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STABILIZATION OF TETRAETHYL LEAD AND
A MOTOR FUEL CONTAINING THE SAME

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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 gasoline 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 cc. per gallon of gasoline. Fuels 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 for this reason require frequent cleaning. Loss of the lead compound through precipitation also tends to lower the anti-knock value of the gasoline.

We have found that certain oil-soluble, surface-active organic sulfonates when added in very small amounts to gasoline containing tetraethyl lead will stabilize the tetraethyl lead and prevent cloud formation and the formation of lead deposits. While we have discovered that many specific compounds will operate successfully to prevent deterioration of the tetraethyl lead with cloud formation and subsequent deposition the compounds of our invention which have proven to be effective have a number of common properties which lead us to believe that the stabilization of the tetraethyl lead may be brought about by any compound having these common characteristics. The stabilizing agents of our invention are oil-soluble in such degree that effective amounts thereof may be dissolved in the gasoline. Our effective stabilizers contain a non-polar group in their molecular structure which has an affinity for mineral oils. For lack of better terminology we call this a lipophile group. Another essential feature of their molecular structure is that they also contain a $-\text{SO}_3\text{X}$ group in which X is a salt-forming radical. Still another common characteristic of our stabilizers is that they all possess surface-active properties.

Although we do not know with certainty the exact mechanism of the stabilizing action a possible explanation may be based upon the analogous action of wetting agents. Those agents generally are of such a molecular structure that one portion of the molecule is preferentially soluble in water and another portion of the molecule is preferentially soluble in oil. A molecule of this type concentrates at the interface be-

tween the oil and water phases and modifies the surface relationships existing there. Such substances are thus said to be surface-active. Our stabilizers are also of the surface-active type and contain in their molecular structure a group preferentially soluble in gasoline and another group, the $-\text{SO}_3\text{X}$ radical, which we believe is preferentially attracted to the deteriorated or partially decomposed tetraethyl lead particles by chemical affinity, partial valency, adsorption or some other mechanism before they have attained a size sufficient to cause cloud formation. Further agglomeration of the tetraethyl lead particles is thus prevented and they are not able to attain a size sufficient to cause cloudiness and precipitation in the gasoline. The lead particles of submacroscopic size are retained in solution or dispersion in the gasoline as discrete particles of undetermined molecular size. The above explanation is given however merely in order that our invention may be more easily understood and while we believe it to be correct we do not wish to be limited thereto.

The amount of stabilizer used depends, of course, upon the amount of tetraethyl lead in the gasoline. We have found that ordinarily 1% to 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 gasolines varies considerably and may run from 0.01% to 0.25% tetraethyl lead based on the weight of the gasoline. The amount of stabilizer which we use will therefore vary from about .0001 to 0.025% based on the total weight of the gasoline. With ordinary commercial gasolines, however, we have found that 0.005% by weight of our stabilizers will stabilize the gasoline 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. They may also be added directly to the ethyl fluid with desired amounts of solvent 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.

We prefer to use our stabilizer in the form of the sodium sulfonate salt as this salt is generally most readily obtained. We may, however, use other salts of sulfonic acids such as the calcium, zinc, lead, potassium, magnesium and ammonium salts, etc., or the sulfonic acid itself may be used and the term "sulfonate" as used in the claims is intended to cover all of these. Among the various sulfonic acid salts found useful in the practice of our invention may be mentioned the dialkyl sulfosuccinates such as the diamyl, dioctyl, dicapryl, diundecyl and dilauryl sulfo-

succinates; the alkyl-aryl sulfonates such as diisobutyl naphthalene sodium sulfonate, diisopropyl naphthalene sodium sulfonate, lauryl phenyl sodium sulfonate, esters of sulfophthalic acid such as the diamyl and dioctyl esters; lauryl sodium beta-sulfobutyrate, which is an ester of a sulfomonocarboxylic acid; esters of sulfosebacic acid; capryl phenyl ether sodium sulfonate; terpenyl alkyl phenyl ether sodium sulfonates; sulfonated esters of talloel fatty acids such as the capryl ester; and the petroleum sulfonates or mahogany soaps which generally consist of a variety of oil-soluble surface-active organic sulfonates of petroleum hydrocarbons.

In order to illustrate the effectiveness of our stabilizers a number of them were tested on a directly comparative basis. In these tests a commercial sample of gasoline containing ethyl fluid was placed in a 4-oz. screw cap glass bottle and placed 12 inches from a mercury sunlamp of the General Electric S1 type. The time in hours required for formation of an observable cloud formation was noted. Samples of the same gasoline but containing stabilizing amounts of our tetraethyl lead cloud formation inhibitor were then exposed to the strong light in the same manner and the time for cloud formation noted. Samples containing lecithin, a material heretofore used for this same purpose, were also tested. The results are given in the following table.

	Time in hours for cloud formation
Gasoline A:	
Control	1.2
Control+0.005% dioctyl sodium sulfosuccinate	12.0
Control+0.005% dioctyl zinc sulfosuccinate	13.6
Control+0.005% dicapryl sodium sulfosuccinate	14.0
Control+0.005% diamyl sodium sulfosuccinate	9.0
Control+0.005% dilauryl sodium sulfosuccinate	7.5
Control+0.005% diundecyl sodium sulfosuccinate	12.5
Control+0.005% diisobutyl naphthalene sodium sulfonate	6.5
Control+0.005% alkyl phenyl sodium sulfonate	7.5
Control+0.005% petroleum sulfonate-sodium salt (65%) (sample A)	12.0
Control+0.005% petroleum sulfonate-lead salt (65%)	7.0
Control+0.005% petroleum sulfonate-sodium salt (50%) (sample B)	7.0
Control+0.005% petroleum sulfonate-sodium salt (50%) (Sample C)	13.0
Control+0.005% lecithin	9.5
Gasoline B:	
Control	1.8
Control+0.005% dioctyl sodium sulfosuccinate	20.0
Control+0.005% dioctyl calcium sulfosuccinate	15.0
Control+0.005% petroleum sulfonate-sodium salt (65%) (sample A)	12.5
Control+0.010% petroleum sulfonate-sodium salt (65%) (sample A)	33.0+
Control+0.005% petroleum sulfonate-lead salt (65%)	12.0
Control+0.010% petroleum sulfonate-lead salt (65%)	20.0+
Control+0.005% lecithin	13.0
Control+0.010% lecithin	20.0

Tests were also made on the gasoline to determine what effect the addition of our stabilizers might have on other gasoline characteristics. There was no lowering of the octane rating even when amounts up to 0.025% of our stabilizer was present in the gasoline. In the copper dish test it was found that in the presence of our stabilizer there was appreciably less gum formation when compared with the tests made on the control sample. In the presence of monobutyl para-amino phenol, a well-known gum inhibitor, it was found that the induction period as measured by the A. S. T. M. oxygen bomb test was not changed appreciably by the addition of effective amounts of our tetraethyl lead stabilizer.

What we claim is:

1. A composition comprising tetraethyl lead and an oil-soluble surface-active organic sulfonate in amounts effective to stabilize said tetraethyl lead against cloud formation.

2. A composition comprising gasoline, tetraethyl lead, and an oil-soluble surface-active organic sulfonate in amounts of 1-10% of the weight of the tetraethyl lead and being effective to stabilize said tetraethyl lead against cloud formation.

3. A composition comprising gasoline, 0.01% to about 0.25% of tetraethyl lead, and an oil-soluble surface-active organic sulfonate in amounts of about 1-10% of the weight of the tetraethyl lead and being effective to stabilize said tetraethyl lead against cloud formation.

4. Gasoline containing 0.01% to about 0.025% of tetraethyl lead and about 0.0001% to 0.025% of an oil-soluble surface-active organic sulfonic acid salt.

5. A motor fuel comprising gasoline, tetraethyl lead in amounts sufficient to impart anti-knock properties to said motor fuel, and an oil-soluble surface-active ester of sulfocarboxylic acid in amounts of about 1-10% of the weight of said tetraethyl lead.

6. A composition comprising tetraethyl lead and an oil-soluble surface-active petroleum sulfonate in amounts effective to stabilize said tetraethyl lead against cloud formation.

7. A motor fuel comprising gasoline, tetraethyl lead in amounts sufficient to impart anti-knock properties to said motor fuel, and an oil-soluble surface-active dialkyl sulfosuccinate in amounts of about 1-10% of the weight of said tetraethyl lead.

8. A motor fuel comprising gasoline, tetraethyl lead in amounts sufficient to impart anti-knock properties to said motor fuel, and dioctyl sodium sulfosuccinate in amounts of about 1-10% of the weight of said tetraethyl lead.

9. A motor fuel comprising gasoline, tetraethyl lead in amounts sufficient to impart anti-knock properties to said motor fuel, and an oil-soluble surface-active petroleum sulfonate in amounts of about 1-10% of the weight of said tetraethyl lead.

10. A motor fuel comprising gasoline, tetraethyl lead in amounts sufficient to impart anti-knock properties to said motor fuel, and a sodium salt of a petroleum sulfonate in amounts of about 1-10% of the weight of said tetraethyl lead.

11. A motor fuel comprising gasoline, tetraethyl lead in amounts sufficient to impart anti-knock properties to said motor fuel, and an oil-soluble surface-active alkyl-aryl sulfonic acid salt in amounts of about 1-10% of the weight of said tetraethyl lead.

12. The method of stabilizing gasoline containing tetraethyl lead against tetraethyl lead

deterioration and cloud formation which comprises adding to gasoline containing tetraethyl lead 0.0001% to 0.025% of an oil-soluble surface-active organic sulfonate.

13. The method of stabilizing gasoline containing tetraethyl lead against tetraethyl lead 5

deterioration and cloud formation which comprises adding to gasoline containing tetraethyl lead 0.0001% to 0.025% of an oil-soluble surface-active petroleum sulfonate.

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