Patented Nov. 9, 1948 2,453,138

UNITED STATES PATENT OFFICE

2,453,138

PROCESS OF DELEADING GASOLINE

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No Drawing. Application May 2, 1946, Serial No. 666,805

7 Claims. (Cl. 196—44)

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

The invention described herein relates to a process for removing tetraethyl lead from leaded gasoline, and more particularly to a process in which the leaded gasoline is treated with a reagent capable of precipitating out the tetraethyl lead and the precipitate then settled out by treatment with a basic adsorbent or absorbent compound such as an amine-treated charcoal.

Because of the fact that most of the internal combustion engines in use today are of the high-compression type and operate more efficiently on fuel of high-octane rating, the base stock of most fuels is treated with tetraethyl lead compounds to increase the octane rating of the fuel. However, certain apparatus of the type used by the Armed Forces in the field and by farmers and others, such as low-compression engines, gasoline lanterns and gasoline stoves, does not operate satisfactorily with leaded gasoline because lead deposits are formed on such vital parts as valves and burner tips. In many cases, unleaded fuel is not readily available to those having need of it, so that a method of quickly and inexpensively deleading leaded gasoline is desirable.

Heretofore, several methods have been devised for deleading leaded gasoline, but it has been found that in actual practice these methods do not produce results as satisfactory as desired because they require too much time, they increase the gum content of the gasoline to an undesirable extent, they remove the dye from the gasoline but very little of the tetraethyl lead, the volume of treating agent required relative to the volume of gasoline deleaded is so large that the methods are impracticable or the gasoline is left with acid constituents or other undesirable constituents.

In one of these methods a relatively small quantity of stannic chloride is mixed with the leaded gasoline. This reacts with the tetraethyl lead to form diethyllead dichloride and diethyltin dichloride which being insoluble in gasoline are precipitated. Any stannic chloride in excess of that required to precipitate out the lead is removed from the gasoline by adding water in order to prevent polymerization of unsaturated hydrocarbons in the gasoline which would increase the gum content to an undesirable extent. Although this process accomplishes the removal of tetraethyl lead from gasoline in a fairly satisfactory manner it requires a good deal of time to complete a deleading operation and results in the

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waste of a rather large quantity of the gasoline being treated. In addition undesirable acid constituents remain in the deleaded gasoline after treatment.

In my improved process for deleading gasoline I initially add to the leaded gasoline a relatively small quantity of anhydrous stannic chloride slightly in excess of the amount required to precipitate out the quantity of tetraethyl lead contained in the gasoline and vigorously stir or shake the mixture. The amount of precipitant required for a particular quantity of gasoline can be determined from the octane value of the gasoline. After the lead has been precipitated (which requires approximately 5 minutes) an adsorbing and absorbing agent comprising an amine treated charcoal is added. In practice this is added to the gasoline at one time and the mixture of gasoline and treating agent shaken or stirred for approximately 3 minutes to secure a uniform distribution of the treating agent in the gasoline mixture. Within 10 minutes after this last stirring the precipitate and charcoal will have settled sufficiently so that removal of the top level of gasoline may be commenced, it being preferably passed through a filter while being drawn off in order to remove any fine bits of precipitate which may have remained suspended in the solution.

Because the amine treated charcoal forms a relatively heavy and compact sludge with the precipitate formed when stannic chloride is added to leaded gasoline a relatively rapid settling of the precipitate is secured so that the total time required to complete a deleading operation is reduced by about one-third of the time required by the processes described in the prior art. In addition a more complete settling occurs so that a greater recovery of the deleaded gasoline treated can be secured, and since no acid is formed in any of the reactions which occur the treated gasoline is free from acid constituents and will not corrode the delicate mechanism of the devices in which the gasoline is used as a fuel. Furthermore, the gum content of the treated gasoline is not increased to any greater extent than in the best of the prior methods of treatment, and in no case to such an extent as to affect the suitability of the gasoline for use as a fuel.

Accordingly, it is an object of the invention to provide a new and improved process for removing tetraethyl lead from gasoline in which the tetraethyl lead is precipitated from leaded gasoline with anhydrous stannic chloride and the precipitate settled out by adding an amine treated charcoal to the mixture.

Another object of the invention is the provision of a new and improved process for deleading gasoline which may be more rapidly carried out and which results in a greater recovery of deleaded gasoline than any of the deleading processes heretofore known and used.

A further object of the invention is the provision of a new and improved process for deleading gasoline which is inexpensive and may be readily carried out on any desired quantity of gasoline with a minimum of equipment so that the process is adaptable for use by the Armed Forces in the field or by others desiring deleaded gasoline when only leaded gasoline is available.

In order to disclose the process sufficiently to permit the practice thereof an example of a deleading operation performed on a 5 gallon lot of leaded gasoline will be described. In every case the container used for containing the gasoline during the deleading operation should be dry because the process is much less efficient if even a small quantity of water is present. To this gasoline 100 ml. of a precipitating agent made by dissolving 1 part by volume of stannic chloride in 4 parts by volume of a solvent such as ligroin is added and the mixture stirred or shaken for approximately 2 minutes to secure an even dispersion of precipitant in the gasoline. This amount of stannic chloride (approximately 20 ml.) is sufficient for the treatment of 5 gallons of gasoline where the tetraethyl lead content varies between 2.22 mls. per gallon and 3 mls. per gallon. The 80 octane gasoline supplied to Army Ground Forces in the field has a lead content falling within this range as does most of the gasoline sold commercially for use in automotive vehicles. If the lead content is considerably below 2.22 mls. per gallon, for example 1.9 ml. per gallon, and the same amount of stannic chloride is used reaction compounds are formed with the absorbing and settling agent which interfere with the quick settling of the reaction products so that the amount of stannic chloride used should be reduced for such gasolines. In case the lead content exceeds 3 mls. per gallon as in 100 octane aviation gasoline, the amount of stannic chloride added should be increased. In every case the proportion of reagent to tetraethyl lead should be approximately the same as in the above example.

Upon completion of the stirring above described the mixture is allowed to stand approximately 3 minutes after which the adsorbing and absorbing agent is added. This is preferably in the form of a slurry formed by mixing approximately 28 gms. of a tertiary amine such as triethylamine

$$[(C_2H_5)_3N]$$

and approximately 65 gms. of activated charcoal in 400 mls. (280 gms.) of ligroin. This will form approximately a pint of slurry and this is poured into the mixture of gasoline and precipitant and stirred for approximately 3 minutes and then allowed to stand until the reaction products and charcoal sludge settle to the bottom of the container before any gasoline is removed. After approximately 10 minutes the charcoal sludge and precipitate will have settled sufficiently to permit removal of some of the gasoline from the upper level of the container, but it should be allowed to stand up to 30 minutes so that all of the recoverable gasoline is cleared of precipitate. When aviation or other gasoline of high octane content is being treated, a longer period (up to 20 minutes) may be required before any clear gasoline can be removed from the treating container and at least 45 minutes must elapse before all the precipitate has settled. Various charcoals have been tested and found to be satisfactory for use in the adsorbing mixture, among them being Nuchar 000 and Nuchar Aqua, both produced and sold by the West Virginia Paper and Pulp Company.

Separation of the treated gasoline from the settled waste may be effected by syphoning it from the treating container, but a minimum of 1000 mls. of fluid should be left in the container because this is approximately the volume of the settled waste when 5 gallons of gasoline is treated as above described. Thus recovery of gasoline averages 95% of the original volume. This is a saving of about ⅓ in the amount of gasoline wasted when the processes of the prior art are used. In order to remove every trace of reaction products, the deleaded gasoline is preferably filtered through a cotton filter.

If deleading is to be carried out as a continuous process, the waste products remaining in the treating container after one deleading operation has been completed is poured out and the deleading operation may be repeated. However, after several consecutive operations the treating container should be washed or rinsed with gasoline.

When stannic chloride is added to a gasoline containing tetraethyl lead diethyllead dichloride and diethyltin dichloride, both of which are insoluble in gasoline, are formed in accordance with the following equation:

$$SnCl_4 + (C_2H_5)_4Pb \rightarrow (C_2H_5)_2SnCl_2 + (C_2H_5)_2PbCl_2$$

To complete this reaction and insure the precipitation of all the tetraethyl lead a slight excess of stannic chloride is required, but it should be kept to a minimum because the excess stannic chloride tends to promote the polymerization of the unsaturated hydrocarbons in gasoline thus increasing the gum content which is undesirable. Generally, it has been found that the most satisfactory results are obtained when stannic chloride is used in the proportion of approximately 2.50 moles to every mole of tetraethyl lead in the gasoline.

Excess stannic chloride should be removed from the solution or neutralized as soon as all the tetraethyl lead has been precipitated which in the ordinary case will occur within 5 minutes after it is added to the gasoline. The probable reaction between the amine present in the amine charcoal mixture (triethylamine in the above example) and the reaction products of the above equation may be expressed in the following equation:

$$(C_2H_5)_2SnCl_2 + N(C_2H_5)_3 \longrightarrow [(C_2H_5)_2SnCl_2 \cdot N(C_2H_5)_3]$$
complex

$$(C_2H_5)_2PbCl_2 + N(C_2H_5)_3 \longrightarrow [(C_2H_5)_2PbCl_2 \cdot N(C_2H_5)_3]$$
complex

These complexes are adsorbed on the charcoal.

Several amines have been tested in carrying out the above process including dimethylaniline, pyridine, tributylamine, N-methylmorpholine, N-ethylmorpholine, and triethylamine, but the latter has two advantages over the others, namely it produces a heavier and more compact sludge so that more gasoline may be recovered, and the waste products settle in less time so that the total time for carrying out a deleading operation is reduced.

In order to expedite the performance of the deleading operation by this method the treating materials used may be packaged in a kit designed

for treating a specific quantity of gasoline of a known octane rating. This kit should include a container of stannic chloride slurry of a volume sufficient to treat a specific volume of gasoline, for example 5 gallons, and a second container of the amine treated charcoal slurry of the required volume for treating the quantity of gasoline for which the kit is designed.

The above described example of a method for deleading gasoline is described for the purpose of disclosing the steps to be performed in carrying out a deleading operation in accordance with my improved method. It will be obvious that modifications may be made in the process disclosed without departing from the scope of the invention, hence I do not wish to be limited to the precise process above described but desire to include within the scope of the invention all those modifications included in the claims set forth below.

I claim:

1. The process of deleading gasoline containing tetraethyl lead which comprises adding stannic chloride to the gasoline and then treating the mixture with a tertiary-amine-treated charcoal to adsorb the reaction products and settle out the same.

2. The process of deleading gasoline containing tetraethyl lead which comprises adding stannic chloride to the gasoline, then after an interval treating the mixture with a tertiary-amine-treated charcoal to adsorb the reaction products and settle out the same, and then after another interval separating the deleaded gasoline from the settled precipitate.

3. The process of deleading gasoline containing tetraethyl lead which comprises precipitating the tetraethyl lead by adding an excess of stannic chloride to the gasoline, then after an interval adding a tertiary-amine-treated charcoal to adsorb the resultant precipitate and excess stannic chloride and settle out the same, and then after another interval separating the deleaded gasoline from the settled precipitate.

4. The process of deleading gasoline containing tetraethyl lead which comprises adding stannic chloride to the gasoline in the proportion of approximately 2.5 moles of stannic chloride to 1 mole of tetraethyl lead to precipitate the latter, then after an interval adsorbing and settling the resultant precipitate by adding a tertiary-amine treated charcoal, and then after an interval separating the deleaded gasoline from the settled precipitate.

5. The process of deleading gasoline containing tetraethyl lead which comprises adding stannic chloride to the gasoline to precipitate out the tetraethyl lead, then after an interval treating the mixture of gasoline and stannic chloride with a mixture of charcoal and a tertiary amine to adsorb and settle out the resultant precipitate, and then after another interval separating the deleaded gasoline from the settled precipitate and reaction products.

6. The process of deleading gasoline containing tetraethyl lead which comprises adding an excess of stannic chloride to the gasoline to precipitate out the tetraethyl lead, then after an interval adding a mixture of triethylamine and charcoal to the gasoline to remove the unreacted stannic chloride and adsorb the resultant precipitate and reaction products, and then after another interval separating the deleaded gasoline from the settled precipitate and reaction products.

7. The process of deleading gasoline containing tetraethyl lead which comprises precipitating the tetraethyl lead by adding a predetermined excess quantity of stannic chloride to a predetermined quantity of the untreated leaded gasoline, agitating the gasoline stannic chloride mixture for a predetermined interval, then after an interval adding a predetermined quantity of a tertiary-amine-treated charcoal to the predetermined quantity of gasoline stannic chloride mixture to adsorb the reaction products and excess stannic chloride and settle the same, agitating the mixture for a predetermined interval and then after an interval separating the deleaded gasoline from the settled precipitate and reaction products.

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