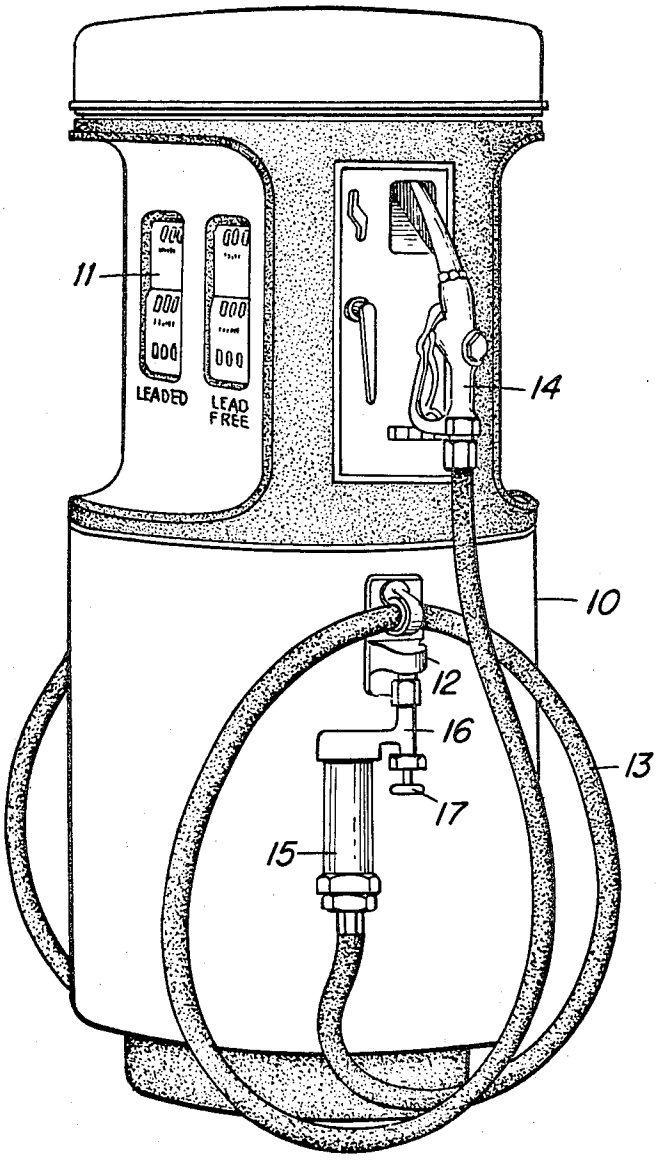
March 26, 1974 I. J. HEILWEIL 3,799,870

LEAD TRAP

Filed March 9, 1973

FIG.1



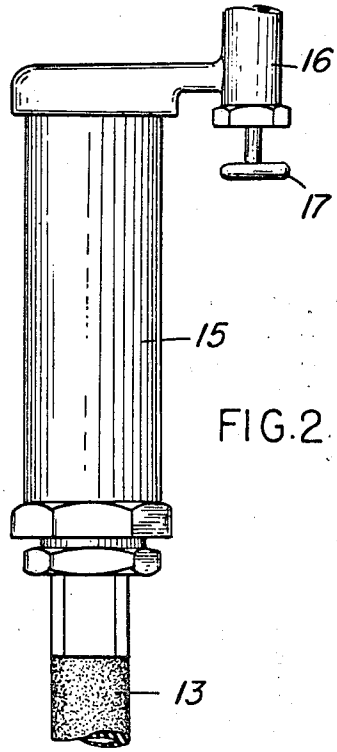


FIG.2

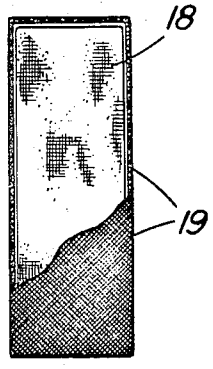


FIG.3

United States Patent Office 3,799,870 Patented Mar. 26, 1974

3,799,870

LEAD TRAP

Israel J. Heilweil, Princeton, N.J., assignor to Mobil Oil Corporation, New York, N.Y.

Continuation-in-part of application Ser. No. 245,339, Apr. 19, 1972. This application Mar. 9, 1973, Ser. No. 339,683

Int. Cl. C10g 17/00, 29/04

U.S. Cl. 208—251 6 Claims

ABSTRACT OF THE DISCLOSURE

In providing lead free gasoline from gasoline which may become contaminated during transportation or storage in vessels also used for transport and storage of leaded gasoline; a lead trap is provided at the point of dispensing to motor vehicles characterized by a material having selective chemisorption properties with respect to tetraalkyl lead.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of now pending U.S. patent application Ser. No. 245,339 filed Apr. 19, 1972.

BACKGROUND OF THE INVENTION

This invention is concerned with transportation and distribution of lead free motor fuels. Residues of alkyl lead from combustion of leaded gasoline tend to poison catalysts available for cleaning up automotive exhaust by oxidation of carbon monoxide and unburned hydrocarbons in the exhaust.

Such poisoning severely shortens the useful life of exhaust combustion catalysts. It has therefore been proposed that lead free gasoline be supplied for use in automobiles equipped with emission control devices in the nature of combustion catalysts.

The normal network of petroleum product distribution involves railroad tank cars, pipelines, water borne tankers, tank trucks and bulk storage tanks. For economical operation these are presently set up to handle different products. For example, the same pipeline will 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 two products will be diverted to storage for the lower grade product, thus avoiding degradation of the higher grade product.

When leaded gasoline, containing tetraethyl lead, tetramethyl lead or a mixture of transalkylation product of the two is contacted with the metal surfaces of transportation and storage facilities, a significant amount of lead is left deposited in scale and on the metallic surfaces. Upon using the same facilities for lead free gasoline, the latter product becomes contaminated to the extent of 0.07 gram of lead per gallon or more. These amounts of lead are sufficient to impair the life of exhaust emission catalysts.

Techniques are known for removal of lead from gasoline. The presently known techniques require considerable time or they would remove from a gasoline those additives which are desired to be retained, such as anti-oxidants, anti-icing additives, metal passivators and the like.

One such system is described in U.S. Pat. No. 2,368,261. Acid activated clay such as bentonite which has been treated with hydrochloric or sulfuric acid, is used in the process of this patent. Leaded gasoline is percolated through the clay to remove 95% of the lead present. Acid activated clays will also remove the additives which are

required for proper protection and functioning of automotive equipment.

Another approach is that described in U.S. Pat. No. 2,392,846. 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 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. Here also the additives desired to be retained will be 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. The resulting decomposition products are not readily soluble in hydrocarbons and hence are adsorbed on high surface desorbents. This avoids the property of tetraalkyl leads which presents the greatest difficulty in this separation namely infinite solubility in hydrocarbons.

SUMMARY OF THE INVENTION

According to the present invention, lead free motor fuel is handled through the normal distribution system of tankers, pipelines, bulk storage etc., alternatively with leaded gasoline in a manner which suits the convenience of the operator in maximum utilization of capital facilities. Means are provided at the point of distribution, namely service station gasoline pumps, for selective removal of such amounts of tetraalkyl lead as may have been picked up by the fuel in storage or transit. This novel means is the combination of a macroreticular resin having high surface area with surface groups which chemisorb tetraalkyl lead with high selectivity. A typical such group is a bromosuccinimide group which may be incorporated in crosslinked polystyrene, phenyl ethers, phenolic and epoxy resins. Other groups bound to a resin and within the scope of this disclosure include thiosuccinic ester, thiocarboxylic acid, thiocarboxylic ester, succinic acid, thiosuccinic acid, benzoic acid and camphor sulfonic acid alone or in the presence of silanes, o-cresol, ferric chloride, cupric nitrate and aluminum chloride. The macroreticular resin might be comprised of one or more of the resins noted above, and one or more of the groups listed above which chemisorb lead might be bonded to such a resin. It should also be noted that while a particular embodiment of the process of this invention is herein described for purposes of illustration, various modifications and adaptions thereof, which will be obvious to those skilled in the art, may be made within the spirit of this invention.

The term "macroreticular resin" is used herein in the sense defined by Kun and Kunin, "Macroreticular Resins III. Formation of Macroreticular Styrene-Divinylbenzene Copolymers", Journal of Polymer Science, vol. 6, 2689–2701 (1968).

A cartridge of such chemisorption agent may be installed at any point in the system for local storage and dispensing of lead free gasoline at the service station.

In a preferred embodiment the cartridge is placed in the discharge line from the service station pump. This permits utilization of presently installed equipment and avoids the changes in design which would be required if the treating agent were installed in the fill pipe to the local storage tank, in the tank itself, in the suction line to the pump or within the pump housing, all of which alternatives are contemplated within the scope of the in-

vention. A further alternative is placement of the lead removal cartridge in the automotive fuel system between the fuel tank of the vehicle and the carburetor. Flow rates are very small compared to those in bulk and retail distribution equipment, permitting long residence times and small volume cartridges.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 of the drawings enclosed herewith represents a typical service station gasoline pump modified according to the present invention.

FIG. 2 is an enlarged view of the canister for containing chemisorption agent in the combination of FIG. 1 and,

FIG. 3 is a view in fragmentary section of a cartridge for containing the chemisorption agent.

DESCRIPTION OF PREFERRED EMBODIMENTS

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 cansister **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** from which it passes through a chemisorption 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 macroreticulate resin of the type which characterizes this invention.

For the usual service station, a cartridge having a diameter of four inches and a length of twelve inches will be adequate to reduce the lead content to acceptable levels over a period 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.

A suitable macroreticulate resin is prepared according to the following specific example:

PREPARATION OF MACRORETICULAR RESINS BASED ON α-OLEFIN-MALEIC ANHYDRIDE-P-DIVINYL BENZENE

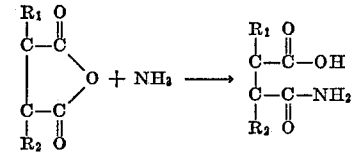
(1) Preparation of macroreticular resin based on styrene-maleic anhydride p-divinyl benzene

Procedure.—Maleic anhydride 4.85 g. is dissolved in 20 cc. dimethyl formamide (DMF) followed by adding 5.2 styrene and 1.30 g. p-divinylbenzene. Next .162 g. AZBN (azobis-isobutyronitrile) is dissolved in the monomer solution, and transferred to a polymerization flask equipped with stirring. Next 200 cc. of n-heptane is added and the temperature brought quickly up to 70° C. under nitrogen. Polymerization is continued for 3 hrs. at 70° C. reaching close to 100% completion. During the polymerization we observe that swollen particles are formed in the flask.

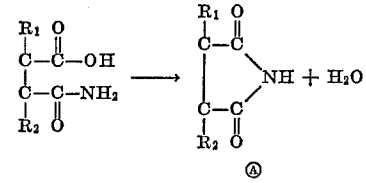
At the end of polymerization, the product is filtered off, and immediately dispersed in benzene (300 cc.) in order to extract out DMF. After 2 hrs. the polymer is recovered by filtration and redispersed in n-heptane (300 cc.) for 1 hr. Next the polymer is recovered by filtrations and dried at ambient temperature. Final product consists of a macroreticular resin in particle form.

(2) Preparation of styrene maleimide-p-divinyl-benzene from the copolymer under (1)

Procedure.—5 g. of styrene-maleic anhydride p-divinyl benzene as prepared in part (1) is swollen in 100 cc. of DMF in a 200 cc. pressure tube. The tube is heated up to 110° C. and pressured up with NH_3 up to 100 p.s.i. The following reaction occurs:



After completing the reaction (no further pressure drop) the reactor is purged with N_2 in order to remove the NH_3. Next step consists of bringing the reactor temperature up to 160–200° C. in order to complete the imidization.

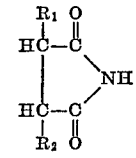


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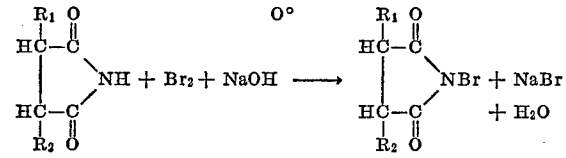
Alternative; Resin A can also be produced directly by substituting maleic anhydride with N-maleimide in the experimental procedure under (1).

(3) Preparation of macroreticular resin consisting of styrene - N-Bromo-succinimide-p-divinyl-benzene copolymer

Experimental procedure.—Resin A above is



Swollen in an ice-cold alkaline solution, Br_2 is added to the solution. The following reaction is carried out.



The product is washed with distilled water in order to remove NaBr followed by vacuum drying at ambient temperature.

The macroreticular resin containing maleic anhydride can be hydrolyzed to the di-acid form or treated with R_2S to the thio-acid form or thio ester (R=H or alkyl group) by conventional methods, and used in practice of this invention.

What is claimed is:

1. In a process for distributing and dispensing motor fuel: transportation means and storage means used alternatively for leaded and unleaded fuels and a plurality of lead free fuel dispensing stations each comprising a storage tank, a pump, a suction line connecting said tank and said pump and a discharge line from said pump; the improvement which comprises a bed of high surface area macroreticular resin having at the surfaces thereof one or more active groups wherein said groups are selected from assemblage consisting of thiocarboxylic acid, thiocarboxylic ester, succinic acid, thiosuccinic acid, thiosuccinic ester, benzoic acid, camphor sulfonic acid, o-cresol, cupric nitrate, and N-bromo-succinimide which are highly selective for the chemisorption of tetraalkyl lead, through which said unleaded fuels are passed in order to remove any lead contamination.

2. A process as claimed in claim 1 wherein said macroreticular resin is comprised of one or more resins selected from the group consisting of phenyl ether, crosslinked polystyrene, phenolic and epoxy resins.

3. A process as claimed in claim 2 wherein said group is N-bromo-succinimide and said macroreticular resin is styrene-p-divinyl-benzene.

4. A method for removing trace amounts of lead from substantially lead free motor fuel, said method comprising flowing the fuel intended to be lead free but which has acquired a minor content of tetraalkyl lead through equipment also used for leaded fuel through a body of high surface area macroreticular resin characterized by one or more groups at the surface thereof which are highly selective for chemisorption of tetraalkyl lead wherein said groups are selected from the assemblage consisting of thiocarboxylic acid, thiocarboxylic ester, succinic acid, thiosuccinic acid, thiosuccinic ester, benzoic acid, camphor sulfonic acid, o-cresol, cupric nitrate, and N-bromo-succinimide.

5. The method as claimed in claim 4 wherein said macroreticular resin is comprised of one or more resins selected from the group consisting of phenyl ether, crosslinked polystyrene, phenolic and epoxy resins.

6. The method as claimed in claim 5 wherein said group is N-bromo-succinimide and said macroreticular resin is styrene-p-divinyl-benzene.

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U.S. Cl. X.R.

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