Jan. 15, 1946. M. FRIEDMAN 2,392,846

METHOD FOR THE REMOVAL OF TETRAETHYL LEAD FROM HYDROCARBONS

Filed Aug. 17, 1944 3 Sheets-Sheet 1

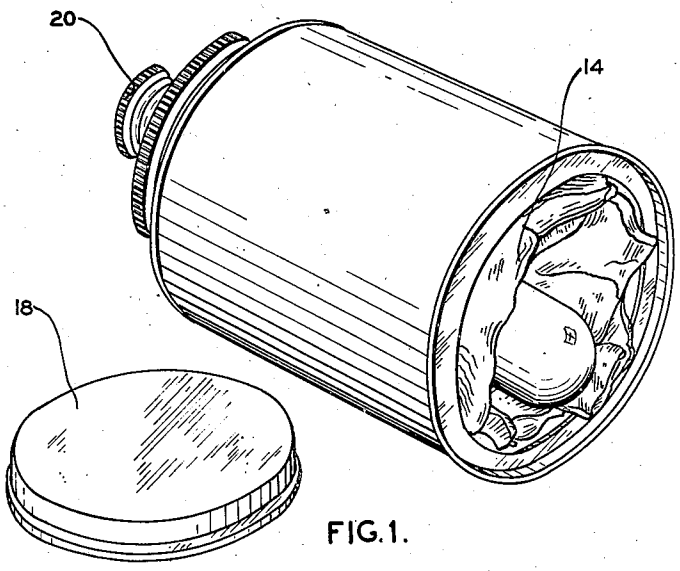


FIG. 1.

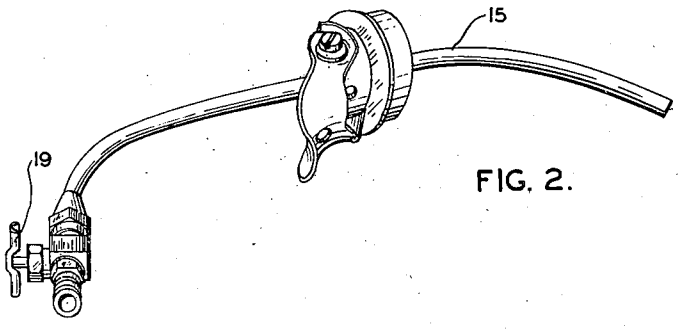
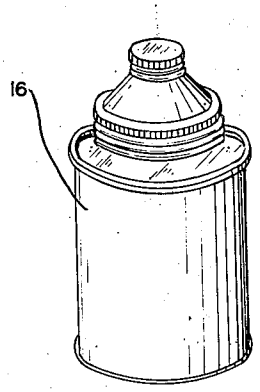


FIG. 2.



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METHOD FOR THE REMOVAL OF TETRAETHYL LEAD FROM HYDROCARBONS

Filed Aug. 17, 1944 3 Sheets-Sheet 2

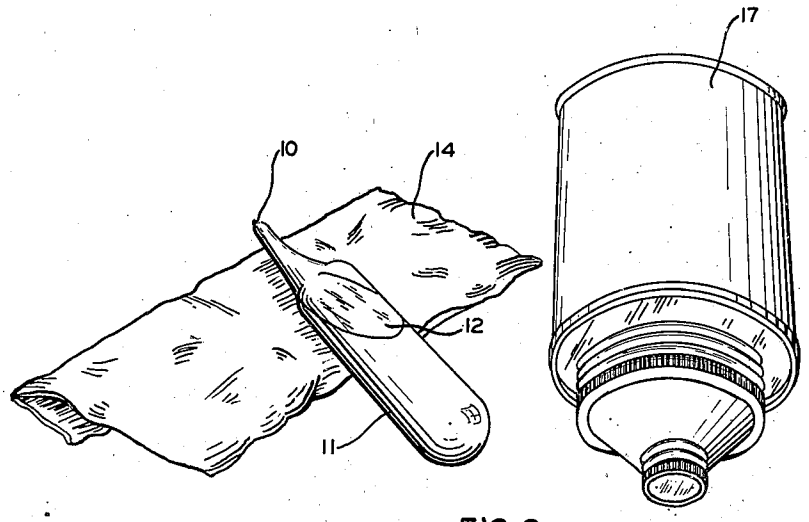

FIG. 3.

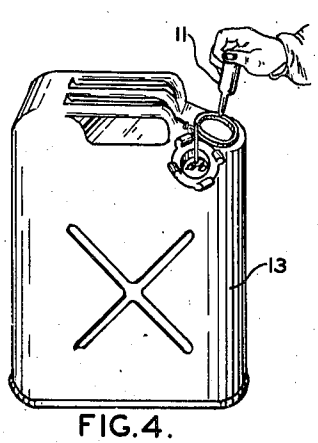

FIG. 4.

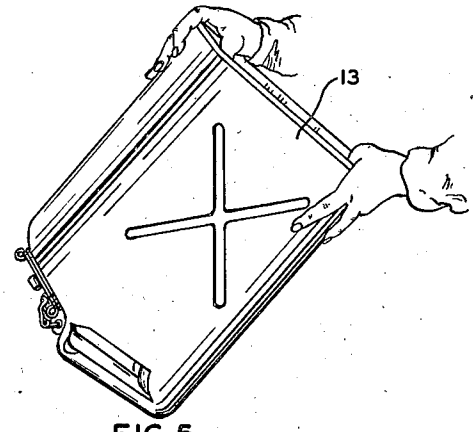

FIG. 5.

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FIG.6.

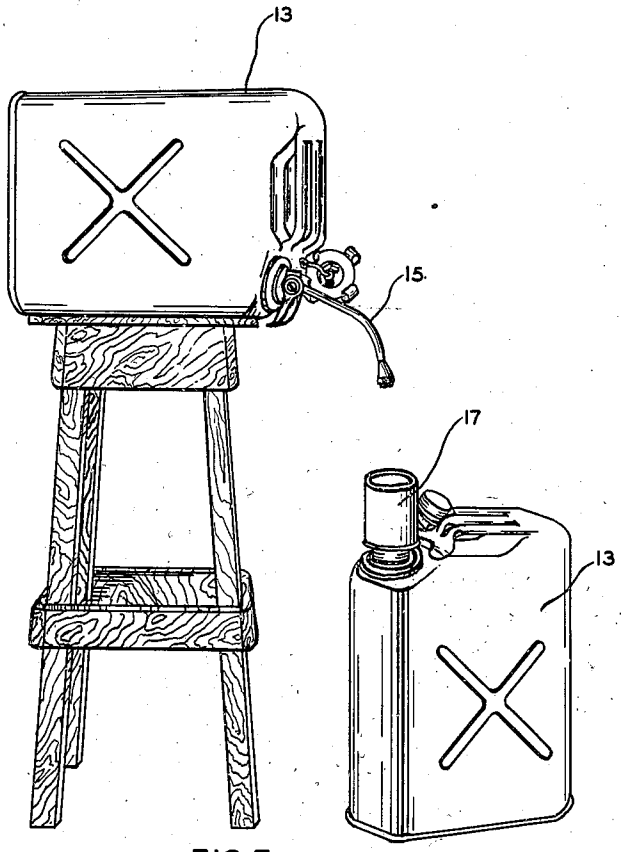

FIG. 7.

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Patented Jan. 15, 1946

2,392,846

UNITED STATES PATENT OFFICE

2,392,846

METHOD FOR THE REMOVAL OF TETRAETHYL LEAD FROM HYDROCARBONS

Maurice Friedman, Asbury Park, N. J., assignor to the United States of America as represented by the Secretary of War

Application August 17, 1944, Serial No. 549,952

4 Claims. (Cl. 196—44)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

The invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment to me of any royalty thereon.

My invention relates to a method for the removal of tetraethyl lead from gasoline by means of chemical agents. No special equipment is required except for the necessary chemicals, anhydrous stannic chloride and activated carbon, and a simple decanting tube. Although the method developed has been designed for use with a 5-gallon container, it can easily be adapted for larger quantities of gasoline. This method is equally effective in removing tetraethyl lead from both 80-octane gasoline, commonly known as "all purpose motor fuel," and 100-octane gasoline, commonly known as "aviation fuel."

In order to obtain maximum efficiency from modern high compression internal combustion engines, it is necessary to use fuels having high octane values. Such fuels are produced by incorporating into the base stock volatile metal compounds, such as tetraethyl lead, along with the so-called lead scavengers such as ethylene dibromide and ethylene dichloride. While such fuels are very effective for the operation of high compression internal combustion engines, they are said to be unsatisfactory for the operation of engines of the low compression type, such as are utilized in motor-generators, or for the operation of other devices, such as field stoves, torches and lanterns, designed for use with fuel free of volatile metal compounds.

Since leaded gasoline is the only type of fuel supplied in the field, much difficulty has been encountered in the operation of power units, field stoves, torches and lanterns, due to the deposition of lead in various parts of these devices. To supply lead-free gasoline in the field is difficult, since the requirements for this type of fuel are comparatively limited and the problem of supply would become complicated if such fuel were to be supplied regularly in the field. Because of this, it has become necessary to devise a simple method for deleading gasoline in the field with a minimum of extraneous equipment.

Gasoline is an extremely complex mixture of hydrocarbons boiling within range of 80° F. to 410° F. Although it is impossible to say exactly how many hydrocarbon compounds are present in a given gasoline, it is generally agreed that due to the vast number of isomers and stereoisomers which are possible, the total number of possibilities is probably 4000. This complexity is further augmented by the presence of olefine and diolefine hydrocarbons which are obtained in the so-called "cracking" processes now commonly used to increase the yeld of gasoline from crude petroleum. These olefine and diolefine molecules are unsaturated with respect to hydrogen, and therefore contain extremely reactive "double bonds" that have a tendency to form addition compounds polymerizing to high carbon chain molecules, which often lead to the deposition of gum in the intake system and combustion chamber of an engine, field stove, torch and lantern. Such gum formation is greatly enhanced and accelerated by the presence of catalytic chemical agents of the type that have possibilities for use as deleading materials.

Tetraethyl lead is a heavy, colorless liquid, soluble in gasoline and inert under ordinary exposure to air, light, heat and water, and unreactive to all but the most active of chemical reagents. Its extreme stability, therefore, makes its removal dependent upon its conversion to some other form of lead compound insoluble in gasoline. Since the tetraethyl lead molecule is very similar structurally and chemically to the hydrocarbons in gasoline, this conversion must necessarily be such that the characteristics of the gasoline are not materially changed, and the formation of harmful reaction completely avoided, or at least kept to a safe minimum.

In view of the complexity of gasoline composition, and of the extreme stability of tetraethyl lead and its similarity to most hydrocarbon molecules, it is immediately apparent that great difficulty would be attached to finding a chemical agent which would selectively react with tetraethyl lead without materially affecting the hydrocarbon molecules present in the gasoline. By my invention I have devised a method and means which effectively removes tetraethyl lead from gasoline without essentially changing the chemical and physical properties of the original fuel.

The method developed in my invention makes use of C. P. or commercial anhydrous stannic chloride, also known as tin tetrachloride, as a means of precipitating tetraethyl lead from gasoline, the probable reaction being:

$$Pb(C_2H_5)_4 + SnCl_4 \rightarrow Pb(C_2H_5)_2Cl_2 + Sn(C_2H_5)_2Cl_2$$

Lead tetraethyl	Stannic chloride	Lead diethyl dichloride	Tin diethyl dichloride

The lead dichloride formed is insoluble in gasoline and can, therefore, be removed by filtration, after agitating with a mixture of activated carbon treated with or without an organic amine for the purpose of breaking up the colloidal solution which is formed and adsorbing or absorbing some

of the reaction products and residual stannic chloride.

The mechanical features of my method are extremely simple and require no extraneous equipment except for the package containing the chemicals, a simple tube for decanting and, of course, a container to carry out the deleading operation. (The one containing the gasoline to be deleaded is used.) The time required to delead 5 gallons of gasoline is approximately 25 minutes, of which only 10 minutes is the actually working time during which the operator is occupied. It is readily possible for one operator to delead three or four batches (15–20 gallons) of gasoline at the same time, thus making it possible to prepare approximately 35 gallons of deleaded gasoline in one hour.

The general object of my invention is to provide a simple method for deleading gasoline in the field with a minimum of extraneous equipment.

Another object of my invention is to provide a small compact container which encloses the chemicals to be used in the deleading process.

Another object of my invention is to provide a small compact container which, upon emptying the contents thereof, can be used as a filtering funnel in the deleading process.

Another object of my invention is to provide an ampoule which is sealed and contains the anhydrous stannic chloride reagent.

A further object of my invention is to provide a package containing activated carbon.

Other objects and advantages will appear hereinafter from the following description and drawings.

Referring to the drawings, which are for illustrative purposes only:

Fig. 1 shows a chemical package, a filter-funnel assembly and a method of packing deleading chemicals.

Fig. 2 is a decanting tube and a complete chemical package.

Fig. 3 shows the deleading chemicals, the package ready for use as a filter-funnel.

Fig. 4 shows an ampoule of stannic chloride being emptied into a container.

Fig. 5 shows the container being agitated after addition of the ampoule of stannic chloride.

Fig. 6 shows a package of activated carbon which will be emptied into the container of Fig. 4 after agitation in Fig. 5.

Fig. 7 shows the container, the decanting tube, the filtering funnel and the receiving container in operation.

In the method of deleading referring to Fig. 3 the tip **10** of the ampoule **11** containing **18—22** ml. anhydrous stannic chloride **12** is broken and its contents emptied into the container **13** in Fig. 4 containing 5 gallons of the gasoline to be deleaded. The gasoline is stirred from 3 to 5 minutes by agitating the container **13** as shown in Fig. 5. The package containing 100–125 grams of the activated carbon **14** as shown in Fig. 6, prepared by finely powdered activated carbon in a closed container, is then emptied into the container **13** in Fig. 4 and the gasoline again agitated as shown in Fig. 5 for a period of from 6 to 10 minutes. Referring to Fig. 7 the decanting tube **15** is inserted and clamped into position, the container **13** is placed on its side as illustrated, and then allowed to stand for 10 minutes, or until such time as is necessary to allow the main mass of reaction sludge to settle to the bottom of the container **13**, as will be indicated by the flow of a clear liquid from the decanting tube **15**.

The package which contained the chemicals **16** in Fig. 2 is converted to a filter and funnel **17** in Fig. 7 by removing the larger end **18** and the smaller end **20** in Fig. 1. This funnel **17** is placed in the mouth of the receiving container **13**, narrow end downward, and the flow rate of the treated gasoline adjusted by means of the valve **19** on the decanting tube **15** so that the funnel **17** will not overflow. The decanting operation is continued, with the container **13** in its original horizontal position, until the flow of gasoline stops. No further attempt at recovering the remaining gasoline is advisable, since the tube **15** has been purposely designed so that all but approximately one to two quarts of gasoline is recovered, the wasted portion being chiefly mixed with the reaction sludge which would clog the filter.

The sludge is swirled around in the container **13** as shown in Fig. 5 and is then discarded. It is not necessary to clean the container **13** between each operation, but safe practice would be to give it one thorough cleaning with gasoline every fifth or sixth deleading operation. The use of water as a cleansing agent is not advisable unless the container **13** is thoroughly dried prior to its reuse, since the presence of even a slight amount of water causes hydrolysis of the stannic chloride thereby adversely affecting its ability to react with tetraethyl lead.

A typical gasoline was deleaded by the procedure given above, and the analyses of the original gasoline and of the deleaded gasoline follow:

	Original gasoline	Deleaded gasoline
Tetraethyl lead, ml./U. S. gallon	2.63	0.20
A. S. T. M. dissolved gum, mgs./100 ml.	5.00	15.00
A. P. I. gravity, degrees A. P. I.	59.34	59.32
Reid vapor pressure, lbs./sq. in.	7.50	7.30
Tin salts		None
Corrosion, A. S. T. M. copper strip	None	None
Color	Red	[1] White
Octane number, CFR motor method	80	64

[1] Colorless.

Distillation range

	Original gasoline	Deleaded gasoline
Initial boiling point, °F.	106	104
10% evaporated @, °F.	142	144
20% evaporated @, °F.	158	160
30% evaporated @, °F.	174	175
40% evaporated @, °F.	188	189
50% evaporated @, °F.	203	204
60% evaporated @, °F.	216	219
70% evaporated @, °F.	236	236
80% evaporated @, °F.	258	258
90% evaporated @, °F.	292	296
Final boiling point, °F.	367	365
Recovery, per cent	98.7	98.0
Residue, do	1.2	1.0
Loss, do	0.1	1.0

From the above analyses, it is immediately apparent that the deleading procedure reduced the tetraethyl lead content of the original gasoline by 93%. The small differences shown for some of the other properties are well within the permissible variation of the analytical test methods themselves, and it can be definitely stated that, with the exception of the dissolved gum value, and of course the tetraethyl lead content, the other properties of the original gasoline have not been materially changed by the deleading operation. The octane number of the deleaded gasoline is lowered due to the removal of tetraethyl lead which was originally used to increase the octane rating of the base stock.

While the form of embodiment of my invention as herein disclosed constitutes a preferred form, it is to be understood that other forms might be adopted, all coming within the scope of the claims.

Having thus described my invention I desire to secure by Letters Patent and claim:

1. The method for treating a mixture of liquid hydrocarbon fuel and organolead compound to remove the latter from said mixture, which comprises adding to a predetermined quantity of said mixture a predetermined quantity of anhydrous stannic chloride, agitating the resultant quantity of mixture and anhydrous stannic chloride for a predetermined time, adding an adsorbent to the agitated mixture and anhydrous stannic chloride, agitating the resultant quantity of mixture, anhydrous stannic chloride and adsorbent for a predetermined time, decanting a resultant portion of clear liquid from the said quantity of material, and finally filtering said resultant portion of said clear liquid.

2. The method for treating a mixture of liquid hydrocarbon fuel and organolead compound to remove the latter from said mixture, which comprises adding to a predetermined quantity of raw mixture a predetermined quantity of anhydrous stannic chloride, agitating the resultant quantity of mixture and anhydrous stannic chloride for a predetermined time, adding activated carbon to the agitated mixture and anhydrous stannic chloride, agitating the resultant quantity of mixture, anhydrous stannic chloride and activated carbon for a predetermined time, decanting a resultant portion of clear liquid from said quantity of material, and finally filtering said resultant portion of said clear liquid.

3. The method for treating a mixture of liquid hydrocarbon fuel and tetraethyl lead to remove the latter from said mixture, which comprises adding to a predetermined quantity of the raw mixture a predetermined quantity of anhydrous stannic chloride, agitating the resultant quanttiy of mixture and anhydrous stannic chloride for a predetermined time, adding activated carbon to the agitated mixture and anhydrous stannic chloride, agitating the resultant quantity of mixture, anhydrous stannic chloride and activated carbon for a predetermined time, decanting a resultant portion of clear liquid from said quantity of material, and finally filtering said resultant portion of said clear liquid.

4. The method for treating a mixture of gasoline and tetraethyl lead to remove the latter from said mixture, which comprises adding to a predetermined quantity of the gasoline and tetraethyl lead a predetermined quantity of anhydrous stanic chloride, agitating the resultant quantity of mixture and anhydrous stannic chloride for a predetermined time, adding activated carbon to the agitated mixture and anhydrous stannic chloride, agitating the resultant quantity of mixture, anhydrous stannic chloride and activated carbon for a predetermined time, decanting a resultant portion of clear liquid from said quantity of material, and finally filtering said resultant portion of said clear liquid.

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