

PATENT SPECIFICATION

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- (21) Application No. 50501/77 (22) Filed 5 Dec. 1977 (19)
(31) Convention Application No. 754461 (32) Filed 27 Dec. 1976 in
(33) United States of America (US)
(44) Complete Specification Published 21 Jan. 1981
(51) INT. CL.³ C10G 25/00
(52) Index at Acceptance
C5E SR



(54) PROCESS FOR REMOVAL OF ALKYL LEAD IMPURITIES FROM LIQUID HYDROCARBONS

(71) We, MOBIL OIL CORPORATION, a Corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This application is directed to a process for the removal of alkyl lead impurities from liquid hydrocarbons.

Lead and its compounds, especially alkyl lead, R_4Pb , are not recognized as naturally occurring in crude oil. However, lead is found in crude oils and their distillate fractions and is usually traced to the lead contamination in gasoline.

It is known to use cupric chloride impregnated on nongraphitic carbon or on silica gel for removing lead contamination from unleaded gasoline; A.A. Zimmerman, G.S. Musser et al., SAE Fuels and Lubricants Meeting. (Houston 6/3-5/75) Technical Paper; Chemical Abstracts vol. 85-1976, 49026 G. It is also known to remove lead from motor fuels for internal combustion engines by contacting the fuel with a strongly acidic cation exchanger (German Patent DT 2,361,025); and to remove dissolved organic lead compounds from various liquid hydrocarbons by pretreatment with $SiCl_4$, $CuCl_2$, $CuBr_2$, I_2 or I_2 combined with an acid followed by contacting the pretreated hydrocarbon with activated carbon and an acid treated clay or silica gel (U.S. 3,893,912). However, significant amounts of lead impurities remain after such treatments. Additional lead contamination may be acquired in shipping, for example, when a naphtha reformer feed is purchased in one location and shipped to another for reforming.

Therefore, this application is directed to a novel process wherein substantially all of the lead contaminants contained in a given liquid hydrocarbon solution are removed. For example, feedstocks to reformer units in refineries should be substantially free of lead impurities to guarantee reasonable economics of operation. Contamination of reformer feedstock by lead impurities put the reformer facilities out of balance and cause unnecessary reformer catalyst poisoning. By means of the process disclosed herein lead contamination in for example naphtha reformer feedstocks of 75 parts per million (ppm) is reduced to less than 5 parts per billion (ppb).

Accordingly, this application is more particularly directed to a process for effecting the removal of alkyl lead contaminant from liquid hydrocarbon media containing said contaminant from liquid hydrocarbon media containing said contaminant which comprises contacting said hydrocarbon at a temperature below the boiling point thereof with a solid sorbent comprising 0.001 to 20% wt. of anhydrous HCl gas adsorbed therein sufficient to effect substantial reduction in the concentration of said contaminant and maintaining said contact until substantially all of said contaminants are removed therefrom.

The novel process in accordance with the invention disclosed herein is generally useful for removing alkyl lead impurities from any liquid hydrocarbon media. It is suitable for treating petroleum oils of lubricating viscosity, distillate fuel oils, gasoline and similar light liquid hydrocarbon products including both mineral oil and synthetic hydrocarbon products. The preferred embodiment is the removal of lead contamination from reformer feeds.

A wide variety of solid sorbents may be advantageously used. These sorbents (supports) can be crystalline or amorphous. Amorphous sorbents, however, have proven to be more advantageous. In any event, the sorbents must have sufficient surface area and porosity to

adsorb an effective amount of the anhydrous HCl. The surface area of the sorbents useful herein is from about 5 m²/g to about 1000 m²/g; the surface area of zeolite crystalline sorbents is usually from about 100 to about 1000 m²/g and preferentially from 100 to about 750 m²/g; the surface area of the amorphous sorbents is usually from about 5 to 750 m²/g and preferably from about 150 - 600 m²/g. The average pore diameter of the sorbent should be from about 3 to about 200 Å; the average pore diameter of zeolite crystalline sorbents used herein is usually less than about 10 Å, i.e., from about 3-9 Å; of amorphous sorbents it is usually from about 10-20 to about 200 Å and preferentially from about 20-100 Å.

Suitable sorbents include synthetic or naturally occurring materials such as faujasite (zeolite X, zeolite Y), mordenite, and various other zeolites as may be suitable, e.g., zeolite ZK-4, zeolite ZSM-5, as well as such inorganic materials as bauxite, clay, silica and/or metal oxides and naturally occurring clays which can be composited with the zeolites, these include the montmorillonite and kaolin families, which include the sub-bentonites and the kaolins commonly known as Dixie, McNamme-Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite and activated carbons. Such clays can be used in the raw state as originally mined or initially subject to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, zeolites employed herein may also be composited with material such as bauxite, alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica, berylia, silica-titania as well as ternary compositions, such as silica-alumina-thoria, silica-alumina, zirconia, silica, alumina-magnesia and silica-magnesiazirconia. Preferred are sorbents selected from the group consisting of various forms of silica, bauxite, mordenite, natural and synthetic clays, amorphous and crystalline aluminosilicates, alumina and silica-alumina mixtures; silica-alumina mixtures may contain about 5 to 95% silica or preferably about 5-25 wt.% or about 75-95 wt.% silica to alumina. The silica-alumina preferably has an average pore diameter of 20 to 100 Å and an average surface area from 150 to 600 m²/g. Thermofor cracking catalysts (TCC) such as fresh, spent or regenerated bead type TCC catalysts may be used herein as sorbents. Especially preferred are sorbents selected from amorphous silica-alumina, silica-clay or other gel-type matrix containing a minor proportion of crystalline aluminosilicate zeolite. Preferred crystalline aluminosilicates are zeolite X or zeolite Y, preferably having an average pore diameter of 8-9 Å and a surface area of 200-1000 m²/g.

The effective amount of adsorbed anhydrous HCl gas will vary dependent upon type of sorbent, adsorption conditions of temperature and pressure as well as reaction parameters. The sorbent disclosed herein will contain from 0.001 to 20 wt.% of adsorbed HCl and preferably from about 0.1 to about 17.5 wt.%, more preferably 1.0 to 17.5 wt.%, based on the total weight of the sorbent.

The process of removing lead contaminants, e.g., tetraethyl or tetramethyl lead, from liquid hydrocarbons is conveniently carried out in a simple flow or batch process. A solution of the lead contaminated hydrocarbon is passed over the sorbent. e.g., NaX-zeolite, amorphous silica, etc., lead compounds in the solution undergo a displacement reaction giving an insoluble alkyl salt, i.e., R₃PbCl and a gaseous product, i.e., RH. The gas escapes through the solution and the insoluble salt remains on the sorbent. The process is carried out at room temperature or at any temperature below the boiling point of the liquid hydrocarbons. Preferred operating conditions are a temperature of from about 25-60°C, LHSV of from about 5-20 and atmospheric or slightly higher pressure. A suitable sorbent, i.e., silica, alumina, mixtures thereof and calcined X and Y zeolites such as calcined NaX, may be included after the lead removal step to remove (i.e. adsorb) any HCl desorbed during the lead removal stage of the process. For a "wet" (having more than about 100 ppm water) hydrocarbon feed, a drying step utilizing the above operating conditions and also utilizing calcined NaX or other suitable dessicant can precede the lead removal step e.g., commercial drying agents comprised of silica, alumina, mixtures thereof, and X and Y zeolites are suitable.

The following examples illustrate the invention: Examples 1, 2 and 3 illustrate the preparation of suitable solvents.

EXAMPLE 1

100 grams NaX 1/16" extrudate were calcined in a glass reactor at 350°C in argon for about 16 hours and cooled at room temperature. A stream of anhydrous hydrogen chloride gas was allowed to contact the zeolite (pore diameter about 7-9 Å; surface area about 750 m²/g), downflow until the loading was complete, i.e., about 15.6-17.5 wt. % of HCl at equilibrium at room temperature. When anhydrous HCl contacts the sorbent, an exothermic reaction zone develops at the top of the reactor. This zone moves down the bed. After the bottom section of the reactor cooled down, in an atmosphere of HCl gas, the reactor was purged with dry argon for about 1 minute to remove any easily-desorbed HCl.

EXAMPLE 2

80 grams of a NaX molecular sieve, 1/16" extrudate, were placed in a glass reactor, calcined at 400°C. in argon for about 16 hours and cooled to room temperature. Anhydrous HCl gas was then passed downflow (as in Example 1) over the calcined sorbent until HCl loading was complete; the NaX extrudate adsorbed about 12.5 g HCl, or about 15.6 wt. % and was otherwise prepared in the manner of Example 1.

EXAMPLE 3

32.1 grams of a commercially obtained amorphous silica-alumina sorbent (Durabead-1) having the following general properties: pore diameter about 80Å; surface area about 200 m²/g. and a silica to alumina ratio of about 9:1, were calcined in argon at 350°C for about 16 hours and cooled to room temperature. Dry HCl gas was then passed downflow over the catalyst until equilibrium at room temperature was reached. 0.345 grams of HCl (≈ 1% wt.) were adsorbed by the sorbent.

EXAMPLE 4

A regular gasoline containing 1.8 g/gal Pb was used as a 10% contaminant in a Pb-free naphtha reformer feed. A suitable reactor containing the NaX sorbent with adsorbed anhydrous HCl as described in Example 1 was connected to a feed pump. Naphtha was introduced at the bottom of the reactor at 0.6 LHSV and at a temperature of about 5°C below the boiling point of the naphtha by means of a metering pump and moved upflow through the bed until it reached the exit at the top of the reactor. The naphtha was then collected as product. Reformer naphtha properties were as shown in Table 1, <5 ppb lead before contamination and 75,000 ppb after contamination. Product naphtha properties are shown in Table 2, after treatment with the sorbent of Example 2 lead contamination was reduced to <5.

TABLE 1

PROPERTIES OF NAPHTHA FEED

	Fresh Naphtha	Contaminated with 10% Regular Gasoline
Gravity, °API	63.0	62.2
Vapor Pressure	2.3	3.3
Water, ppm.	44	-
Lead, ppb.	<5	75,000 (75 ppm)
Chloride, Cl ⁻	absent	absent
Distillation, °F		
5%	188	-
10%	198	-
30%	215	-
50%	237	-
70%	264	-
90%	296	-
EP	335	-

TABLE 2

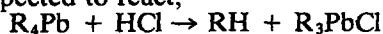
Properties of Naphtha Treated
With HCl/NaX, 0.6 LHSV, 10 vol/vol of Contact Mass

	25°C	90°C
Gravity, °API	62.2	-
Lead, ppb.	<5	<5
Chloride, Cl ⁻	absent	absent

EXAMPLE 5

One gallon of a hexane/toluene mixture (70/30 vol.) containing 174 ppm Pb was pumped upflow, 0.5 LHSV and at room temperature, through a sorbent system as described in Example 3 followed by another gallon containing 340 ppm lead. Finally, 1500 ml containing 450 ppm lead were used. 10 ml samples of product were taken for diagnostic Pb analyses by Test Method A (described below) at 24 hour intervals. In addition, 500 ml samples were taken at about 25%, 65%, and 75% HCl depletion points for ppb Pb analyses by Test Method B (described below). Table 3 summarizes data obtained on samples of Pb-contaminated light hydrocarbon mixtures treated with the silica-alumina/HCl sorbent system of Example 3 at room temperature.

Data in Table 3 show that the stoichiometry of the reaction is one mole of HCl to one mole of R_4Pb . Thus, for the amount of HCl adsorbed, 0.345 gm. (9.45 mmols), a maximum of 1.958 gm. of Pb would be expected to react,



where R_4Pb is a commercial mixture of tetraalkyl lead; i.e., tetraethyl, tetramethyl, trimethylethyl, diethyl-dimethyl etc.

Table 3 further shows that a 99.2% of HCl used, the contact mass reduces 450 ppm Pb in the feed to 38 ppm and at a point $\approx 100\%$ to > 300 ppm and that alkyl lead compounds react with available HCl in the catalysts until all the HCl is depleted.

TABLE 3

REMOVAL OF R_4Pb FROM LEAD CONTAMINATED¹
LIQUID HYDROCARBONS² BY TREATMENT WITH
HCl/SILICA-ALUMINA AT 25° AND 0.5 LHSV

Pb, ppm in Feed (g/gal)	Pb, gm Removed by Contact Mass	Sorbent: Example 3 Pb in Treated Naphtha		% of Adsorbed HCl Used
		ppb ^a	ppm ^b	
174 (0.49)	0.41	<5	<0.1	-
340 (0.98)	0.45-0.48	<5	<0.1	25
	0.76	-	<0.1	38
	0.91	-	<0.1	46
	1.13	-	<0.1	58
450 (1.26)	1.16-1.30	<5	<0.1	59-67
	1.30	-	<0.1	67
	1.30-1.43	29	<0.1	67-73
	1.46	-	0.4	75
450 (1.26)	1.46-1.93	-	4.1	75-99
	1.93	-	32	99
	1.94	-	38	99.2
	>1.96	-	>300	≈ 100

1--A commercially available mixture of tetraalkyl leads, i.e., tetramethyl, tetraethyl, trimethyl-ethyl, diethyl-di-methyl etc., was used at the contaminant.

2--Moisture content <100 ppm.

a--Test Method A

b--Test Method B (ASTM D3237).

Test Method A is used to determine lead in reformer naphthas and similar light hydrocarbon stocks at concentrations below 100 ppb, i.e., trace amounts of lead. Lead present as alkyllead contamination and as naphthenates and other compounds decomposed by bromine are determined. Other metals do not interfere.

OUTLINE OF METHOD A

A 500-ml sample is reacted in an appropriate sample bottle with 454g (5N) bromine diluted in carbon tetrachloride to 1 liter, for 2 minutes at room temperature, and then extracted with water. The extract is transferred to a test tube and aspirated into the burner of an atomic absorption spectrometer. The absorbance of the 2170Å line is measured and converted to lead content by means of a calibration curve.

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Test Method B (ASTM D3237) is used to analyze unleaded materials such as fuels containing 0.5 ppm or more of lead.

OUTLINE OF METHOD B

The atomic absorption spectrophotometer is adjusted with the aid of commercially obtained standardization solutions. The sample material is then aspirated directly into the instrument and the absorption is measured.

As is readily apparent from the data in the foregoing Tables, the sorbent system and method of use thereof is a significant improvement in the art.

TABLE 4

REMOVAL OF R₄Pb FROM KUWAIT LEAD¹ CONTAMINATED NAPHTHA BY TREATMENT

with 10 ML. HCl/SILICA-ALUMINA
AT 25°C

Catalyst		Sorbent: Example 3		
Pb in Feed ppb =	Cumulative Vol. Ml.	LHSV hr 1 at 25°C	Pb in Treated Naphtha, ppb =	
88	600	5	<5	
	1200	10	<5	
25	1700	15	<5	
	2200	20	<5	

1. See Table 3 for Pb contaminant used.

TABLE 5

REMOVAL OF R₄Pb FROM KUWAIT LEAD¹ CONTAMINATED NAPHTHA BY TREATMENT WITH 10 ML. HCl/SILICA-ALUMINA AT 20.5 LHSV

Catalyst		Sorbent: Example 3		
Pb in Feed ppb =	Cumulative Vol. Ml.	Temperature °C at 20.5 LHSV	Pb in Treated Naphtha, ppb =	
88	2700	26	<5	
	3200	45	<5	
	3700	60	<5	

1. See Table 3 for Pb contaminant used.

EXAMPLE 6

Samples of naphtha (see Table 1) were contaminated by the addition of about 0.2 ml of a 5 g Pb/gal. gasoline to 1 gallon of Kuwait naphtha to give 88 ppb of lead contamination; and processed as described above using the sorbent of Example 3; see Tables 4 and 5.

The data in Tables 4 and 5 illustrate that reformer feeds containing as little as 88 ppb contamination can be even further reduced to safe reformer levels, i.e., <5 ppb by the process of this invention.

Although preferred embodiments have been exemplified, variations can be resorted to and are within the scope of this invention as one of ordinary skill in the art will readily understand.

WHAT WE CLAIM IS:-

1. A process for removing alkyl lead contaminant from liquid hydrocarbons which comprises contacting such hydrocarbon with a solid sorbent comprising 0.001 to 20% wt. of anhydrous hydrogen chloride adsorbed thereon.

2. A process according to Claim 1 where the sorbent has an average pore diameter of 3 to 200 Å and an average surface area of 5 to 1000 m²/g.

3. A process according to Claim 1 or Claim 2 where said sorbent comprises silica, bauxite, mordenite, a natural or synthetic clay, an amorphous or crystalline aluminosilicate, alumina, or silica-alumina.

4. A process according to Claim 3 wherein said sorbent is fresh, spent, or regenerated



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Test Method B (ASTM D3237) is used to analyze unleaded materials such as fuels containing 0.5 ppm or more of lead.

OUTLINE OF METHOD B

5 The atomic absorption spectrophotometer is adjusted with the aid of commercially obtained standardization solutions. The sample material is then aspirated directly into the instrument and the absorption is measured. 5
As is readily apparent from the data in the foregoing Tables, the sorbent system and method of use thereof is a significant improvement in the art.

10 **TABLE 4** 10

REMOVAL OF R₄Pb FROM KUWAIT LEAD¹ CONTAMINATED NAPHTHA BY TREATMENT

15 with 10 ML. HCl/SILICA-ALUMINA 15
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Catalyst	Sorbent: Example 3			
Pb in Feed ppb =	Cumulative Vol. Ml.	LHSV hr 1 at 25°C	Pb in Treated Naphtha, ppb =	
88	600	5	<5	
	1200	10	<5	
25	1700	15	<5	
	2200	20	<5	25

1. See Table 3 for Pb contaminant used.

30 **TABLE 5** 30

REMOVAL OF R₄Pb FROM KUWAIT LEAD¹ CONTAMINATED NAPHTHA BY TREATMENT WITH 10 ML. HCl/SILICA-ALUMINA AT 20.5 LHSV

Catalyst	Sorbent: Example 3			
Pb in Feed ppb =	Cumulative Vol. Ml.	Temperature °C at 20.5 LHSV	Pb in Treated Naphtha, ppb =	
88	2700	26	<5	
	3200	45	<5	
	3700	60	<5	40

45 1. See Table 3 for Pb contaminant used. 45

EXAMPLE 6

50 Samples of naphtha (see Table 1) were contaminated by the addition of about 0.2 ml of a 5 g Pb/gal. gasoline to 1 gallon of Kuwait naphtha to give 88 ppb of lead contamination; and processed as described above using the sorbent of Example 3; see Tables 4 and 5. 50

The data in Tables 4 and 5 illustrate that reformer feeds containing as little as 88 ppb contamination can be even further reduced to safe reformer levels, i.e., <5 ppb by the process of this invention.

55 Although preferred embodiments have been exemplified, variations can be resorted to and are within the scope of this invention as one of ordinary skill in the art will readily understand. 55

WHAT WE CLAIM IS:-

1. A process for removing alkyl lead contaminant from liquid hydrocarbons which comprises contacting such hydrocarbon with a solid sorbent comprising 0.001 to 20% wt. of anhydrous hydrogen chloride adsorbed thereon.
2. A process according to Claim 1 where the sorbent has an average pore diameter of 3 to 200Å and an average surface area of 5 to 1000 m²/g.
3. A process according to Claim 1 or Claim 2 where said sorbent comprises silica, bauxite, mordenite, a natural or synthetic clay, an amorphous or crystalline aluminosilicate, alumina, or silica-alumina.
- 65 4. A process according to Claim 3 wherein said sorbent is fresh, spent, or regenerated 65

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bead thermofor cracking catalyst.

5. A process according to Claim 3 or Claim 4 wherein said sorbent is an amorphous silica-alumina, silica-clay, or other gel-type matrix containing a minor proportion of crystalline aluminosilicate zeolite.

6. A process according to any of Claims 3 to 5 wherein the crystalline aluminosilicate is zeolite X or zeolite Y.

7. A process according to Claim 6 wherein said crystalline aluminosilicate has an average pore diameter of 8-9Å and a surface area of 200-1000 m²/g.

8. A process according to any preceding claim wherein the amount of adsorbed hydrogen chloride is from 0.1 to 17.5 wt. %.

9. A process according to any preceding claim wherein the amount of adsorbed hydrogen chloride is from 1.0 to 17.5 wt. %.

10. A process according to any of claims 1 to 3 and 8 or 9 wherein the sorbent is silica-alumina having an average pore diameter from 20 to 100Å and an average surface area from 150 to 600 m²/g.

11. A process according to Claim 10 wherein the silica/alumina comprises from 5 to 95 wt. % silica.

12. A process according to any preceding claim wherein said contaminant is tetra-alkyl-lead.

13. A process according to any preceding claim wherein said hydrocarbons are comprised in a naphtha suitable as reformer feedstock.

14. A process according to any of Claims 1 to 12 wherein said hydrocarbons are comprised in a motor fuel.

15. A process according to Claim 14, wherein said motor fuel is an unleaded gasoline.

16. A process according to any preceding claim which is continued until less than 5 parts per billion of said alkyl lead contaminant remain in said hydrocarbons.

17. A process according to any preceding claim which is carried out at a temperature of 25 to 60°C and a LHSV of 5 to 20.

18. A process according to any preceding claim wherein the liquid hydrocarbons are contacted with a drying agent before said contacting with said sorbent.

19. A process according to any preceding claim wherein hydrogen chloride present in the hydrocarbons from which said contaminant has been removed is sorbed therefrom by contact with a suitable sorbent.

20. A process for removing alkyl lead contaminants from liquid hydrocarbons substantially as described in any one of Examples 4, 5 and 6.

21. Liquid hydrocarbons from which alkyl lead contaminants have been removed by the process of any one of the preceding Claims.

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