United States Patent [19]

Whitehurst et al.

[11] **3,793,185**

[45] **Feb. 19, 1974**

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

[75] Inventors: **Darrell D. Whitehurst**, Titusville; **Stephen A. Butter**, East Windsor; **Paul G. Rodewald**, Rocky Hill, all of N.J.

[73] Assignee: **Mobil Oil Corporation**, New York, N.Y.

[22] Filed: **May 30, 1973**

[21] Appl. No.: **365,358**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 319,099, Dec. 27, 1972.

[52] **U.S. Cl.** ..... **208/251 R**, 208/252, 208/253, 252/411, 252/414

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

[58] **Field of Search** 208/251, 252, 263, 253; 252/411, 413, 414

[56] **References Cited**

UNITED STATES PATENTS

2,453,138	10/1948	Kharasch	208/251
3,176,041	3/1965	Ayers	208/263
3,751,507	8/1973	Walker	208/263
2,745,793	5/1956	Jezl et al.	208/251
3,213,033	10/1965	Hindin et al.	252/413
2,504,134	4/1950	Kharasch	208/251

Primary Examiner—Delbert E. Gantz
Assistant Examiner—Juanita M. Nelson
Attorney, Agent, or Firm—Andrew L. Gaboriault; Michael G. Gilman; Coe A. Bloomberg

[57] **ABSTRACT**

A novel use for sorbents involving the selective removal of heavy metals from liquid streams has been discovered. More specifically it has been discovered that these sorbents selectively remove alkyl lead moieties from gasoline. The sorbents are comprised of metal halides (preferably tin tetrachloride or antimony pentachloride) bonded to a suitable substrate through at least one amine or alkyl halide functional group. The sorbents can be effectively regenerated.

34 Claims, 12 Drawing Figures

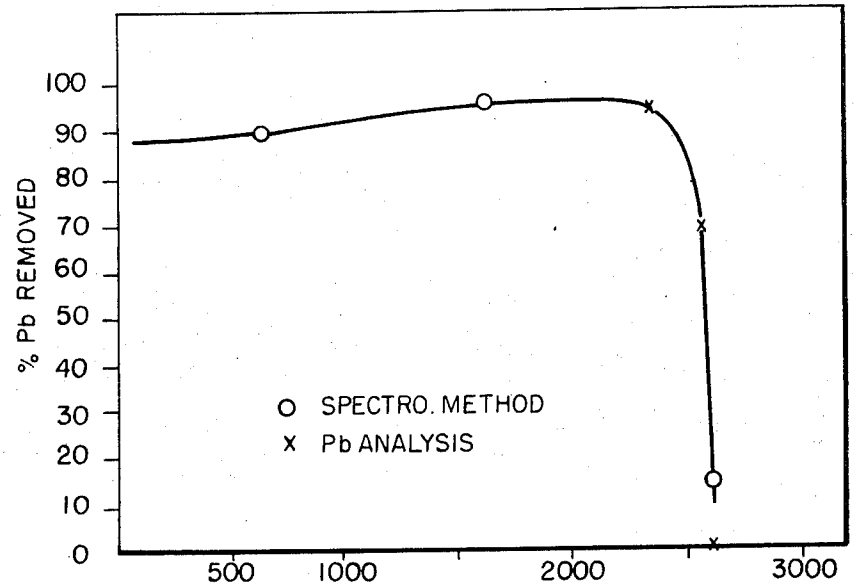
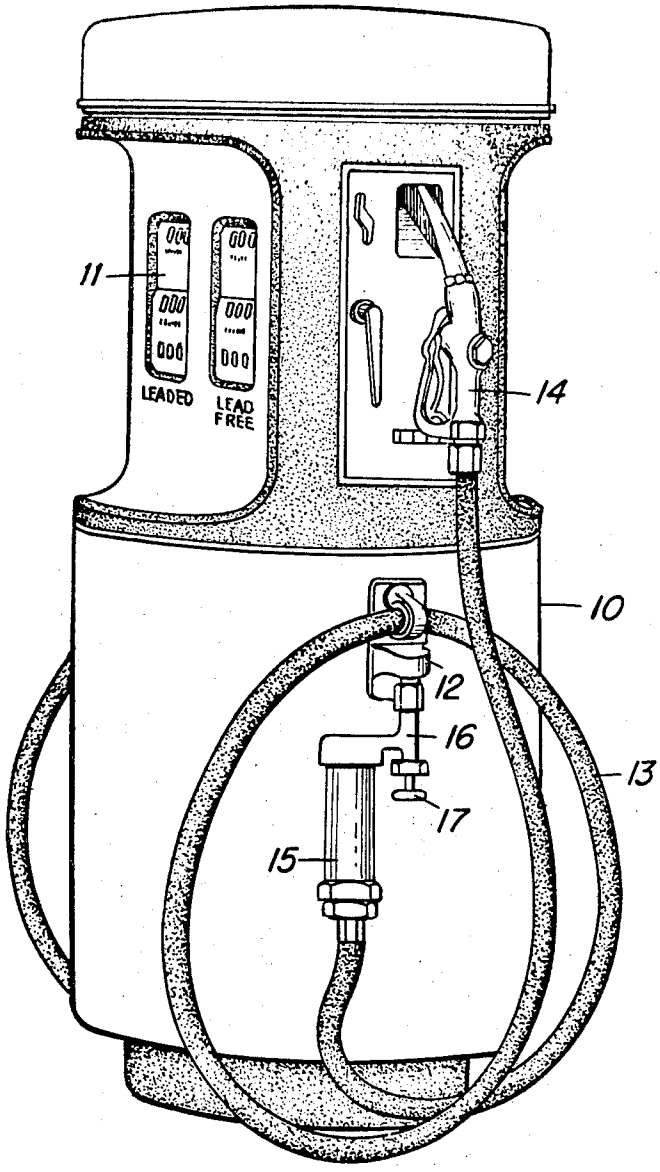


FIG. 1



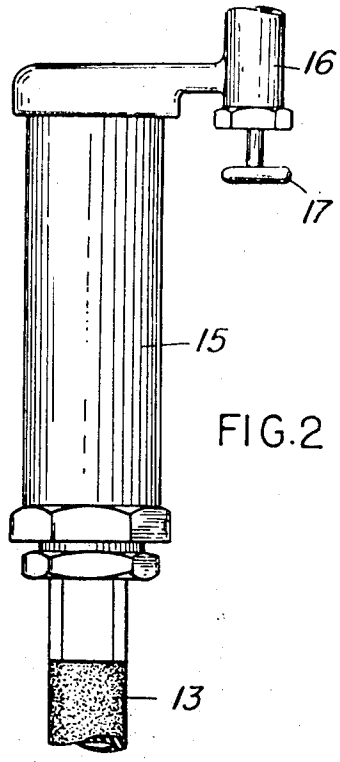


FIG. 2

FIG. 3

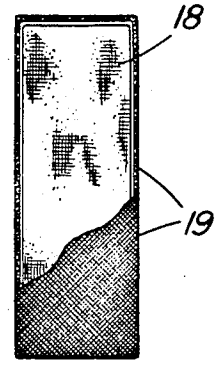


FIGURE 4

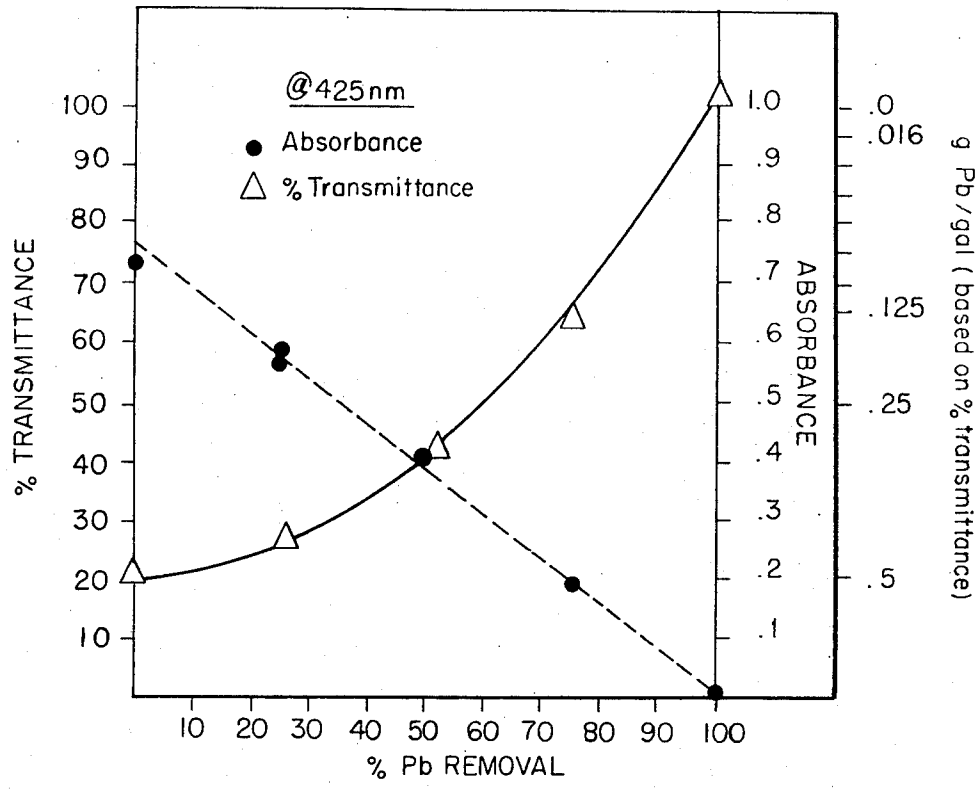
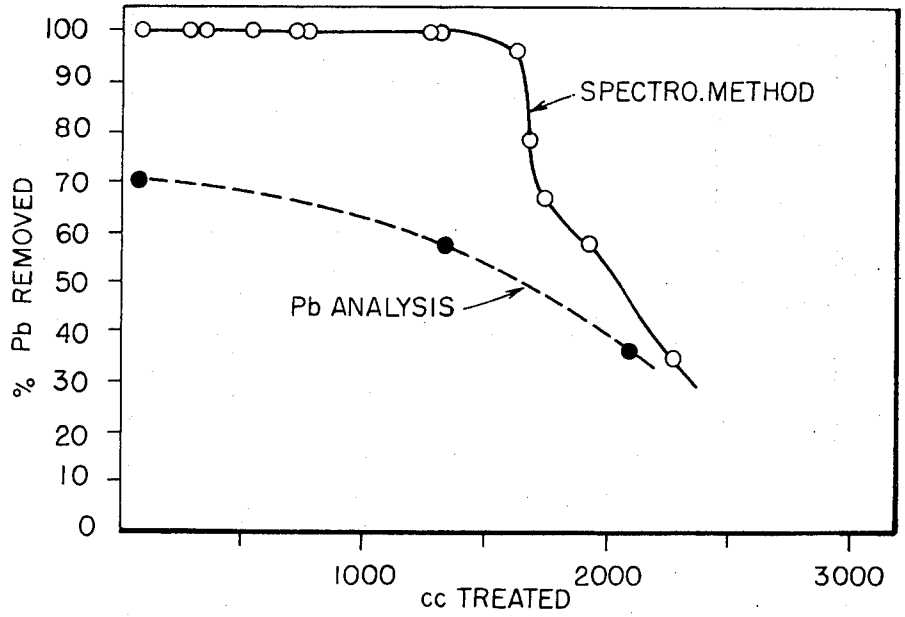


FIGURE 5



LEAD REMOVAL CAPACITY OF PR-44 (12 LHSV)

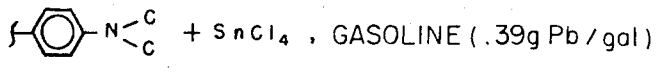
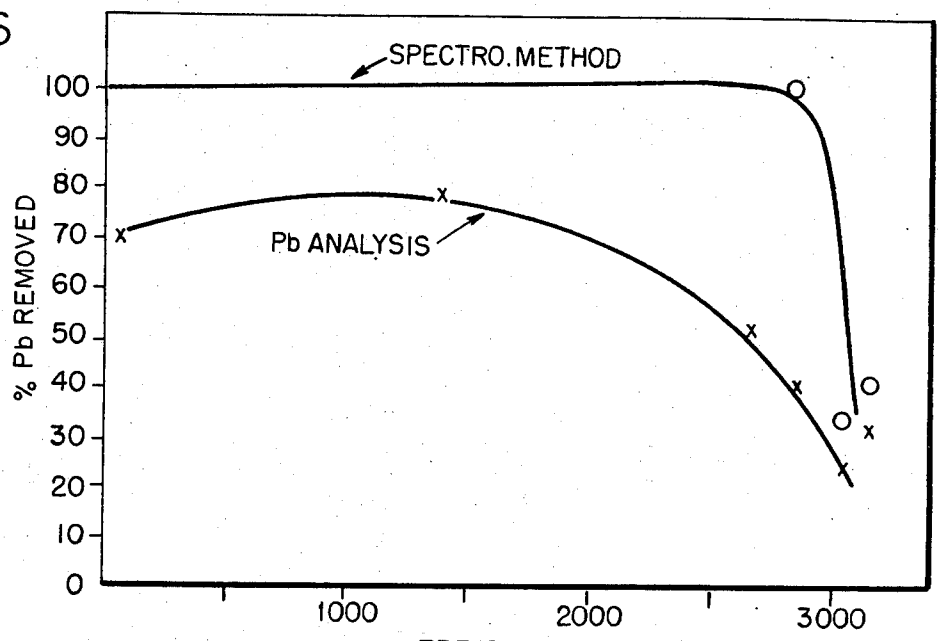


FIGURE 6



LEAD REMOVAL CAPACITY OF PR-48 (12 LHSV)

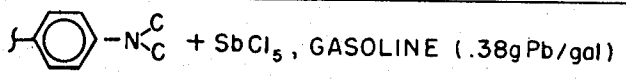
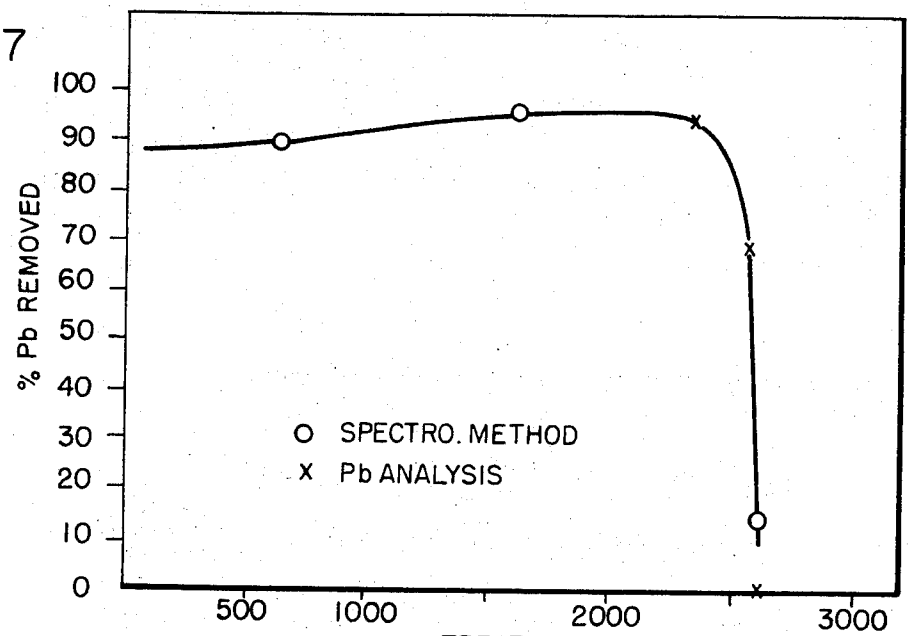
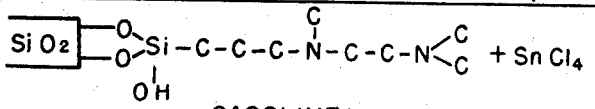


FIGURE 7

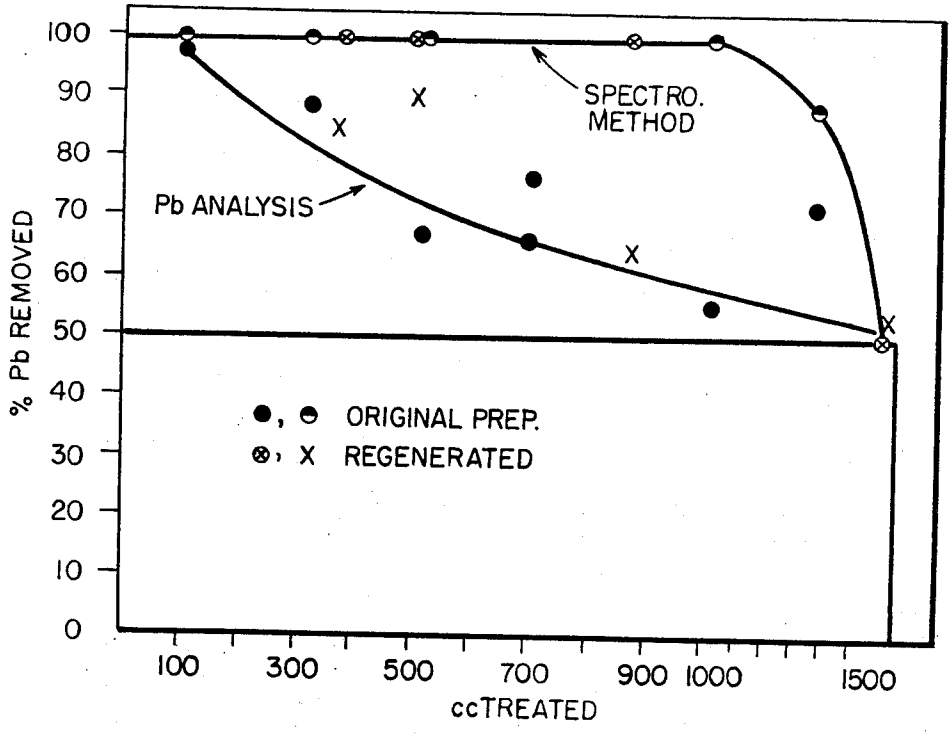


LEAD REMOVAL CAPACITY OF PR-46 (12 LHSV)

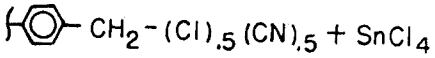


GASOLINE (.38g Pb/gal)

FIGURE 8



LEAD REMOVAL CAPACITY OF SB-13 (11-13 LHSV)



GASOLINE (.33 - .39g Pb/gal.)

FIGURE 9

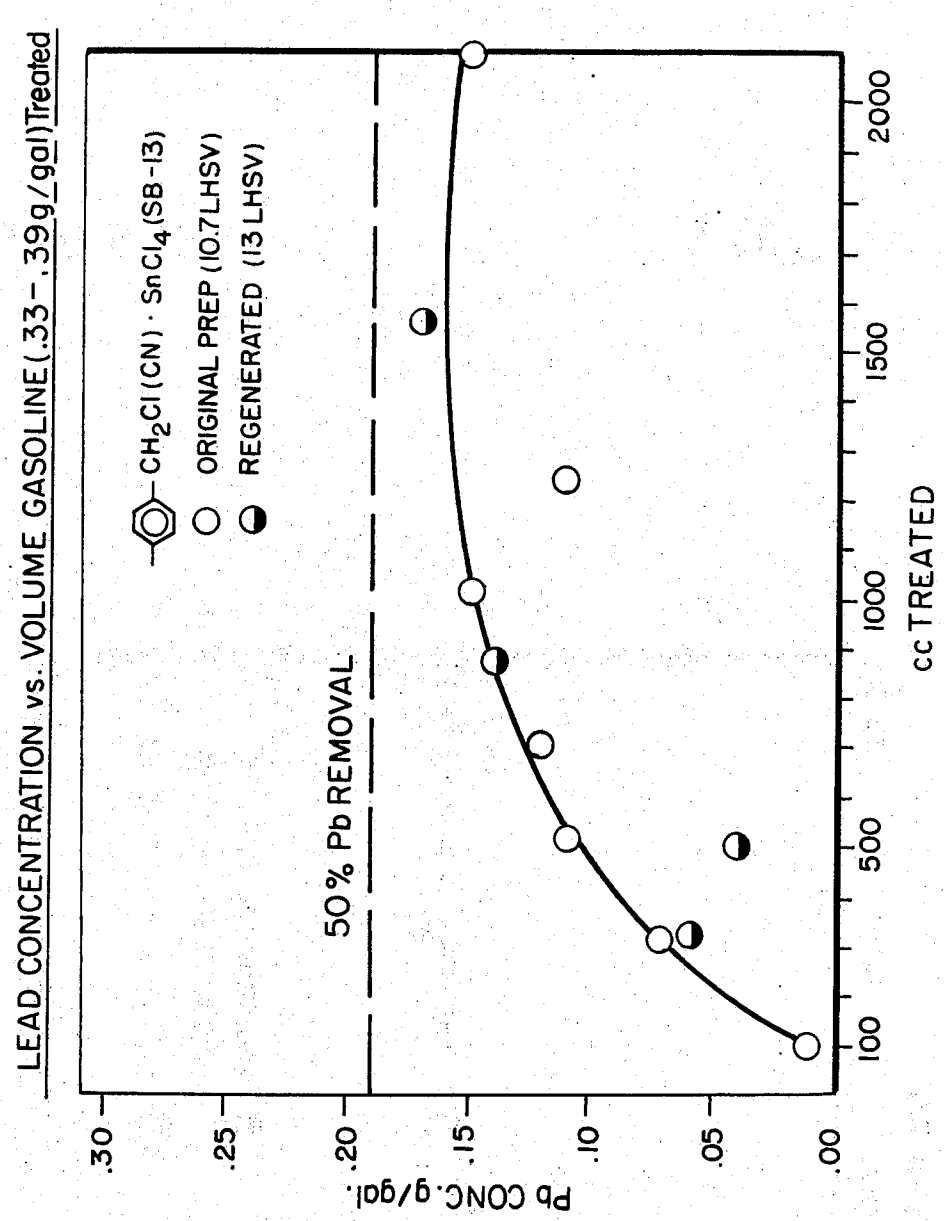
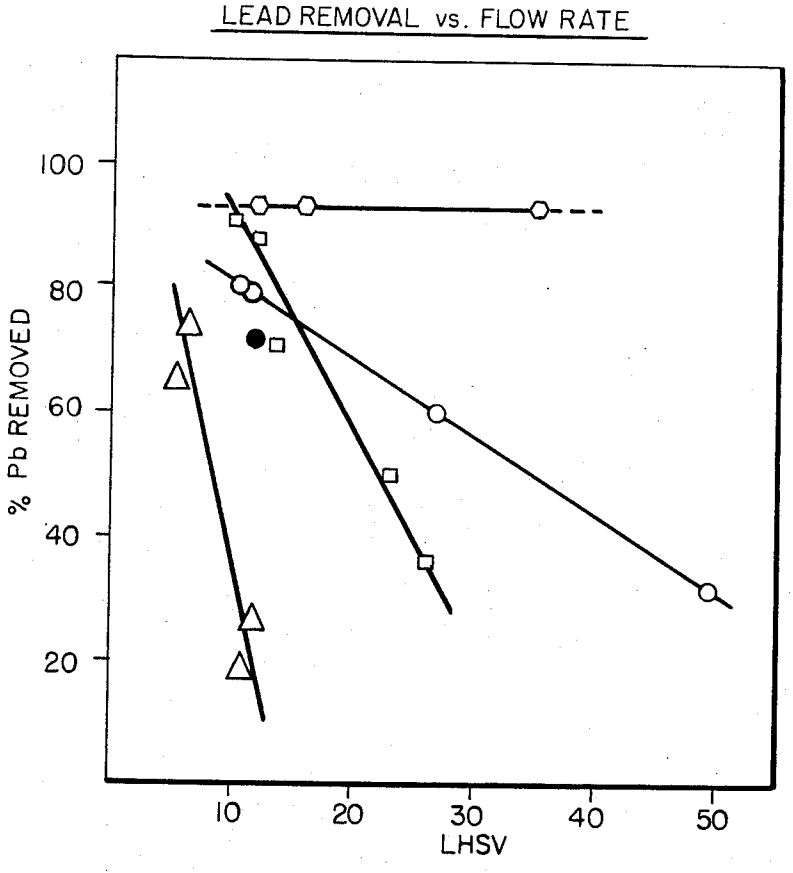

LEAD CONCENTRATION vs. VOLUME GASOLINE (.33-.39 g/gal) Treated
$CH_2Cl(CN) \cdot SnCl_4$ (SB-13)
ORIGINAL PREP (10.7 LHSV)
REGENERATED (13 LHSV)
50% Pb REMOVAL
Pb CONC. g/gal.
.00
.05
.10
.15
.20
.25
.30
100
500
1000
1500
2000
cc TREATED

FIGURE 10



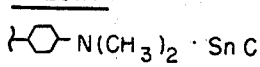
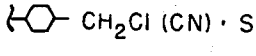
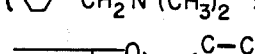
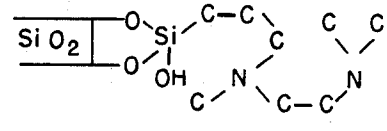
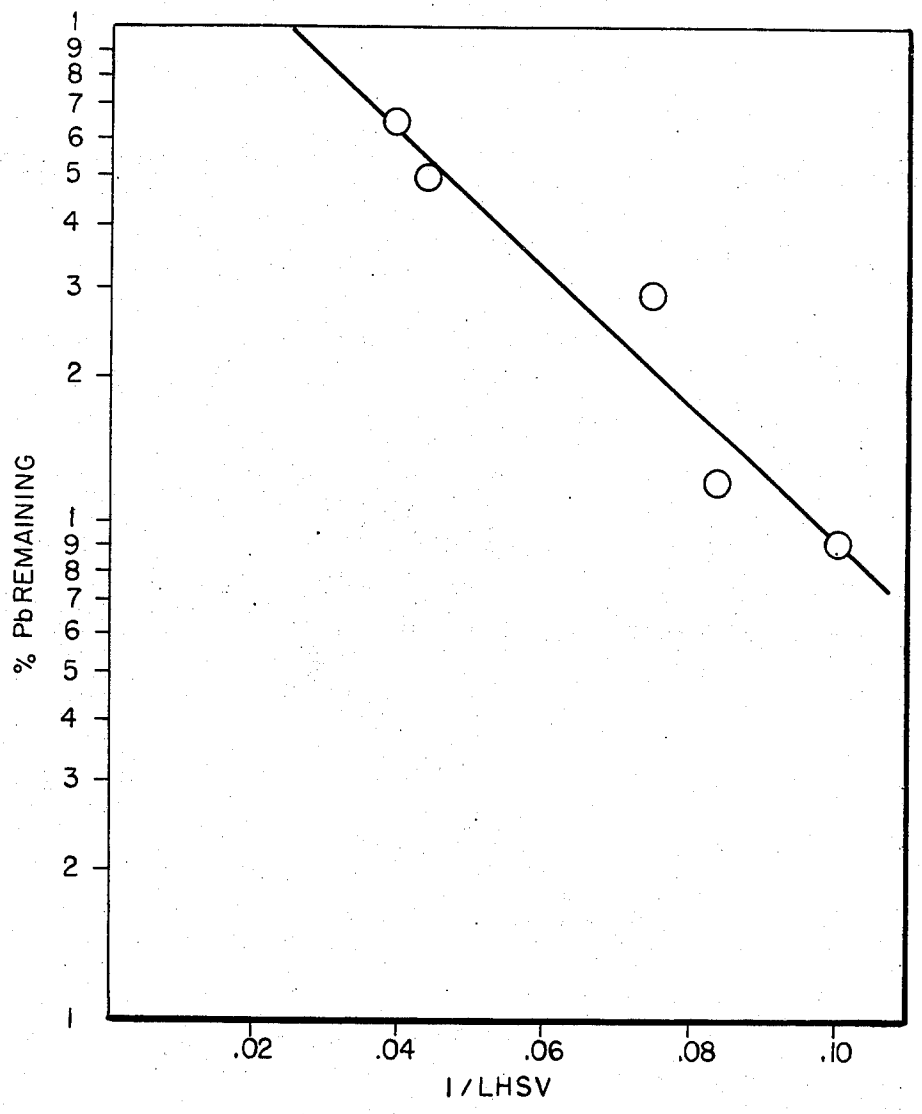
	RESIN	Pb Conc. g/gal	S.A. M^2/gm
○		0.10 (● = .36)	> 100
□		0.38	20
△		0.33	~ 30
⬡	 (PR46)	0.36	340

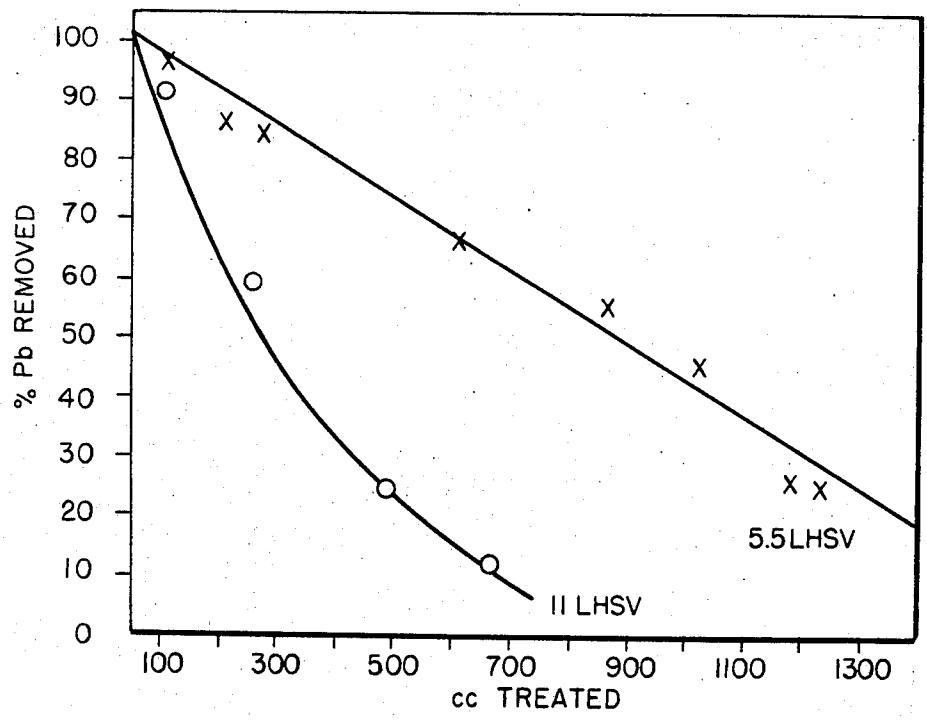
FIGURE 11



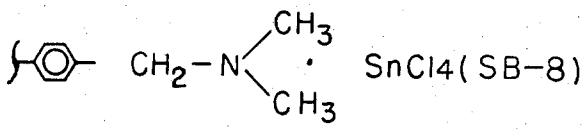
Pb CONTENT OF EFFLUENT vs. CONTACT TIME

($SnCl_4$ – ACTIVE HALOGEN RESIN SB-13)

FIGURE 12



LEAD REMOVAL CAPACITY AND CONTACT TIME



INFLUENT Pb CONC. = 0.33g/gal.

SORBENT FOR REMOVAL OF HEAVY METALS

RELATED CASE

This application is a continuation-in-part of now pending U.S. application Ser. No. 319,099 filed Dec. 27, 1972.

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 is 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 combustible exhaust gases 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. Furthermore the presence of lead complexes in engine exhaust is considered objectionable by some. Therefore the removal of lead from gasoline might be desirable separate and apart from its characteristic of poisoning 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. The lead level reduction is to be accomplished by July 1, 1974. 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 of 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 de-

sired 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 all gasoline manufacturers 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. It is an objective of this invention to selectively remove these metals from hydrocarbon streams by such means as will not remove gasoline additives, such as detergent additives, from gasoline streams. It is an objective of this invention to provide for means for removing lead alkyls from gasoline, such means being capable of regeneration. 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 10 A. and a minimum surface area of about 10 m^2/g; the substrate being modified by at least one functional group of an amine, alkyl halide or the like which acts as a bridging member between the substrate and at least one metal halide; mixed functional groups of amines or other weak Lewis bases with alkyl halides being particularly effective; the metal being a Group IB, IIB, IIIA, IVA, VA, VIA or VIII metal having an atomic number of at least 13, for the removal of heavy metals from non-aqueous liquid solutions, and more particularly for removing lead from gasoline. For purposes of this disclosure, the metal group designations referred to are as defined in *Lange's Handbook of Chemistry* at 58–61 (10th ed. 1967). The gasoline is passed through said sorbent at a space velocity of up to 300 LHSV and a temperature of about −50°C. to 100°C.

Halides of the following metals work particularly well: iron (Fe), copper (Cu), silver (Ag), zinc (Zn), cadmium (Cd), mercury (Hg), aluminum (Al), tin (Sn), lead (Pb), phosphorous (P), arsenic (As), antimony (Sb), bismuth (Bi), sulfur (S), selenium (Se) and tellurium (Te). Those salts having a Lewis acid character exhibited unusually superior results.

The sorbents were prepared by a batch sorption technique in a manner which may be generally described as follows: 10cc of a metal halide such as tin chloride was added while stirring to approximately 150cc of a solvent such as acetone in a 500cc Erlenmeyer flask. To this mixture approximately 50cc of functionalized sorbent matrix was added. The flask was stoppered and the mixture was shaken occasionally over a period of about one half hour. The mixture including the added matrix was then transferred to a chromatographic column and washed twice with approximately 50cc volumes of a solvent such as acetone. The sorbent was dried by passing P_2O_5 dried nitrogen through the sorbent bed. An aliquot of the sorbent was swelled with the gasoline being used.

In a preferred embodiment, the metal salts of stannic chloride and/or antimony pentachloride bonded to a substrate having a surface area of at least 10 m^2/g. with pore diameter of at least 10A., through an amine bridging member produced an extraordinary ability to remove lead tetraethyl and tetramethyl compounds from gasoline. As illustrated by Table 7, described later in this disclosure in greater detail, a sorbent having a substrate of silica, a metal halide of stannic chloride bonded to the substrate by means of a tertiary amine reduced the lead concentration of gasoline from 0.36 g/gal. to 0.01 g/gal for 150 bed volumes of operation.

Furthermore, as depicted in Table 9, also described in greater detail later in this disclosure, the sorbent which comprises an embodiment of this invention removes lead moieties and other heavy metals selectively; important and needed additives such as cleansing detergents are not substantially removed.

While not wishing to be limited by a specific theory of operability, it is believed that the lead removal by the sorbents of this invention may be represented by the following notation:

$$\underset{\text{matrix}}{SnX_4} + R_4Pb \rightleftharpoons \underset{\text{matrix}}{SnX_3R} + \underset{\text{matrix}}{R_3PbX} \rightleftharpoons \underset{\text{matrix}}{SnX_2R_2} + \underset{\text{matrix}}{R_2PbX_2} \rightleftharpoons \text{etc.}$$

where X is a halogen and R is an alkyl. The above notation and the operation which it represents will be amplified later in the specification, and specifically in the section where the examples are described.

Another embodiment of this invention involves the method of regenerating a sorbent as previously described by means of acid extraction. In the preferred embodiment, a volume of sorbent which is "spent," that is, no longer active for lead removal due to prolonged use, is washed sequentially with about 15 volumes of benzene, methanol and water. Then about 25 volumes of about 20 percent hydrochloric (HCl) is

passed over the sorbent. The sorbent is then washed free of acid and dried. The regenerated sorbent is then reactivated with a solution of the metal halide (a preferred sorbent is acetone) in a proportion of about 1:15 metal halide to sorbent as it is passed over the sorbent. Finally the "regenerated" sorbent is washed with 10 volumes of solvent and air dried.

Other embodiments of this invention comprise the system and method of employing the previously described sorbent at any point in a system for distributing and dispensing motor fuels or in an automobile fuel system so as to substantially remove lead.

BRIEF DESCRIPTION OF THE DRAWINGS

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.

FIGS. 5–8 are curves comparing turbidometric analysis with atomic absorption analysis for four selected sorbents.

FIG. 9 is a set of curves illustrating lead concentration as a function of volume of leaded gasoline treated.

FIG. 10 is a series of curves illustrating lead removed as a function of flow rate.

FIG. 11 is a curve illustrating lead content of effluent as a function of contact time.

FIG. 12 is a set of curves illustrating lead removal capacity as a function of contact time.

DESCRIPTION OF PREFERRED 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 is 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. For stations having larger substantially "lead free" gasoline throughput, either the cartridge may be changed more often, or a larger cartridge may be installed between the fuel tank and the dispensing pump. (As previously noted, this disclosure contemplates utilizing the sorbent at any point in a system for distributing and dispensing motor fuels.). Again referring to FIG. 2, 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.

Applicant has discovered that performance of the previously described sorbent can be appreciably enhanced by the addition of an absorption material such as charcoal. Such an absorption or deliquesent material may either be mixed with sorbent particles contained in the canister 15 or be located upstream or downstream of the sorbent. When the absorption material is utilized to remove trace amounts of water in gasoline a preferred embodiment entails the location of the absorption material upstream of the sorbent.

EXAMPLES 1–8

The sorbents were prepared by a batch sorption technique in a manner which may be generally described as follows:

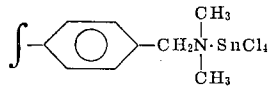
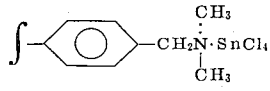
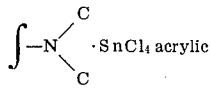
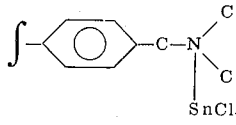
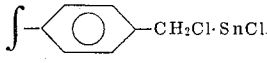
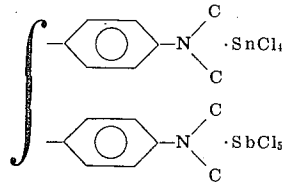
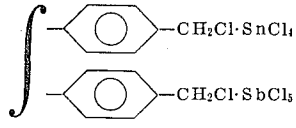
10cc of a metal halide such as tin chloride was added while stirring to approximately 150cc of a solvent such as acetone in a 500cc Erlenmeyer flask. To this mixture approximately 50cc of functionalized resin matrix was added. The flask was stoppered and the mixture was shaken occasionally over a period of about one half hour. The mixture including the added resin was then transferred to a chromatographic column and washed twice with approximately 50cc volumes of a solvent such as acetone. The resin was dried by passing P_2O_5 dried nitrogen through the resin bed.

These tests consisted of contacting approximately three to six volumes of gasoline containing 2.5 grams of lead/gallon gasoline with one volume of sorbent under ambient conditions, followed by a lead analysis of the contacted gasoline. The period of contact time is noted in the first 5 examples. (The lead analyses after 20 minutes, one hour and three hours roughly correspond to those found under flow conditions at space velocities of 9, 3 and 1 LHSV, respectively).

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 10 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. Results of examples 1–8 are illustrated by Table 1.

TABLE 1

Example number	Sorbent designation	Sorbent complex	Solvent	Time	Metal removal (percent Pb)	Remarks
1	SB-6		ETOET	20 min 1 hr	90 100	
2	SB-8		$(CH_3)_2CO$	20 min 1 hr 2 hr	0 45 71	3 hr.—66% 1 wk.—100%
3	SB-9		$(CH_3)_2CO$	Up to 1 wk	0	
4	SB-10		$(CH_3)_2CO$	20 min 1 hr 2 hr	0 23 95	1 wk.—100%
5	SB-11		$(CH_3)_2CO$	20 min 1 hr 2 hr	0 77 94	1 wk.—96%
6	BI	DEAE cellulose·$SnCl_4$			68	
7	PR-65-A		o-Dichlorobenzene	1 hr	100	
8	PR-65-B		do	1 hr	100	

Comparison of example 3 with the other example results tabulated in Table 1 gives an indication of the importance of the substrate surface area. The acrylic substrate used in example 3 had a surface area substantially lower than the other substrates used, and as the results indicate, the lead removal ability of the sorbent formed with it was substantially lower than the other examples.

It is contemplated that substrates of the type described in this disclosure include spent cracking catalysts and inorganic oxides such as clays and pumice.

EXAMPLES 9–12

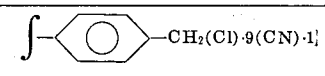
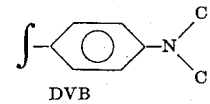
Metal halides having Lewis acid character were attached to various substrates as noted in Table 2. The table also indicates the solvent used during metal halide incorporation and the volume of gasoline passed over 10 parts by volume of sorbent while still maintaining at least 50 percent removal of the initial lead at 11–13 LHSV.

The leaded gasoline to be treated was passed over the sorbent under the following continuous flow conditions:

The general procedure involved passing volumes of about 0.4 gram of lead/gallon of gasoline fuel through a 10 part by volume quantity of resin supported on a glass frit. The flow rates were controlled by varying the percent of stroke on a variable displacement pump, while a 1 to 2 part by volume gasoline hydraulic head was maintained above the resin by a fine adjustment stopcock.

The sorbents utilized in examples 9–12 were analyzed in a manner similar to the procedure described in examples 1–8.

TABLE 2.—PERFORMANCE OF VARIOUS METAL HALIDE REDISTRIBUTION REAGENTS IN LEAD REMOVAL FROM GASOLINE

Example number	Sorbent designation	Sorbent [a]	Metal halide	Solvent used during metal halide incorporation	$V_{1/2}$ cc./10 cc. (sorbent) [b]
9	PR-30	 EGDM	$SnCl_4$	Acetone	1,200
10	PR-34	Same as above	$SbCl_5$	Benzene	1,400
11	PR-44	 DVB	$SnCl_4$	Acetone	1,600
12	PR-48	Same as above	$SbCl_5$	Chloroform	2,700

[a] Subscript denotes crosslinking agent. EGDM=Ethylene glycol dimethacrylate. DVB=Divinylbenzene
[b] Capacity at LHSV=10–13.

EXAMPLES 13–19

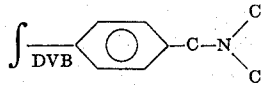
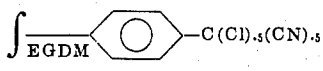
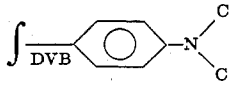
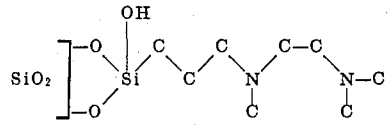
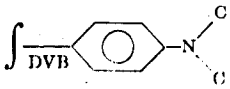
A number of sorbents containing tin chloride ($SnCl_4$) or antimony pentachloride ($SnCl_5$) were analyzed for tin or antimony content before and after processing a gasoline of about 0.4 grams of Pb/gallon of fuel. The lead content of the used sorbents was also determined by chemical analysis, and the results summarized in Table 3. The gasoline flow conditions were identical to those described in the procedure recited in examples 9–12.

Those sorbents which efficiently removed lead and had large capacities in general showed little or no loss of tin or antimony to be processed gasoline. Lead removal by the sorbents in general paralleled the volume of gasoline processed in which 20 percent of the lead was removed. In example 18 nearly 3 percent by weight lead was incorporated into the sorbent. At such a high level of lead, its recovery by acid extraction would appear to be economically feasible.

EXAMPLES 20–29

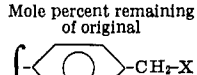
A class of sorbents with tin chloride in combination with active halogen was further modified by the addition of weak Lewis bases (nitriles). The relative concentration of halogen to nitrile; swelling of the sorbent after nitrile modifying treatment and stannic chloride addition; the weight percentage of tin incorporated with the sorbent; and the volume of gasoline passed over 10 volumes of the treated sorbent until 50 percent of the initial lead (0.4 gm/gal.) at 11–13 LHSV could no longer be removed were measured and summarized in Table 4. The gasoline flow conditions were identical to those described in the procedure recited in examples 9–12.

TABLE 3.—TIN RETENTION AND LEAD PICKUP BY VARIOUS SORBENTS CONTAINING $SnCl_4$

Example	Sorbent designation	Sorbent matrix	Weight percent Sn initial	Weight percent Sn [1] final	Weight percent Pb [1] final	Volume of [1] 0.33–0.39 g. Pb/gal. gasoline deleaded (cc./10 cc. sorbent)
13	SB-11		.22	.07	.02	343
14	SB 21		1.32	.8	.04	665
15	SB-8		11.4	12.2	.04	1,240
16	SB-13		2.61	2.45	1.4	2,142
17	PR-44		7.1	2.91	1.2	2,294
18	PR-46		4.3	3.6	2.8	2,626
			Wt. percent Sb			
19	PR-48		14.0	14.6	.28	3,144

[1] All runs were terminated shortly after the sorbent no longer removed >20% of the lead (~.4 g./gal.) at LSHV=11-13.

TABLE 4.—SORBENT EFFICIENCY OF $SnCl_4$ PLUS BENZYL HALIDE CONTAINING POLYMERS

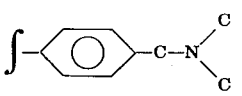
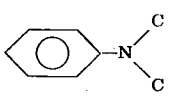
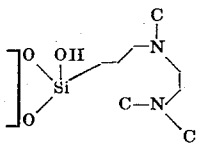
Ex. No.	Sorbent designation	Base resin number	Cross linking agent*	Modifying treatment	Wt. percent Cl in original	Mole percent remaining of original  CH_2—Cl	Mole percent remaining of original CH_2CN	Swelling (Δcc./gm.) After treatment	Swelling (Δcc./gm.) After $SnCl_4$	Wt. percent Sn+[4] incorporated	Vol.$_{1/2}$ LHSV-11-13	Percent Sn efficiency
20		5	E (gel)	None		100		0	0			
21	SB-11	4	D	do	11.2	100				.22	150	28
22	SB-21	2	E	do	20.0	100		.65		1.32	500	19
23	PR-30	2	E	KCN/H_2O (58° C.) 16 hr	20.0	90	10	.42	.05	2.5	1,200	32
24	SB-13	1	E	$NaCN/H_2O$ (warm) 16 hr.	17.1	50	50	.45	.35	2.61	>2,000	>43
25	PR-36	2	E	KCN/DMSO (50° C.) 16 hr.	20.0	20	80			1.50	700	28
26	SB-13R	1	E	SB-13 regenerated	20.0	50	50				1,600	
27	PR-32	2	E	KCN/H_2O (40° C.) 72 hr.	20.0			.28			230	Low
28	PR-39	3	E	$NaOH/H_2O$ (50° C.) 16 hr.	18.4	~100					300	Low
29	PR-33	2	E	Sonicated (125 w) 10 min.	20.0	100			.58		300	Low

*E is ethylene glycol dimethylacrylate. D is divinylbenzene.

EXAMPLES 30–35

The tin distribution in a number of sorbent matrices was determined by electron microprobe techniques; leaded gasoline was passed over a 10 part by volume sample of each sorbent until the sorbent was no longer

TABLE 5.—SORBENT EFFICIENCY AND PHYSICAL PROPERTIES OF SELECTED $SnCl_4$ CONTAINING MATRICES

	Tertiary amine series			Active halogen series		
Example number	30	31	32	30	31	32
Sorbent designation	S B-8	P R-44	P R-46	S B-11	S B-21	S B-13
Sorbent matrix				DVB	EGDM	EGDM
Surface area ($m.^2/gm.$)	~30	67	340	<5	19	20
Swelling [a] (Δ cc./g.)		.48	~0		.65	.45
Density, found (g./cc.)		.55	.4			.63
Density, calculated (g./cc.)	.53	.57	.41	.74	.74	.74
Pore volume (cc./g.)	.6	.6	1.15	.1-.3	.207	2.04
Percent pore size dist.:						
>300 A	Major		8.5	Major	94.2	94.9
300-100 A			59.3		1.5	0.3
100-50 A		Major	32.2		4.2	4.8
<50 A			Small			
Percent Sn	11.4	7.1	4.3	.22	1.32	2.61
Percent Cl [b]	6.2			[11]	[21]	[9.7]
Percent X [b]	[5.32]N	[3.28]N	[0.5]N			

Example number	33	34	35	33	34	35
Sorbent designation	S B-8	P R-44	P R-46	S B-11	S B-21	S B-13
Sn distribution (fresh) [c]		u	u	s(11%)	s(10%)	s(14%)
Pb distribution (used) [d]		u	u	(u-s)	(u-s)	(u-s)
Initial percent Pb removal/pass	~90	80	95	90	90	85
Vol. $_{1/2}$ [e] (cc.)	300	1,600	2,400	150	500	>2,000
Moles Sn/10 cc. sorbent	5.51	3.43	1.49	.14	.83	1.64
Moles Pb removed at vol.$_{1/2}$	.08	.54	1.00	.04	.16	>.71
Percent Sn efficiency [f]	1.5	16	67	29	19	>43

[a] Determined for non-Sn containing sorbents, gasoline solvent.
[b] Bracketed numbers refer to the sorbent matric prior to Sn incorporation.
[c] s (11%)=shell distribution, the depth of the shell=(11%) of the radius from the exterior surface inward; u=uniform distribution.
[d] (u-s)=uniform distribution in the center portion of the particle where Sn was *not* found.
[e] Volume of gasoline passed over 10 cc. of sorbent while still maintaining at least 50% removal of the initial Pb (.4 g./gal.) at 11-13 LHSV.
[f] The percent of the original Sn which operated efficiently in removing lead.

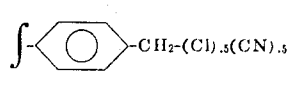
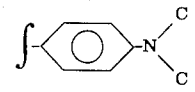
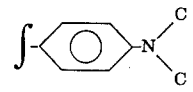
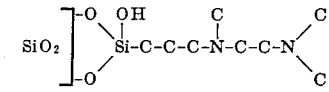
able to remove 50 percent of the initial lead concentration (0.4 gm/gal) at 11–13 LHSV according to the flowing test procedure recited in examples 9–12; and finally the lead distribution in the sorbent was determined by microprobe techniques. The percent tin efficiency, that is the percent of the original tin which operated to remove lead, was calculated for each sorbent.

Table 5 illustrates the physical properties or characteristics of various sorbents all of which contained tin chloride ($SnCl_4$). The table shows the amount of tin (Sn) initially deposited on each sorbent, and the uniformity of the distribution throughout the sorbent.

EXAMPLES 36–39

Four sorbents were tested at LHSV 11–13 under the flowing test procedure recited in examples 9–12. Under these conditions the lead removal was high, generally above 80 percent. The treated gasoline was tested to determine its nitrogen component concentration to determine the amount of indigenous basic nitrogen compounds in gasoline removed during the lead removal process. A separate analysis of a detergent additive was also made. Results are shown in Table 6.

TABLE 6.—THE EFFECT OF LEAD REMOVAL ON THE NITROGEN AND NITROGEN BASED DETERGENT CONTENT OF GASOLINE

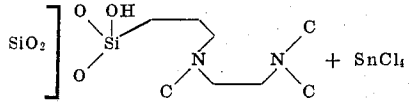
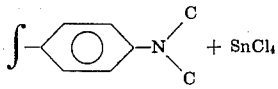
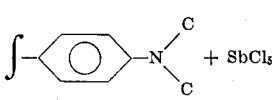
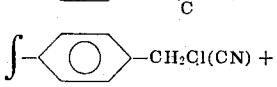
Example number	36		37		38		39	
Sorbent designation	SB-13		PR-44		PR-48		PR-46	
Substrate								
Metal halide	$SnCl_4$		$SnCl_4$		$SbCl_5$		$SnCl_4$	
	"N" content (p.p.m.)	Parts by volume fuel processed (cc.)	"N" content (p.p.m.)	Parts by volume fuel processed (cc.)	"N" content (p.p.m.)	Parts by volume fuel processed (cc.)	"N" content (p.p.m.)	Parts by volume fuel processed (cc.)
	12	Original	13	Original	14	Original	14	Original
	2.0	375	4.5	78	3.6	80	3.1	722
	3.0	500	5.7	1,364	3.5	1,394	4.2	1,614
	3.0	870	6.7	1,918	5.1	2,680	7.9	2,626
	6.9	1,570			6.2	3,034		
			No detergent removal in 1st 400 cc.		No detergent removal in 1st 400 cc.		33% detergent removal in 1st 400 cc. (no removal after 400 cc.)	

(a) Original content was 24#/1,000 bbl. or 3.6 p.p.m. "N".
(b) In all cases 10 parts by volume of sorbent was used to remove the lead at 11–13 LHSV.

EXAMPLES 40–46

Four sorbents, similar or identical to those tested in examples 36–39 were tested at space velocities ranging from 11–40 LHSV. The sorbents were tested by passing 75–150 bed volumes of leaded gasoline over each sorbent and measuring the lead content of the gasoline before and after treatment. The initial lead concentration was varied from 0.10 to 0.39 grams of lead per gallon of gasoline. The results of the test are shown in Table 7.

TABLE 7

Sorbent	Example number	Space velocity	Lead concentration, g./gal. Feed	Lead concentration, g./gal. Product[a]
	40	12	.36	.01
	41	40	.36	.01
	42	13	.36	.16
	43	11	.10	[b].04
	44	28	.10	[b].02
	45	13	.38	.07
	46	13	.39	[b].11

[a] Lead analysis after 150 bed volumes except as noted.
[b] After 75 bed volumes.

EXAMPLES 47

A cyanide-treated chloromethylated polystyrene resin (sorbent designating SB-13) which had been promoted with stannic chloride, and which had been rendered inactive by satisfactorily treating over 200 volumes of leaded gasoline (0.33–0.39 grams/gal.), was washed with portions of benzene, methanol and water. 250 volumes of 20 percent hydrochloric acid was then passed over the resin which was next washed with 250 volumes water, methanol and finally air-dried. Two volumes of stannic chloride in 30 volumes of acetone was then passed over the resin, followed by 100 volumes of acetone; the resin was then dried in air.

This regenerated sorbent was again used to remove lead from gasoline leaded to a 0.33–0.39 gm/gal. level. The results of the lead removal capability of the regenerated sorbent are plotted in FIG. **9.**

EXAMPLES 48–51

A gasoline having a lead level of 0.36 gram/gallon was diluted with a very low lead level gasoline until the mixture's lead level was reduced to 0.10 gram/gallon. Four sorbents were then tested at varying LHSV ranging from about 5 to 50 under the flowing test procedure recited in examples 9–12. The response of the low lead gasoline to space velocity variation was consistent with the results at higher lead levels. The efficiency of sorbent designated as PR-44 was compared at two different lead levels (0.36 gram of lead/gallon and 0.10

gram/gal). As noted in FIG. 7, the efficiencies were substantially identical.

EXAMPLE 52

The sorbent designated SB-13 was subjected to the gasoline flowing conditions recited in examples 9–12. The gasoline had a lead concentration of about 0.4 gm/gal, and the space velocity was varied from approximately 10 to 50 LHSV. The lead removal ability of the sorbent at the various space velocities was determined by atomic absorption analysis; the results are plotted in FIG. 11.

EXAMPLE 53

The sorbent designated SB-8 was subjected to the gasoline flowing conditions recited in examples 9–12. The gasoline had a lead concentration of about 0.4 gram/gallon, and the sorbent was tested at space velocities of 5.5 and 11 LHSV. The lead removal capability of the SB-8 sorbent at the two space velocities was determined after various volumes of gasoline had been passed over the sorbent through the use of atomic absorption analysis; the results are plotted on FIG. 12.

EXAMPLE 54

The preparation of a silica based sorbent containing primary and secondary amine functional groups and attached stannic chloride is described below.

The xylene used as solvent in catalyst preparations was dried by azeotropic distillation using a Dean-Stark trap. The silica used was Davison Grade 59 (properties of which are given in the table below) ground to 12/100 mesh and dried in a vacuum over at approximately 120°C for about 4 hours.

Davison Grade 59 Silica Gel

Silica Content (Dry Basis)	99.0% (Min.)
Total Volatile at 1750°F	4.5% (Max.)
Apparent Density	Approx. 25 lbs. per cubic foot
Specific Heat	0.22 BTU/16°F
Surface Area	340 Sq. Meters/gm
Pore Diameter (average)	140 Angstroms
Pore Volume	1.15 CC/gm

CHEMICAL ANALYSIS
Typical (Dry Basis)

Silica as SiO_2	99.50
Iron as Fe_2O_3	0.01
Aluminum as Al_2O_3	0.10
Titanium as TiO_2	0.02
Calcium as CaO	0.07
Sodium as Na_2O	0.06
Zirconium as ZrO	0.03
Trace Elements	0.03

MOISTURE ADSORPTION
Typical

10% R.H.	1.71
20% R.H.	2.88
40% R.H.	4.96
60% R.H.	7.80
80% R.H.	16.96
100% R.H.	93.50

Approximately 150g silica suspended in about 750 ml. xylene was added 30.5g N-(β-aminoethyl) -γ-aminopropyltrimethoxysilane. The mixture was stirred under reflux (about 105°C) for approximately 4 hrs. and cooled. The liquid was decanted and the solid product was washed 3 times with about 400 ml. portions of n-hexane, stirred in hot distilled water for about ¾ hr. (to promote complete reaction and also remove unreacted silane) washed with water, and dried in a vacuum oven at about 130°C for approximately 16 hr. This material contained about 4.50 wt.% C, 1.23 wt.% H and 1.1 wt.% N.

To about 60 cc. acetone in an approximately 250 cc. Erlenmeyer flask was added with stirring 4.0 cc. stannic chloride. Then about 20cc. of the above functionalized silica was added. The flask was stoppered and the mixture was shaken occasionally over a period of about ½ hour. The sorbent was then transferred to a chromatographic column and washed three times with about 25cc. volumes of acetone. The sorbent was dried by passing P_2O_5-dried nitrogen through the sorbent bed. The final product was designated PR-81 and contained 4.3 wt.% Sn.

EXAMPLE 55

The preparation of a silica based sorbent containing tertiary amine functional groups and attached stannic chloride is described below.

Approximately 110 g. portion of the functionalized silane of Example 1 was suspended in about 250 ml. of 88 percent formic acid and about 185 ml. 37 percent formaldehyde and stirred under reflux (~98°C) for approximately 12 hr. After cooling, the liquid was decanted. The solid was washed 3 times with about 300 ml. distilled water, suspended in about 300 ml. distilled water and sufficient 1 N NaOH (~90 ml.) was added until the solution was neutral. The product was then filtered out, washed with about 300 ml. distilled water, stirred in about 700 ml. 90°C distilled water for approximately 1 hr., filtered and dried in a vacuum oven at about 130°C for approximately 16 hr. Analysis: 4.5% C, 1.23% H, 1.1% N. Tin chloride was incorporated in an identical manner to that of Example 1. The final product was designated PR-80 and contained 3.2 wt.% Sn.

EXAMPLES 56–57

The above sorbents (PR80 and PR81) were used to remove lead alkyl contaminants from a commercial gasoline. The initial concentration of lead was about 0.4g/gal. The flow rate varied between 12 and 24 LHSV and under these conditions the sorbents were effective for removing more than 55 percent of the lead alkyl from the volumes of gasoline as listed below in Table 8.

TABLE 8

Example	Sorbent Designation	Capacity (volumes of gasoline/volume of sorbent
56	PR-80	>425
57	PR-81	>480

EXAMPLES 58–59

The sorbents PR 80 and PR 81 were found to be more effective at elevated temperatures as shown in Table 9 where the instantaneous lead removal increased markedly on raising the temperature. The sorbents being studied were aged due to use and were op-

erating at 12 LHSV. Increased capacities at higher temperatures were also observed.

TABLE 9

Sorbent Designation	Example	Instantaneous Pb Removal at 25°C	Instantaneous Pb Removal at 55°C	Capacity for more than 55% Pb Removal at 55°C (volumes/vol. of sorbent)
PR-80	58	74%	94%	>475
PR-81	59	56%	87%	>525

EXAMPLE 60

The sorbent containing primary amine functional groups designated PR-100 was prepared as in Example 1 from antimony pentachloride and an aminopolystyrene resin containing 2.35 percent nitrogen. The sorbent was used to remove lead alkyl contaminants from gasoline containing 0.105 g. Pb/gal. The flow rate was 12 LHSV. Under these conditions the sorbent was effective in removing more than 55 percent of the lead alkyl from 230 volumes gasoline/volume sorbent.

EXAMPLE 61

The sorbent designated PR-91 was prepared in Example 54 from antimony pentachloride and the functionalized silica. The sorbent contained 8.37 percent antimony and was used to remove lead alkyl contaminants from a commercial gasoline containing 0.22g Pb/gal. The flow rate was 12–48 LHSV and the temperature was −20°C. Under these conditions the sorbent was effective in removing more than 55 percent of the lead alkyl from 380 volumes gasoline/volume sorbent. The gasoline detergent was not removed.

EXAMPLE 62

γ-Alumina having a surface area of about 200 M^2/g was functionalized as in Example 54 to give a product containing about 2.09% N. This product was then treated with antimony pentachloride to give the sorbent (PR-118) containing about 5.82% Sb. The sorbent was then used to remove lead alkyl contaminants from a gasoline blend containing about 0.0805 g. Pb/gal. The flow rate was approximately 12–24 LHSV. Under these conditions the sorbent was effective in removing over 50 percent of the lead alkyl from more than 600 volumes gasoline/volume sorbent.

What is claimed is:

1. A method for effecting removal of heavy metal contaminants from a substantially hydrocarbon solution containing the same which comprises contacting said solution with a sorbent for said metal contaminants comprising a substrate having a minimum surface area range of about 10 m^2/g to 800 m^2/g and having pores with a minimum pore diameter range of about 10 A. to 500 A., said substrate being modified by at least one amine functional member, said substrate being further modified by at least one metal halide, the metal of said metal halide being a Group IB, IIB, IIIA, IVA, VA, VIA or VIII metal having an atomic number of at least 13, said functional member acting as a bridging member between said substrate and said metal halide; and removing said solution having a significantly lower heavy metal moiety concentration.

2. The method as claimed in claim **1** wherein said minimum surface area is about 10 m^2/g.

3. The method as claimed in claim **2** wherein said minimum pore diameter is about 10 A.

4. The method as claimed in claim **3** wherein said metal is selected from the group consisting of Fe, Cu, Ag, Zn, Cd, Hg, Al, Sn, Pb, P, As, Sb, Bi, S, Se and Te.

5. The method as claimed in claim **4** wherein said metal halides have Lewis acid character.

6. The method as claimed in claim **5** wherein said heavy metal contaminants are lead alkyl moieties said substantially hydrocarbon liquid solution is gasoline, and said contacting is carried out at about −50°C. to 100°C. and at space velocities of up to about 300 LHSV.

7. The method as claimed in claim **6** wherein said metal halide is tin tetrachloride.

8. The method as claimed in claim **6** wherein said metal halide is antimony pentachloride.

9. The method as claimed in claim **6** wherein said substrate is an oxide of at least one of the elements selected from the group consisting of B, Bi, Al, Si, Ga, Sn, Ti, Zr, V, Cr, Mo, W, Mg and Fe.

10. The method as claimed in claim **9** wherein said element is Al.

11. The method as claimed in claim **9** wherein said element is Si.

12. The method as claimed in claim **9** wherein said element is Ti.

13. The method as claimed in claim **9** wherein said sorbent is further modified by the addition of nitriles having weak Lewis base character.

14. The method as claimed in claim **11** wherein said oxide is SiO_2.

15. The method as claimed in claim **14** wherein said amine functional member is a primary amine.

16. The method as claimed in claim **14** wherein said amine functional member is a secondary amine.

17. The method as claimed in claim **14** wherein said amine functional member is a tertiary amine.

18. The method as claimed in claim **17** wherein said tertiary amine is N,N′,N′-trimethyl-γ-propyl ethylene diamine.

19. The method as claimed in claim **18** wherein said metal halide is tin tetrachloride.

20. The method as claimed in claim **18** wherein said metal halide is antimony pentachloride.

21. In a process for distributing and dispensing motor fuel comprising transportation means and storage means used alternatively for leaded and unleaded fuels and at least one substantially lead-free fuel dispensing station comprising storage means; pumping means; conduit means connecting said storage means and said pump; and conduit discharge means from said pump; the improvement which comprises contacting said fuel with a sorbent comprising a substrate having a minimum surface area range of about 10 m^2/g to 800 m^2/g and having pores with a minimum pore diameter range

of about 10 A. to 500 A., said substrate being modified by at least one amine functional group, said substrate being further modified by at least one metal halide the metal of said metal halide, being a Group IB, IIB, IIIA, IVA, VA, VIA or VIII metal having an atomic number of at least 13, said functional member acting as a bridging member between said substrate and said metal halide, said contacting being carried out at about −50°C. to 100°C. and at space velocities of up to about 300 LHSV; and removing said substantially lead-free gasoline.

22. The process as claimed in claim **21** wherein said minimum surface area is about 10 m^2/g.

23. The process as claimed in claim **22** wherein said minimum pore diameter is about 10 A.

24. The process as claimed in claim **23** wherein said metal halides have Lewis acid character.

25. The process as claimed in claim **20** wherein said amine functional group is a primary amine.

26. The process as claimed in claim **20** wherein said amine functional group is a secondary amine.

27. The process as claimed in claim **20** wherein said amine functional group is a tertiary amine.

28. The process as claimed in claim **23** wherein said tertiary amine is N,N′,N′-trimethyl—γ—propyl ethylene diamine.

29. The process as claimed in claim **28** wherein said metal halide is tin tetrachloride.

30. The system as claimed in claim **28** wherein said metal halide is antimony pentachloride.

31. The process as claimed in claim **28** wherein said sorbent is located in said pump discharge means so that said fuel passes through said sorbent as it is pumped.

32. The process as claimed in claim **31** wherein a absorption material is located upstream of said sorbent to effect water removal.

33. The method claimed in claim **1** wherein said method further comprises regenerating said sorbent by removing said metal contaminants by means of acid extraction, followed by adding a metal halide.

34. A method of regenerating a lead removal sorbent comprising a porous substrate bonded to a metal halide by means of an amine functional member, said method of regeneration comprising sequentially washing a spent sorbent, that is, one no longer active for lead removal due to prolonged use, with about 15 volumes of benzene, methanol and water; passing about 25 volumes of about 20 percent hydrochloric acid over said spent sorbent; washing sequentially said acid reacted sorbent with about fifteen volumes of 0.1 N NaOH and methanol; drying said sorbent; passing a metal halide over said sorbent in a proportion of about 1:5 metal halide to sorbent, said metal halide being in solution with a solvent in a proportion of about 1:15 metal halide to solvent as it is passed over the sorbent; washing said sorbent with about 10 volumes of solvent; and drying said sorbent.

* * * * *

PO-1050
(5/69)

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,793,185 Dated February 19, 1974

Inventor(s) Darrell D. Whitehurst, et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 11	In Table 5, pore volume of example number 32, "1.15" should be --1.16--.
Column 19, line 29	"System" should be --process--.

Signed and sealed this 13th day of August 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents