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MOTOR FUEL PRODUCTS

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The present invention relates to improvements in motor fuel products, more particularly, motor fuel products of the type incorporating the highly effective metallo-organic anti-knock or detonation-inhibiting agents, such as the commonly employed tetra-ethyl lead.

In the production of motor fuels of high anti-knock value, it is customary to employ as a base a gasoline or motor fuel distillate which consists in part or in whole of products resulting from the pressure cracking of heavy hydrocarbon oils, and having, when treated to make them satisfactory for use, a sufficient stability with regard to gum formation to permit of storage for considerable periods or of being subjected to the usual evaporation test for gum without formation of substantial proportions of gum or gum forming constituents. Such products are, in general, relatively low in anti-knock value, and their anti-knock value is improved by the addition of minute proportions of highly effective anti-knock agents, more particularly, the metallo-organic compounds, such as the alkyl compounds of lead, selenium, tin, arsenic, and antimony, iron carbonyl and the like. Of these, the most commonly employed is tetra-ethyl lead, generally in admixture with an alkyl halide, such as ethylene dibromide or ethylene chlorbromide. These admixtures of alkyl halides and tetra ethyl lead are well known as "ethyl fluid" and are referred to in this application as ethyl fluid or tetra ethyl lead solution. In order to suitably measure and control their addition to the gasoline, the tetra-ethyl lead and accompanying alkyl halide are usually dissolved in a suitable solvent, miscible with the gasoline or motor fuel, such as kerosene, solvent naphtha, or the like, and various dyes may be incorporated in the liquid. This concentrated solution, in general, contains from 25 to 50% and usually about 40% of the active metallo-organic compound.

I have found that the addition of an anti-knock compound, and particularly of metallo-organic compounds such as tetra-ethyl lead, even in the minute amounts required for their anti-knock effect, deleteriously affects the stability of the gasoline or motor fuel distillate, greatly increasing its tendency to form gum on storage and the amount of gum developed in the ordinary tests therefor. This tendency to increased gum formation, and particularly on storage, may be indicated by an accelerated test known as the oxygen absorption induction test, which we prefer to conduct in the manner described in an article by Voorhees and Eisinger, published in the Proceedings of the American Petroleum Institute, January 3, 1929, page 170. In accordance with this test, the amount of oxygen absorbed under certain standard conditions by 100 cubic centimeters of the gasoline or motor fuel distillate at a temperature of about 210° F. with an oxygen atmosphere under a pressure of 2.5 atmospheres is determined, and the period prior to the time at which the rate of absorption becomes 1 cc. per minute is designated as the oxygen absorption induction period.

The gasoline or motor fuel distillates to which the anti-knock material is added are in general products of pressure distillation carried out under substantial pressures, ordinarily in excess of 100 lbs. gauge and generally under pressures of 250 to 900 lbs. and at temperatures ordinarily not exceeding 950° F. Such products, when subjected to the usual refining treatment for removal of sulfur and of highly colored constituents are relatively low in anti-knock value, ordinarily having an octane number not above 60 to 65; and as stated above, they do not develop gum forming constituents on storage and develop no detectable quantities of gum when subjected to a gum test. As indicating their satisfactory qualities in this respect, their oxygen absorption induction period is ordinarily above 350 minutes, and usually above 500 minutes. However, when sufficient anti-knock agent, such as the concentrated tetra-ethyl lead solution known as "ethyl fluid" or tetra ethyl lead solution is added, there is a marked decrease in their oxygen absorption induction period, the decrease generally being by more than 10 to 12% and frequently by as much as 25 to 30% or even more. The decrease in the oxygen induction period is indicative of a substantial increase in development of gum forming constituents on storage and of gum formed when subjected to the usual evaporation tests.

The following table illustrates the effect upon the gum or resin formation properties of gasoline or motor fuel distillates of the addition of sufficient proportions of a concentrated solution of tetra-ethyl lead, generally called "ethyl fluid" or tetra ethyl lead solution in proportions to impart to the product an octane number of at least 74.

Sample	Oxygen induction period in minutes	
	Without tetra-ethyl lead	With tetra-ethyl lead
A	570	392
B	530	424
C	502	340
D	690	200
E	385	230

The proportion of "ethyl fluid" or ethyl solution containing 40 to 50% of tetra-ethyl lead required to impart the desired anti-knock rating to such fuels may vary from 0.5 to 4 cc. per gallon of the gasoline distillate material.

It has now been discovered that this deterioration or greater instability with respect to gum formation and resinification by the presence of minute quantities of such organo-metallic compounds added to secure an improved anti-knock rating may be decreased or completely counteracted by incorporating in the product containing the organo-metallic compound small proportions of stabilizing aromatic compounds having a substituting group from the class including the hydroxyl, amino and substituted amino groups. The proportions of such compounds added may vary from 0.001% or somewhat less to 0.005% or even 0.01%, based on the weight of gasoline product, or from 0.025 to 0.27 grams per cubic centimeter of tetra-ethyl lead or other organo-metallic compound employed. Such compounds are inert with respect to the organo-metallic compound employed and to the aliphatic halide compounds which usually accompany it. The compounds which I have found particularly suitable for use are the condensed polynuclear compounds having a substituting group selected from the class consisting of the hydroxyl and amino groups, such as alpha-naphthol, beta-naphthol, alpha - naphthylamine, beta - naphthylamine, the hydrogenated naphthylamines, such as tetra-hydronaphthylamine, dihydroxynaphthalene, amino-naphthol, and the like.

For example, in a particular case, a gasoline or motor fuel distillate derived from a high pressure cracking process, after sweetening treatment, was found to have a satisfactory stability with respect to gum formation, having an oxygen absorption induction period of 690 and showing on the usual gum test, less than 1 mg. gum per 100 cc. and showing substantially no development of gum forming constituents on storage. On the addition of a minute amount of ethyl fluid (less than 1 cc. per gallon), the oxygen absorption induction period dropped to 200 minutes and it was found that gum developed on storage and on the usual gum test, the amount of gum formed rose to an excessive figure, being greater than 5 mg. per 100 cc. On the addition thereto of small proportions of alpha-naphthol, this deterioration was largely counteracted and the material stabilized to a satisfactory extent with respect to gum and resin formation. Thus, the addition of 0.002% alpha-naphthol increased the oxygen absorption induction period to 490 and the addition of 0.004% of alpha-naphthol increased it to 590, these figures being indicative of satisfactory gum stability. Other specific compounds of the class hereinbefore set forth produced similar results, largely or completely counteracting the action of the organo-metallic compound and restoring the stability of the fuel product.

I may also employ, to counteract the deleterious effect of such organo-metallic compounds upon hydrocarbon distillates of this character various polyhydroxy aromatic compounds such as hydroquinone, resorcinol, catechol, pyrogallol, nicotine pyrogallate, amyl gallate, and the like; and amino phenols, such as para-aminophenol, diaminophenol, para and ortho-methyl-aminophenols, hydimethyl-aminophenol, benzyl-aminophenols, hydroxyazobenzene, butyl and isopropyl-aminophenols, dihydroxy-diphenylamine, paraphenetidine, and the like. The proportions employed are within the ranges hereinbefore stated, the specific proportion required varying with the specific character of the hydrocarbon distillate and the proportion of the organo-metallic compound employed. The specific proportion of any ingredient required may be readily determined by the application of the oxygen absorption test, hereinbefore referred to.

It has been found that a satisfactory method of introducing the inhibiting agent is by incorporating it in the concentrated solution of the organo-metallic compound. In such case, it is in general necessary to modify the solvent employed in the concentrated solution of the organo-metallic compound to permit of incorporation therein of the requisite amounts, varying from 10 to 25%, of the desired inhibiting substance. Thus, instead of a solvent consisting substantially entirely of kerosene or other similar fluid, I may employ a solvent consisting of a mixture of kerosene and benzol containing 25 to 50% of the latter, a mixture of kerosene and acetone containing from 20 to 50% of acetone, or a mixture of kerosene, acetone and benzol in approximately equal proportions. A suitable concentrated fluid or solution for the purpose contains 60% tetra-ethyl lead, 25% ethylene dibromide and the remainder, the mixed solvent of the character hereinbefore set forth. With this is incorporated 0.025 to 0.27 grams of the anti-oxidant or aromatic reducing agent per cubic centimeter of tetra-ethyl lead; for example, I may employ 0.132 to 0.266 and preferably about 0.175 to 0.20 grams of alpha-naphthol per cubic centimeter of tetra-ethyl lead in the fluid. This concentrated fluid is then added to the hydrocarbon motor fuel distillate of low anti-knock value in proportion to impart to it the desired anti-knock rating, generally an octane rating of 74 or higher. The proportion of the concentrated fluid required for this purpose may vary from 0.5 cc. to 4 or 5 cc. per gallon, but, in general, with cracked hydrocarbon distillate of satisfactory gum stability, as indicated in general by an oxygen absorption induction period of at least 300, but with a low anti-knock rating, from 0.5 to 1.5 cc. are sufficient to impart anti-knock ratings of 74 octane number or higher, equivalent to the addition of 3 cc. or more standard ethyl fluid to a straight-run Mid-Continent gasoline.

What I regard as new, and desire to secure by Letters Patent, is:

1. A motor fuel product comprising principally an unsaturated hydrocarbon distillate boiling within the gasoline boiling range and initially stable with respect to gum formation, an added small proportion of tetra ethyl lead solution as a knock suppressing agent, the addition of which results in an impaired stability of the motor fuel with respect to gum formation, and a small amount of an amino hydroxy benzene whereby said impairment of gum stability is corrected.

2. The process of restoring the gum stability of a cracked gasoline initially stable with respect to gum formation but whose gum stability has been impaired by the addition of a tetra ethyl lead solution as a knock suppressing agent, comprising adding to said gasoline a small amount of an amino hydroxy benzene wherein one amino hydrogen has been substituted by a hydrocarbon radical.

3. A motor fuel product comprising a cracked hydrocarbon distillate boiling within the gasoline boiling range and initially stable with respect to gum formation, as indicated by an induction period of at least 300 minutes; a small proportion of tetra ethyl lead as a knock suppressing agent, the addition of which results in an impairment of the stability of the motor fuel with respect to gum formation; and a small amount, not exceeding

about 0.01%, of an amino hydroxy benzene compound to inhibit said impairment of gum stability.

4. The process of restoring gum stability of a motor fuel comprising cracked gasoline which is initially stable with respect to gum formation and whose gum stability has been impaired by the addition of tetra ethyl lead as a knock suppressing agent, comprising adding to said gasoline of impaired gum stability not more than 0.01% of a hydrocarbon substituted-amino hydroxy benzene whereby said impairment of gum stability is substantially inhibited.

5. The method of restoring the gum stability of a motor fuel containing cracked gasoline which has been impaired by the addition of less than 1 cc. of ethyl lead solution per gallon of motor fuel, comprising adding to said motor fuel not more than 0.01% of an amino hydroxy benzene compound wherein one amino hydrogen has been substituted by a hydrocarbon radical.

6. The method of preventing tetra ethyl lead solution from impairing the gum stability of an initially gum stable motor fuel containing cracked gasoline, which comprises incorporating in said motor fuel an amino hydroxy benzene compound wherein one amino hydrogen has been substituted by a hydrocarbon radical.

7. The method of preventing tetra ethyl lead solution from impairing the gum stability of an initially gum stable motor fuel containing cracked gasoline, which comprises incorporating in said motor fuel not more than 0.01% of an aryl substituted-amino hydroxy benzene.

8. The method of preventing tetra ethyl lead solution from impairing the gum stability of an initially gum stable motor fuel containing cracked gasoline, which comprises incorporating in said motor fuel a small amount of a benzylaminophenol.

9. The method of preventing tetra ethyl lead solution from impairing the gum stability of an initially gum stable motor fuel containing cracked gasoline, which comprises incorporating in said motor fuel not more than about 0.01% of para benzylaminophenol.

10. A motor fuel product consisting principally of an unsaturated hydrocarbon distillate boiling within the gasoline boiling range and initially stable with respect to gum formation, a small proportion of tetra ethyl lead solution as a knock suppressing agent, the addition of which results in an impaired stability with respect to gum formation; and a small amount of a benzylaminophenol whereby said impairment of gum stability is corrected.

11. The method of preventing tetra ethyl lead solution from impairing the gum stability of an initially gum stable motor fuel containing cracked gasoline, which comprises incorporating in said motor fuel a small amount of an amino hydroxy benzene wherein an amino hydrogen has been substituted by an alkyl radical.

12. A motor fuel product comprising principally an unsaturated hydrocarbon distillate boiling within the gasoline boiling range and initially stable with respect to gum formation as indicated by an induction period of at least 300 minutes, a small proportion of tetra ethyl lead solution as a knock suppressing agent, the addition of which results in an impaired stability with respect to gum formation, and a small amount of a methyl-amino phenol to inhibit said impairment of gum stability.

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