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STABILIZATION OF TETRAETHYL LEAD AND A MOTOR FUEL CONTAINING A STABILIZED TETRAETHYL LEAD

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This invention relates to the stabilization of tetraethyl lead and particularly to the stabilization of tetraethyl lead in motor fuels.

It is common practice to add to motor fuels a composition generally known as "ethyl fluid" consisting principally of tetraethyl lead and small amounts of ethylene dibromide, ethylene dichloride and other substances, in order to increase the anti-knock value of the motor fuel. Most of the gasoline now being sold contains some of this fluid, the amount varying from about 1–3 ccs. per gallon of gasoline. Fuel for special purposes such as aviation gasoline may contain even more.

It has been found that upon storage, and especially upon exposure to sunlight, the tetraethyl lead tends to deteriorate or decompose with the production of a haze or cloud formation in the gasoline and with subsequent deposition of a white precipitate. These lead deposits are most noticeable in sight glasses and in the glass bowls of gasoline pumps which become fouled and require frequent cleaning. Loss of the lead compound through precipitation also tends to lower the anti-knock value of the motor fuel.

We have found that the addition of a very small amount of a surface-active organic sulfate to motor fuels containing tetraethyl lead will stabilize the tetraethyl lead and prevent cloud formation and deposition of deteriorated or partially decomposed tetraethyl lead. The compounds of this group of tetraethyl lead stabilizers are anionically surface active; that is, they ionize in the presence of water in such a way that the cationic portion of the molecule is relatively small and ineffective as compared with the anionic portion of the molecule which is comparatively large, negatively charged and capable of exerting a considerable surface active effect. The ionization of the anionically surface active organic sulfates of our invention may be illustrated by the sulfuric acid ester of lauryl alcohol as follows

$$[C_{12}H_{25}OSO_3]^- + [H]^+$$

Another important characteristic of our stabilizers is that they contain in the anionic portion of the molecule one or more non-polar groups having an affinity for gasoline. These groups in the anionic portion of the molecule tend to solubilize the compound in gasoline and should preferably be alkyl chains of 4 or more carbon atoms. Those organic sulfates having branched chains in the anionic portion of the molecule, as for example the sulfuric acid ester of 3,9-diethyl tridecanol-6 have better gasoline solubility than the straight chain alkyl or alkyl aryl sulfates and are accordingly the preferred compounds of our invention.

The anionically surface active organic sulfates which may be employed in accordance with our invention to stabilize tetraethyl lead include the higher straight chain alkyl sulfuric acid esters such as lauryl, cetyl and stearyl sodium sulfates; the sulfuric acid esters of branched chain secondary alcohols such as 3,9-diethyl tridecanol-6 and 7-ethyl-2-methyl undecanol-4 and the salts of these acid esters. Other secondary alcohol sulfates of this group are 5-ethyl nonyl-2-sodium sulfate, 6-ethyl decyl-3-sodium sulfate, 5,11-diethyl pentadecyl-8-sodium sulfato eicosane. Other anionically surface active sulfates which may be employed include the sulfated monoalkyl ethers of glycerol, the sulfates of mixed fatty acid monoglycerides, alkyl aryl ether sulfates and various other industrial products of indefinite composition such as the sodium salt of sulfated capryl esters of talloil fatty acids, sodium salts of sulfated oils such as sperm, olive, castor and teaseed oils, Montan wax alcohol sulfates, sulfated mixtures of higher alcohols obtained as a byproduct in the manufacture of synthetic methanol, sulfates obtained by absorption of cracking still gases in strong H_2SO_4, and the like. Although some of these materials are prepared according to conventional sulfonation procedures and are designated in the art as sulfonated products, they are in fact sulfates and are, of course, included within the scope of our invention as limited by the appended claims.

It is also to be noted that while we have indicated most of these compounds to be the sodium salt this is done as a matter of convenience since other stable salts such as the potassium, calcium, barium, zinc, ammonium, amine or amidine salts could also be employed. In fact, the acid ester itself can be employed except for the undesirable addition of an acidic substance to the motor fuel.

Although we do not intend to be bound by any proposed explanation of the mechanism of the stabilizing action of our compounds their effectiveness appears to be due to the surface active properties of the anionically active molecule which is probably attracted to and peptizes the extremely small particles of the deteriorated or partially decomposed tetroethyl lead, thus preventing their growth and precipitation from the motor fuel. Accordingly, any sulfuric acid ester or its salt which is anionically surface active will be found to stabilize tetraethyl lead in gasoline in accordance with our invention.

The amount of stabilizer used depends, of course, on the amount of tetraethyl lead in the gasoline. We have found that ordinarily 1–10% by weight of our stabilizers based on the weight of tetraethyl lead in the gasoline is sufficient for most practical purposes. The amount of tetraethyl lead in gasoline varies considerably and may run from 0.01 to 0.25% of tetraethyl lead based on the weight of the gasoline. The amount of stabilizer which we use will therefore vary to about 0.0001 to 0.025% based on the total weight of the gasoline. With ordinary commercial gasolines, we have found that 0.005% 50 parts per million) by weight of our stabilizers will stabilize the tetraethyl lead satisfactorily.

Our stabilizers may be added to the gasoline directly or, preferably, dissolved in a suitable solvent such as naphtha, alcohol or benzene and then added to the gasoline in desired proportions. Some of the individual compounds are difficultly soluble in gasoline directly and may be dispersed therein in effective amounts by means of a mutual solvent such as petroleum sulfonate in which the ester is first dissolved before it is added to the gasoline. We therefore characterize as oil-dispersible both those compounds which are gasoline soluble and those which can be dispersed therein by other means.

Our stabilizers may also be added to motor fuels containing adjuncts such as benzene or alcohol for the purpose of stabilizing tetraethyl lead contained therein. They may also be added directly to the ethyl fluid with additional amounts of solvent, if desired, and sold and shipped in this form. In this way the addition of tetraethyl lead to the gasoline and addition of stabilizer occur simultaneously, thus avoiding any chance of decomposition after the addition of ethyl fluid.

In order to illustrate the effectiveness of our stabilizers a number of them were tested under conditions tending to accelerate the decomposition of the tetraethyl lead. In these tests commercial samples of gasoline containing ethyl fluid were poured into 4 ounce screw cap bottles and placed 12 inches from a mercury sunlamp of the General Electric S—1 type. The time required for the appearance of an observable cloud formation was noted. Samples of the same gasolines but containing 0.005% of our tetraethyl lead cloud formation inhibitor were also exposed to the strong light in the same manner as the control samples and the time for cloud formation noted. Variations in the time in which the control samples clouded are due to the fact that different gasolines containing varying amounts of ethyl fluid were employed in these tests. The results are given in the following table:

Stabilizer	Time in hours for cloud to appear	
	Control	Stabilized
3,9-diethyl tridecyl-6 sodium sulfate	2.0	6.0
Lauryl sodium sulfate	1.5	2.0
Sodium salt of sulfated teaseed oil	2.0	6.0
Sodium salt of sulfated capryl ester of talloil fatty acids	0.5	5.3
Sulfated mixture of higher alcohols	1.0	2.5

What we claim is:

1. A composition comprising tetraethyl lead and an oil-dispersible anionically surface active member of the group consisting of acid esters of sulfuric acid and salts thereof, said esters containing alkyl groups having at least 4 carbon atoms.

2. A composition comprising tetraethyl lead and an oil-dispersible anionically surface active member of the group consisting of acid alkyl esters of sulfuric acid and salts thereof, said esters containing alkyl groups having at least 4 carbon atoms.

3. A composition comprising tetraethyl lead and an oil-dispersible anionically surface active member of the group consisting of higher alcohol sulfuric acid esters and salts thereof.

4. A composition comprising tetraethyl lead and an oil-dispersible anionically surface active member of the group consisting of higher primary alcohol sulfuric acid esters and salts thereof.

5. A composition comprising tetraethyl lead and an oil-dispersible anionically surface active member of the group consisting of higher secondary alcohol sulfuric acid esters and salts thereof.

6. A composition comprising gasoline, tetraethyl lead and an oil-dispersible anionically surface active member of the group consisting of acid esters of sulfuric acid and salts thereof, said esters containing alkyl groups having at least 4 carbon atoms in amounts from 1–10% of the weight of the tetraethyl lead and being effective to stabilize tetraethyl lead against cloud formation.

7. A composition comprising a motor fuel of the gasoline type containing 0.01% to about 0.25% tetraethyl lead and an oil-dispersible anionically surface active member of the group consisting of acid esters of sulfuric acid and salts thereof, said esters containing alkyl groups having at least 4 carbon atoms.

8. A gasoline containing motor fuel containing tetraethyl lead in amounts sufficient to impart anti-knock properties to said motor fuel and an oil-dispersible anionically surface-active member of the group consisting of aliphatic alcohol-sulfuric acid esters and salts thereof, said esters containing alkyl groups having at least 4 carbon atoms in amounts of about 1–10% of the weight of tetraethyl lead.

9. A gasoline containing motor fuel containing tetraethyl lead in amounts sufficient to impart anti-knock properties to said motor fuel and an oil-dispersible anionically surface active member of the group consisting of aliphatic secondary alcohol-sulfuric acid esters and salts thereof, said esters containing alkyl groups having at least 4 carbon atoms in amounts of about 1–10% of the weight of the tetraethyl lead.

10. A gasoline containing motor fuel containing tetraethyl lead in amounts sufficient to impart anti-knock properties to said motor fuel and an oil-dispersible anionically surface active member of the group consisting of fatty oil sulfates and salts thereof in amounts of about 1–10% of the weight of the tetraethyl lead.

11. A gasoline containing motor fuel containing tetraethyl lead in amounts sufficient to impart anti-knock properties to said motor fuel and an oil-dispersible anionically surface active member of the group consisting of sulfated teaseed oil and salts thereof in amounts of about 1–10% of the weight of the tetraethyl lead.

12. Gasoline containing 0.10% to about 0.25% of tetraethyl lead and about 0.001% to 0.025% of an oil-dispersible anionically surface active member of the group consisting of acid esters of sulfuric acid and salts thereof, said esters containing alkyl groups having at least 4 carbon atoms.

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