

# UNITED STATES PATENT OFFICE

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## GASOLINE TREATING PROCESS

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This invention concerns a novel process for improving the quality of gasoline type petroleum fuels. In accordance with this invention hydrocarbons boiling within the gasoline boiling range are subjected to a refining treatment consisting of contacting the gasoline with lead tetraacetate. This process is particularly applicable to the treatment of cracked gasolines and is effective to materially improve what may be called the "engine cleanliness" of the gasoline.

In the petroleum refining industry attempts are being made to provide higher quality gasoline fuels by altering characteristics of the gasoline resulting in the formation of engine deposits on combustion. It has particularly been found that gasoline produced by cracking processes has inferior burning characteristics as indicated by the condition of the engine after a period of use. Particularly in the case of cracked gasolines, sludge forming constituents and constituents forming polymers or other materials, cause deposition of what is known as "varnish" in an engine. Consequently, at the present time efforts are being made to improve this particular characteristic of a gasoline fuel.

It is not yet understood which constituents of gasoline, or particularly which constituents of cracked gasolines, cause the problem of engine varnish formation. However, it has now been found that in some manner, not entirely understood, after gasoline is treated with lead tetraacetate the quality of the gasoline is materially improved. It is theorized that the refining effect of the lead tetra-acetate may be due to the polymerization or condensation and removal of diolefins which are known to be formed as the result of cracking operations.

In accordance with this invention therefore a gasoline is refined by treating the gasoline with lead tetra-acetate. The conditions of treatment are not particularly critical as the refining effect apparently occurs readily and rapidly. Thus it is entirely suitable to contact lead tetra-acetate with the gasoline to be refined at ordinary temperatures and pressures for a period of about 45 minutes or less. In general, about 1 to 6% of lead tetra-acetate by weight, based on the gasoline, is to be employed. As a result of this treatment, a precipitate is formed which must be removed from the gasoline to provide the finished gasoline product. The precipitate elimination may be conducted in any desired manner such as by settling, filtration, or centrifuging. However, it is particularly preferred that the gasoline be freed of precipitate by distilling the gasoline to permit

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recovery of the finished gasoline as an overhead product.

In order to fully disclose the nature of this invention and to exemplify the conduct of the invention the following examples are presented. In these examples the evaluation of the gasoline before and after treatment as regards the engine cleanliness of the gasoline are reported in terms of the "fluoborate deposit factor." This deposit factor is determined in a laboratory test found to correlate with actual engine cleanliness determinations. The test utilizes the coupling reaction which takes place between diazotised p-nitroaniline and certain unsaturated compounds (which cause engine fouling) to form a colored compound. Intensity of color formed after a given time interval is an index of the deposit forming compounds present. In running the test the fraction of the sample boiling over 275° F. and purified by treatment with dilute acid and alkali and steam distillation to 3% bottoms is used. A known quantity of this fraction is added to a solution of p-nitroaniline diazonium fluoborate (NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N=NBF<sub>4</sub>) in acetone, and the optical density measured at intervals in a Hellige-Diller emission photometer. The optical density is plotted against time and the value after 20 minutes read from the curve. The optical density multiplied by the ratio of the fraction boiling over 275° F. to the whole sample, gives the diazonium fluoborate deposit factor.

### Example I

A sample of naphtha obtained by the thermal cracking of a gas oil fraction was subjected to treatment with lead tetra-acetate. The naphtha tested boiled in the range of about 136 to 423 degrees F. and had the following inspections:

Engler distillation:	
Initial boiling point	° F. 136
Mid boiling point (50% distilled)	° F. 275
Final boiling point	° F. 432
A. P. I. gravity	48.8
Gum (G. M.)	mg. 26.0
Bromine number	34.1
A. S. T. M. motor octane number	72
CFR octane number	80

The treatment consisted of mixing 125 cc. of the naphtha with 3.7 gms. of lead tetra-acetate. The mixture was maintained for 45 minutes at room temperatures and pressure. At the end of this time a white precipitate had formed which was filtered from the gasoline. Samples of the naphtha corresponding to the naphtha before

and after treatment were then subjected to the diazonium fluoborate deposit factor test. It was found that the optical density of the naphtha before treatment was 0.638 while after treatment the optical density had been decreased to 0.108, indicating a material improvement in the quality of the thermal naphtha.

#### Example II

A sample of commercial gasoline boiling in the range of 95 to 405 degrees F. and having the following inspections was treated with lead tetra-acetate:

Engler distillation:

Initial boiling point	°F.	95
30% distilled	°F.	176
45% distilled	°F.	212
65% distilled	°F.	266
Final boiling point	°F.	405
A. P. I. gravity		60.5
Reid vapor pressure		3.4
Bromine number		26.4
A. S. T. M. octane No.		75
C. F. R. octane No.		81

In this case 300 cc. of the gasoline were mixed with 10 gms. of lead tetra-acetate for a period of 45 minutes. Thereafter the resulting precipitate was filtered and the gasoline was tested. On testing it was found that the original gasoline had a deposit factor of 10.80, while after treatment the deposit factor was 4.52. These data again bear out the material improvement in engine cleanliness of the gasoline obtained by the lead tetra-acetate treatment. It is particularly notable that this improvement was obtained by treating a base gasoline consisting of a mixture of virgin gasoline, catalytically cracked gasoline, and other gasoline components.

#### Example III

Thermal naphtha of the same nature as that identified in Example I was subjected to the identical lead tetra-acetate treatment. In this case however, tests were conducted to determine the gum content of the gasoline before and after treatment as indicated by ASTM Test D-381-49. It was found that the thermal naphtha before treatment had an ASTM gum content of 168 mg. per 100 ml. However, after lead tetra-acetate treatment the ASTM content of the naphtha had increased to 244.2 mg. per 100 ml. This thermal naphtha was therefore subjected to a distillation operation in which the gasoline was removed as the overhead product. In distilling the gasoline to permit recovery of 95% of the gasoline, it was found that the ASTM gum content of the gasoline was reduced to only 3 mg. per 100 ml. This example particularly shows the desirability of following the lead tetra-acetate treatment with a distillation operation in which the gasoline is distilled to free the gasoline from precipitate formed during the treatment and from gum forming constituents which remain behind as a bottoms product. It is apparent that the distillation may be carried out to recover substantially all of the gasoline, since the data indicates that

the gum forming constituents are selectively retained during distillation as still bottoms.

As indicated therefore, the process of this invention comprises treating gasoline with about 1 to 6% by weight of lead tetra-acetate. As indicated, the treatment may be conducted at ordinary temperatures and pressures or if desired, at higher temperatures and pressures; depending on the refining effect desired. The time of reaction may be varied from a maximum of about 45 minutes down to any desired lower limit of contacting. After lead tetra-acetate treatment, if desired, the resulting precipitate may be removed by filtration or the equivalent to provide the finished gasoline. However, when it is desirable to simultaneously lower the gum content of the gasoline, it is particularly contemplated that the treated gasoline be subjected to distillation.

What is claimed is:

1. The process for refining a gasoline consisting of contacting gasoline with a small percentage of lead tetra-acetate and thereafter separating the gasoline from the resulting precipitate.

2. The process defined by claim 1 in which about 1 to 6% of lead tetra-acetate, based on the weight of the gasoline, is employed.

3. The process for improving the quality of a gasoline comprising the steps of mixing about 1 to 6% of lead tetra-acetate with the said gasoline for a period less than about 45 minutes, whereby a precipitate is formed, thereafter separating the said gasoline from the said precipitate.

4. The process defined by claim 3 in which the said separation is carried out by filtration.

5. The process of claim 3 in which the said separation is carried out by centrifuging.

6. The process defined by claim 3 in which the said separation is carried out by distillation.

7. The process defined by claim 3 in which at least a part of the said gasoline constitutes a cracked gasoline.

8. The process for improving the quality of a hydrocarbon mixture boiling in the gasoline boiling range consisting of maintaining the mixture in contact with about 1 to 6% of lead tetra-acetate for a period of not more than about 45 minutes, and thereafter subjecting the mixture to a distillation operation in which at least about 95% of the gasoline is removed as an overhead product.

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#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

Number	Name	Date
81,071	de Gerbeth	Aug. 18, 1868
400,633	Cazin	Apr. 2, 1889
1,394,987	Fleming	Oct. 25, 1921
1,823,553	Burke	Sept. 15, 1931

#### FOREIGN PATENTS

Number	Country	Date
153,585	Germany	July 21, 1904