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2,863,745

MOTOR FUEL

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This invention relates to fuels and more particularly to leaded gasolines for high compression, spark ignition engines.

It has long been recognized that for greater economy with respect to fuel requirement and greater efficiency in the operation of a gasoline engine high compression ratios are desired. As a result, several automobile manufacturers have increased the compression ratios of their spark ignition engines to 8.5 to 1 and even as high as 9 to 1, the future trend of the automotive industry indicating that substantially all engines will be operating at such high compression ratios in the foreseeable future. In order to obtain smooth engine operation at these high compression ratios, it has been necessary to employ a fuel having a high octane number. To obtain a high octane number most fuels require the addition of an anti-knock agent such as tetraethyl lead. While the addition of tetraethyl lead to gasoline improves its octane number, the resulting fuel has certain disadvantages arising from the presence of the lead. One of the chief objections to the use of leaded gasolines arises from the tendency of the fuel upon being burned to form decomposition products of lead which products are deposited on the walls of the combustion chambers of the engine and on the electrodes and insulators of the spark plugs, thus reducing the efficiency of the engine and offsetting to some extent the increased efficiency obtained by the high compression ratios. The net effect of these deposits is that the octane number requirement of the engine gradually increases as the engine is operated until some equilibrium octane number requirement is reached. The equilibrium octane number requirement of some engines which have been in operation for 100 or more hours may be 10 to 15 numbers higher than the octane number requirement of the same engines at the start of their operation.

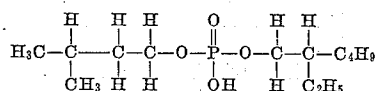
In an attempt to overcome the detrimental effect of the deposits of lead decomposition products in an engine, various "scavenging" agents have been added to the fuel to change the form of the lead decomposition products to those which are more volatile and thus less likely to be deposited within the engine. For example, various volatile alkyl halides such as ethylene dibromide and/or ethylene dichloride have been used with tetraethyl lead to produce the corresponding halides of lead which are more volatile than the oxides. The volatile alkyl halides, however, have not completely overcome the deposition of the decomposition products. The decomposition products comprise various salts including the oxides, sulfates, bromides and chlorides of lead. These decomposition salts deposited within the combustion chamber of the engine have been found to alter adversely the ignition characteristics. The adverse effect encountered as a result of the deposits of the decomposition salts is frequently evidenced by "engine knocking." The "knocking" thus encountered is that associated with preignition of the fuel in the combustion chamber of a spark ignition engine.

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This "knocking" associated with preignition should not be confused with "knocking" due to explosive autoignition of the unburned portion of the fuel-air mixture to be traversed by the normal flame from the spark plug.

We have discovered that a motor fuel, and particularly a gasoline to which a mixture consisting of tetraethyl lead and an ethylene halide has been added in an amount sufficient to produce a leaded fuel having a research octane number of at least 90, can be improved with respect to its tendency to preignite in an engine by incorporating in said gasoline a small amount of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate.

The cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate is prepared by reacting isoamyl octyl acid phosphate with cocoamine. Cocoamine is a commercially available product prepared by converting coconut oil fatty acids into their corresponding amines. Cocoamine consists mostly of mono-lauryl amine with minor amounts of adjacent homologues having eight to eighteen carbon atoms. The cocoamine salt of isoamyl octyl acid phosphate and its preparation are fully described in U. S. Patent No. 2,371,851 which issued on March 20, 1945, to Herschel G. Smith and Troy L. Cantrell. As disclosed in said patent, the cocoamine salt of isoamyl octyl acid phosphate can be readily prepared by reacting cocoamine with isoamyl octyl acid phosphate in approximately equimolecular ratios, the reaction being so controlled as to produce substantially neutral reaction mixtures having a pH value within the range of 5.5 to 7.5, as illustrated in Examples 1 and 2 of that patent. The isoamyl octyl acid phosphate employed is a di-ester of orthophosphoric acid having the following formula:



This compound is also known as 3-methylbutyl,2-ethylhexyl acid orthophosphate.

The amount of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate which is incorporated in the fuel depends upon the amount of tetraethyl lead in the fuel. In general, the amount is based upon that amount theoretically required to convert the lead introduced into the fuel in the form of tetraethyl lead to lead orthophosphate. Good results are obtained by using at least 0.3 times the theoretical amount required. In general, it is not necessary to employ more than 1.5 times the amount theoretically required. Amounts greater than 1.5 times the theoretical amount can be employed, but for economic reasons, we prefer to use only the amount required to give the desired improvement. When less than 0.3 times the theoretical amount is used the preignition characteristic of the leaded gasoline in engines having compression ratios in the order of 9 to 1 is not substantially improved. The theoretical amount of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate required to convert the lead in tetraethyl lead to lead orthophosphate on a molecular proportion basis is two mols of the cocoamine salt to three mols of tetraethyl lead.

In view of the fact that the amount of tetraethyl lead in the gasoline varies from one fuel to another, it is difficult to state on a weight basis the amount of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate based upon the weight of gasoline. However, once knowing the amount of tetraethyl lead present in the gasoline the amount of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate required can be readily calculated. Based upon fuels containing three

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cubic centimeters of tetraethyl lead per gallon of gasoline, we have determined that the amount of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate required in accordance with our invention is between 0.06 and 0.3 percent by weight based on the weight of a 60° API gravity gasoline. It will be understood of course that when commercially available products are used the optimum amount of product on a weight basis will vary depending upon the purity of the product. If, for instance, a commercially available anti-knock mixture comprising tetraethyl lead and ethylene halides is used, the percent by weight of the cocoamine salt will be less than if substantially pure tetraethyl lead is used. For example, if three cubic centimeters of a tetraethyl lead mixture comprising 61.5 percent by weight of tetraethyl lead is used, the amount of the cocoamine salt required in one gallon of a 60° API gravity gasoline to give between 0.3 and 1.5 theories is between about 0.037 and about 0.185 percent by weight. A cocoamine material consisting of about 84 percent by weight of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate will be used in greater proportions than the pure product. In order to incorporate between 0.06 and 0.3 percent by weight of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate in gasoline when using the 84 percent concentrate, it would be necessary to employ between about 0.07 and about 0.35 percent by weight of the concentrate. Since the above weight percents are based upon three cubic centimeters of tetraethyl lead, the percents will vary directly with the lead content as more or less than three cubic centimeters of tetraethyl lead are employed. In any event, the amount of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate used is sufficient to inhibit or substantially prevent preignition of a gasoline containing tetraethyl lead and an ethylene halide in an amount normally tending to cause preignition of the gasoline in the combustion chamber of an engine.

The motor fuel to which the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate is added can comprise a mixture of hydrocarbons boiling in the gasoline boiling range. However, the problem of preignition is primarily present in heavily leaded gasolines having a research octane number of at least about 90. The gasoline to which the tetraethyl lead is added can be either a straight-run gasoline or a gasoline obtained from a conventional cracking process, or mixtures thereof. The gasoline to which the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate is added in accordance with our invention can also contain components obtained from processes other than cracking, such as alkylation, isomerization, hydrogenation, polymerization, hydrodesulfurization, hydroforming, "Platforming," or combinations of two or more of such processes, as well as synthetic gasoline obtained from the Fischer-Tropsch and related processes.

In addition to the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate, the leaded gasoline of our invention can contain other conventional additive agents including upper cylinder lubricants, oxidation inhibitors, anti-freeze agents, metal deactivators, dyes, and the like.

The cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate presents no particular problem with respect to its addition to gasoline. While the cocoamine salt can be added directly to the gasoline, one convenient method of adding it to the fuel is by forming a concentrate thereof with a light lubricating oil and thereafter adding the concentrate to the fuel.

In order to illustrate the improved preignition characteristics obtained with a fuel of the invention, a test was employed in which the fuel was burned in a stationary Cadillac engine having a 9 to 1 compression ratio.

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The engine conditions at the time of the preignition evaluation were as follows:

Speed----- 1000 and 2000 R. P. M.
Spark advance----- 10°
Air:fuel ratio----- 11.5:1 and 10.3:1 at
1000 and 2000 R. P. M., respectively

In this test the load and throttle position are varied, dependent upon when preignition is encountered. At the start of the test the engine is under no load. The throttle is gradually increased until preignition is observed. If full throttle is reached without preignition, the engine is operated at full throttle for 30 seconds or less if preignition occurs sooner. If preignition is not encountered after 120 hours (5 days), the test is usually discontinued. The data set forth in Table I was obtained when the Cadillac engine was operated under the above test procedure with a reference gasoline, normally tending to preignite, containing about 1.5 cubic centimeters (2.49 grams) of tetraethyl lead and about 1.47 grams of a mixture of ethylene dibromide and ethylene dichloride per gallon of gasoline and a similarly leaded gasoline containing about 1.4 cubic centimeters (2.32 grams) of tetraethyl lead, about 1.37 grams of a mixture of ethylene dibromide and ethylene dichloride, and 0.67 gram (0.3 times the theory) of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate. In each instance, the gasoline had CFR research method octane numbers of about 92 (unleaded) and 95 to 96 (leaded).

Table I

Hours of Operation	Amount of Preignition			
	With Reference Gasoline at—		With Leaded Gasoline Containing 0.67 Gram of the Cocoamine Salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate per Gallon of Gasoline at—	
	1,000 R. P. M.	2,000 R. P. M.	1,000 R. P. M.	2,000 R. P. M.
0-----	none-----	none-----	none-----	none-----
24-----	mild-----	mild-----	do-----	mild-----
48-----	violent-----	violent-----	do-----	violent-----
72-----	do-----	do-----	do-----	none-----
96-----	do-----	do-----	do-----	Do-----
120-----	do-----	do-----	do-----	Do-----

It will be noted from the data in Table I that the engine operating with the reference gasoline showed mild preignition within 24 hours and that violent preignition occurred within 48 hours. When the same engine was operated with the improved gasoline of the invention, there was no sustained preignition even after 120 hours of operation. While violent preignition did occur after 48 hours when operating at 2000 R. P. M., the preignition thereafter disappeared. When the engine was further operated, preignition did not occur even after 161 hours.

The above test was repeated with a gasoline containing about 1.4 cubic centimeters (2.32 grams) of tetraethyl lead, 1.37 grams of a mixture of ethylene dibromide and ethylene dichloride, and 0.96 gram (0.4 times the theory) of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate. No preignition occurred either at 1000 R. P. M. or at 2000 R. P. M. after 156 hours of operation. This gasoline had CFR research method octane numbers of about 92 (unleaded) and 95 to 96 (leaded).

While our invention is described above with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such examples and embodiments and may be variously practiced within the scope of the claims hereinafter made.

We claim:

1. A motor fuel consisting essentially of a gasoline con-

taining tetraethyl lead and an ethylene halide in an amount normally tending to cause preignition of said gasoline in the combustion chamber of a spark ignition engine and at least 0.3 times the theoretical amount required to convert the lead to lead phosphate of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate.

2. A motor fuel consisting essentially of a gasoline containing tetraethyl lead and an ethylene halide in an amount normally tending to cause preignition of said gasoline in the combustion chamber of a spark ignition engine, said fuel containing between 0.3 and 1.5 times the theoretical amount required to convert the lead to lead phosphate of the cocoamine salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate.

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