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STABILIZATION OF GASOLINE AND OF ADDITION AGENTS THEREFOR

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This invention is based on the finding of the unique and unsual properties of certain di- or trialkyl phenols in stabilizing certain substances commonly employed as motor fuel or gasoline additives. In particular, it pertains to the stabilization of aromatic amines and to the stabilization of hydrocarbon compositions such as gasoline which contain these amines alone or in combination with metal antiknock additives such as tetraalkyl lead, metallic carbonyls, etc.

It is an object of the invention to produce stabilized aromatic hydrocarbon amines. These stabilized or inhibited aromatic amines may be dissolved in gasoline or other motor fuel; hence, it is an object of the invention to provide motor fuels containing aromatic amino compounds which fuels are stabilized against oxidation or decomposition. Another purpose is to provide motor fuels containing tetraalkyl lead and/or metallic carbonyl compounds which compounds are stabilized by the additives of the present invention. An additional object is to provide improved motor fuels such as aviation gasoline having high anti-knock ratings and improved oxidation or storage stability. Further objects will be apparent from the following description.

Aromatic amino compounds, upon exposure to air, often exhibit a tendency to change color as their period of contact with oxygen lengthens. This color change is the first noticeable sympton of oxidative decomposition which, since it is catalytic in nature, proceeds, if unchecked, at an accelerated rate until the amino compounds are entirely altered in composition and usefulness.

A particular employment for aromatic amino compounds, especially those of low molecular weight, is in motor fuels such as gasoline in which they exert a beneficial anti-knock effect. It will be appreciated, therefore, that if such aromatic amines are produced for incorporation in gasoline, it is especially desirable that they be stabilized against oxidation, since if such decomposition sets in either before or after their addition to the base fuel, it will not only decrease their own value as a fuel component but may also promote the decomposition of the base fuel, resulting in gum formation, increased knock rating, volatility changes, etc.

Aromatic amines have also been added to cracked gasolines in small quantities in order to decrease the gum forming tendencies of the gasoline. Since such inhibition of the oxidation of the gasoline is achieved by the preferential oxidation of the amino inhibitor, it will be realized how difficult it may be to find a substance which

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will stabilize such aromatic amines themselves, both before and after their addition to gasoline.

For this problem, the broad class of known gasoline inhibitors has been found ineffective. Indeed many of them act as pro-oxidants or oxidation accelerators for the amino compounds. Commonly used gasoline stabilizers which have been found to be pro-oxidants for aromatic amines include: para benzyl amine phenol, alpha-naphthol, 4-tertiary butyl catechol, hydroquinone, pyrogallol, beta-naphthol, para phenylene diamine and diphenyl phenylene diamine. Other pro-oxidant substances included thiophenol, thiodiglycollic acid, FeS, sulfanilic acid, salicylic acid, brom benzene, dianisidine, iodine, iron or galvanized iron surfaces, sodium nitrite, benzoyl peroxide, lead peroxide, copper phenyl propionate, manganese oleate and stannous chloride. Gasoline inhibitors which were found to be without inhibiting effect on aromatic amines included: phenyl-alpha-naphthylamine, mixtures of crecylic acids boiling between about 220° C. and 240° C., 2, 3, 5, 6-tetra methyl phenol, penta-methyl phenol, 2, 3, 5-trimethyl phenol, para, para' dihydroxy diphenyl, guaiacol, durohydroquinone, thymol, resorcinol, anthraquinone, etc.

It has now been found, however, that a particular group of polyalkyl phenols in which the alkyl groups are attached at the 2, 6 or 2, 4, 6 positions, as hereafter more fully described, have unique stabilizing properties for aromatic amino compounds, either when the amines are alone or when they are dissolved in gasoline. The stabilizing agents of the present invention are polyalkyl phenols in which the 4 or para position is occupied by a hydrogen atom or a methyl or ethyl group and of the two ortho positions, 2 and 6, one is occupied by a primary, secondary or tertiary alkyl radical and the other by a primary or secondary alkyl radical. It will thus be seen that the polyalkyl phenol may contain only one ortho tertiary alkyl radical (the second ortho radical being primary or secondary) but may contain two ortho secondary alkyl radicals, two ortho primary alkyl radicals or one ortho primary and one ortho secondary alkyl radical.

The ortho alkyl radicals (only one of which, as just stated, may be a tertiary alkyl) may conveniently be methyl, ethyl, n-propyl, iso-propyl, n-, iso-, secondary and tertialy butyl, and the various primary, secondary or tertiary amyl, hexyl, heptyl, octyl, and homologous radicals. In general, radicals containing not more than about 16 or 20 carbon atoms are preferred, those 2,6 or 2,5,6-poly alkyl phenols containing a total

of not more than about 12 carbon atoms in all alkyl groups being particularly desirable (i. e. those having a maximum of about 18 carbon atoms counting the nuclear carbon atoms). The alkyl radicals should generally be such as to render the phenols soluble in the composition to which they are added. Too high a number of carbon atoms causes the compounds to be waxy and difficultly soluble. However, particularly in gasolines of appreciable aromatic contents, phenols with relatively large ortho wax radicals containing up to, say, 35 or 40 or even more carbon atoms may be suitable, especially if those radicals contain branched chains. The ortho radicals may also comprise one or more aromatic groups such as phenyl, tolyl, benzyl, etc., although strictly aliphatic radicals are generally superior.

The above limitations regarding the nature and placement of the several hydrocarbon radicals on the phenol are very important. In this connection, it is of interest that 2,4,6-tri tertiary alkyl phenols, for example, 2,4,6-tri tertiary butyl phenol, are actually pro-oxidants for aromatic amines—that is, they are worse than no inhibitor at all. Other 2,4,6-trialkyl phenols found to be pro-oxidants for aromatic amines are 2,6-di-tertiary butyl-4-methyl or ethyl phenols and 2,6-dimethyl-4-tertiary butyl phenol.

The aromatic amines generally added to gasoline for their anti-knock value are usually mononuclear monoamines having not more than a total of 6 carbon atoms in all alkyl radicals. Particular mention may be made of the following: aniline, N-, mono- and di-methyl or higher alkyl anilines (which may also be substituted in the nucleus); mono-, di-, and trimethyl and higher nuclearly alkylated anilines (which may also be substituted on the N atom), such as toluidines, xylidines, cymidine, cumidine, pseudo cumidine, etc., as well as suitable substituted derivatives. Mixtures of aromatic amines, as well as the individual amines, may be employed and polyamines may also be used. Likewise, aromatic-rich petroleum fractions may be nitrated and reduced to give mixtures such as described in U. S. Patents 1,844,362 and 2,252,099, which mixtures may be blended in a motor fuel according to the present invention.

However, the trialkyl phenolic inhibitors will also stabilize mononuclear amines having a greater number of carbon atoms than indicated above, i. e. greater than 6, as well as poly-cyclic aromatic hydrocarbon amines, e. g. various naphthylamines, alkyl naphthylamines, aryl naphthylamines, anthracylamines and the like.

It is understood that the inhibitor must be well distributed throughout the substance to be protected. Thus, if the amine is a liquid under normal conditions, the inhibitor should be in true or colloidal solution. If it is a solid, the inhibitor may be incorporated by first melting the amine, distributing the necessary amount of inhibitor as by dissolving it, and then allowing the mixture to solidify; or else by merely spraying the inhibitor or a solution thereof onto the solid amine. In undiluted aromatic amines, the content of the polyalkyl phenol may range from about 0.01% to 1% (by weight), preferably about 0.1% to 0.5%.

Stabilization of typical amines is shown by the following data: A liquid mixture of amino xylenes was examined for color at intervals, and the time elapsed to allow the darkening from 2 to 6 A. S. T. M. color at 90° F. in the presence of air, was determined. The following results are typical:

Inhibitor	Time
No inhibitor	About 1 week.
0.2% 2,4-dimethyl-6-tertiary butyl phenol	3 months.

In contrast, some of the commercial gasoline inhibitors reduced the time of darkening to about one day.

Blends of gasoline containing aromatic amines and the polyalkyl phenolic inhibitors were also tested with highly satisfactory results. For example, a blend of unleaded 100 octane aviation gasoline containing 2½% v. xylidine and 0.002% 2,4-di-methyl-6-tertiary butyl phenol showed no change in color or gum content after 22 hours in the dark at 80° C.

Quantitative determinations of the effectiveness of inhibitors of the present invention in stabilizing xylidine were made by determining the light transmission through various xylidine samples for a specific wave length (λ=550 mu) using a Coleman spectrophotometer. Since the formation of colored products and oxidation of the xylidine occur simultaneously on aging, the decrease of light transmitted through the solution is an indication of the extent of oxidation. The following determinations were made at 70° C., one atmosphere of air and employing inhibitor concentrations of 0.2% w.

Inhibitor	Time to reach 10% transmission	Increase in 10% transmission due to inhibition, as percent of blank
	Hours	
None	35	0
2,4,6-trimethyl phenol (mesitol)	186	430
2,6-dimethyl phenol	119	250
2,4-dimethyl-6-secondary butyl phenol	111	220
2,4-dimethyl-6-tertiary amyl phenol	110	210
2,4-dimethyl-6-tertiary octyl phenol	79	130
2,4-dimethyl-6-tertiary butyl phenol	69	97

It has also been found that combinations of the present polyalkyl phenols and aromatic amines, such as the earlier enumerated monocyclic aromatic amines having less than a total of about 7 carbon atoms in all alkyl groups, exhibit an inhibiting or stabilizing effect on gasoline, which effect is greater than the calculated total of the inhibition produced by each additive alone. This effect is particularly noticeable in saturate or initially stable gasoline such as aviation gasoline composed of straight run, cyclopentane, aromatics, alkylate, hydroformed fractions and the like, which initially stable gasoline has been rendered unstable by the incorporation of tetraalkyl lead.

In such leaded gasolines containing aromatic amines an unusual degree of stability may be obtained by employing two or more of the phenolic inhibitors. For example, 2,4-dimethyl-6-tertiary butyl phenol is an outstanding stabilizer of tetraalkyl lead whereas some of the other phenolic inhibitors of this invention are more effective stabilizers for aromatic amines than is 2,4-dimethyl-6-tertiary butyl phenol. Therefore, in a leaded aviation gasoline containing aromatic amines, for instance, one may advantageously employ both 2,4-dimethyl-6-tertiary butyl phenol and another of the herein described polyalkyl phenols, such as 2,4,6-trimethyl phenol, 2,6-

dimethyl phenol, 2,4-dimethyl-6-secondary butyl phenol, 2,4-dimethyl-6-tertiary amyl phenol, 2,4-dimethyl-6-tertiary octyl phenol, and the like.

Effective total amounts of the polyalkyl phenolic inhibitors in a gasoline are generally between about 0.0001% to 0.1% (by weight), a preferred range being from about 0.001% to about 0.01% or 0.1%. The aromatic amines may be employed in about 0.25%–3% (by volume) in a gasoline although higher or lower quantities can also be used. The upper limit is usually prescribed by maximum boiling range specifications of the gasolines. Since the amines are relatively high boiling, they may raise the upper boiling range of the gasoline above permissible limits if used in excessive amounts. On the other hand, amounts of the amines below the lower limit indicated give, as a rule, insufficient improvement in knock rating to warrant their use. About 1% has been found to be particularly advantageous. The combination of aromatic amines and the specific polyalkyl phenols has a synergistic stabilizing effect when applied particularly to saturated, initially stable gasolines rendered unstable by the addition of metal anti-knock compounds, as well as to unsaturated, initially unstable gasolines (such as cracked gasolines) with or without metal anti-knock compounds. Up to about 6 cc. per gallon of tetraethyl lead or an equivalent amount of another tetraalkyl lead may normally be added to gasolines.

Solubilizers for the aromatic amines may also be present, particularly in gasolines which contain but a small amount of aromatic constituents. Such mutual solvents may be low molecular weight alcohols, ethers, ketones, in particular five or six carbon atom unsymmetrical ketones, aromatics such as benzene, toluene, etc.

A further advantage in the use of the combination of aromatic amino and polyalkyl phenol is that when the inhibitor effectiveness of the compounds begins to wear off, a sharp break in the induction period does not occur, but rather the formation of deterioration products proceeds slowly and a visible precipitate forms only after extended aging. This is in marked contrast to the action of most oxidation inhibitors whose effectiveness is usually terminated quite suddenly at the end of their period of stabilization with the rapid formation of degradation products in the gasoline and the consequent prompt termination of the usefulness of the motor fuel.

The synergistic effect of aromatic amines and the present polyalkyl phenols in gasoline may be seen from the following tests made with pure xylidine (5-amino-1,3-dimethyl benzene) in a 100 octane aviation gasoline composed of approximately 45% straight run gasoline, 45% alkylate and 10% cyclopentane and containing 4 cc. of tetraethyl lead per gallon.

Additive	Time required to form 5 mg. of A. S. T. M. gum/100 ml., hours
None	2.33
1% xylidine	4.5
2,4-dimethyl-6-tertiary butyl phenol (1 mg./100 ml.)	37.5
2,4-dimethyl-6-tertiary butyl phenol (1 mg./100 ml.)+1% xylidine	78

It has also been found that the combination of the present polyalkyl phenols with aromatic amines shows extraordinary stabilizing power for

metallic carbonyl compounds contained in gasoline or other motor fuel.

It is known that numerous metallic carbonyl compounds possess desirable anti-knock properties when incorporated in a hydrocarbon fuel. However, various difficulties have beset their particular utilization, notable among which has been their chemical instability and ease of decomposition on standing, as well as their tendency to catalyze the breakdown of the hydrocarbon fuel, producing such effects as gum formation and the like. Although the anti-knock function of metallic carbonyls in gasoline may often be performed in part by other compounds such as tetraethyl lead, there are particular applications in which such other substances are not applicable as in a "break in" fuel or in a heavily leaded fuel to which the addition of more tetra-alkyl lead would have little effect.

Metallic carbonylic compounds contemplated by the present application are, for example, the various carbonylic compounds of iron, nickel, cobalt, molybdenum, mercury, etc., as well as their various applicable derivatives. Among these may be mentioned $Fe(CO)_4$, $Fe(CO)_5$, $Fe_2(CO)_{15}NO$, $FeNi(CO)_9$, $Ni(CO)_4$, $Co(CO)_3NO$, $Mo(CO)_6$, $Hg(Co(CO)_4)_2$. Compounds which decompose under engine conditions to produce metallic carbonyls may also be employed, such as complexes of carbonyls with ammonia, amines, alkanol amines, etc.

In general, an amount of metallic carbonylic compound in the range of about 0.25 to 3 cc./gallon is adequate for a break-in fuel, although up to about 10 cc./gallon may be used. In addition, there may be present up to about 6 cc. of commercial tetra-alkyl lead per gallon as well as various solutizers such as alcohols, ketones, esters, pyridine, aromatic constituents such as benzene and the like.

Advantage of this triple combination of polyalkyl phenol, aromatic amine and metallic carbonyl may be seen from the following oxygen stability test on a straight run aviation gasoline blend containing 4 cc. of tetra-ethyl lead per gallon and having an octane number of 91 (without the iron pentacarbonyl).

Additives	Concentration, mg./100 ml.	Induction period at 110° C. and 100 p. s. i. oxygen for—	
		Original gasoline	Gasoline+½ cc. $Fe(CO)_5$[2] per gal.
None		5.00	1.08
24M6B [1]	1 mg.	14.25	5.75
4-tertiary butyl catechol	2 mg.	2.75	3.50
4,4'dihydroxy-3,3' dimethyl diphenyl.	do.	6.00	2.42
Alpha naphthol	do.		2.92
24M6B [1]+3,5-xylidine	1 mg.+1% v.	40	40
24M6B [1]+anthranilic acid.	1 mg.+2.5 mg.	15	5.58

[1] 2,4-dimethyl-6-tertiary butyl phenol.
[2] Iron pentacarbonyl, 90% practical Eastman Kodak Co. product.

This application is a continuation-in-part of my copending United States patent applications, Serial No. 441,876, filed May 5, 1942; Serial No. 478,290, filed March 6, 1943; Serial No. 493,683, filed July 6, 1943; and Serial No. 502,707, filed September 15, 1943.

The invention claimed is:

1. A composition comprising gasoline hydrocarbons containing a knock-reducing amount of a mononuclear aromatic amine in which the total

number of carbon atoms in all alkyl radicals is less than 7 and a stabilizing amount of a diortho-para polyalkyl phenol in which the para substituent is selected from the group consisting of hydrogen atoms and methyl and ethyl radicals, one ortho radical being selected from the group consisting of primary, secondary and tertiary alkyl radicals, the other ortho radical being selected from the group consisting of primary and secondary alkyl radicals.

2. A composition comprising gasoline hydrocarbons containing a knock-reducing amount of a mononuclear aromatic amine in which the total number of carbon atoms in all alkyl radicals is less than 7 and a stabilizing amount of a diortho para polyalkyl phenol having a maximum of about 18 carbon atoms and in which the para substituent is selected from the group consisting of hydrogen atoms and methyl and ethyl radicals, one ortho radical being selected from the group consisting of primary, secondary and tertiary alkyl radicals, the other ortho radical being selected from the group consisting of primary and secondary alkyl radicals.

3. A composition comprising gasoline hydrocarbons containing about 0.25%–3% (by volume) of a mononuclear aromatic amine in which the total number of carbon atoms in all alkyl radicals is less than 7 and about 0.001%–0.1% (by weight) of a diortho para polyalkyl phenol in which the para substituent is selected from the group consisting of hydrogen atoms and methyl and ethyl radicals, one ortho radical being selected from the group consisting of primary, secondary and tertiary alkyl radicals, the other ortho radical being selected from the group consisting of primary and secondary alkyl radicals.

4. A composition comprising gasoline hydrocarbons containing a tetraalkyl lead compound, a knock-reducing amount of a mono nuclear aromatic amine in which the total number of carbon atoms in all alkyl radicals is less than 7 and a stabilizing amount of a diortho para polyalkyl phenol having a maximum of about 18 carbon atoms and in which the para substituent is selected from the group consisting of hydrogen atoms and methyl and ethyl radicals, one ortho radical being selected from the group consisting of primary, secondary and tertiary alkyl radicals, the other ortho radical being selected from the group consisting of primary and secondary alkyl radicals.

5. A composition of matter comprising a mixture of gasoline hydrocarbons which has been rendered potentially unstable by the addition of tetraalkyl lead, about 0.25% to 3% (by volume) of a mononuclear aromatic amine in which the total number of carbon atoms in all alkyl radicals is less than 7 and a total of about 0.001% to 0.1% (by weight) of two phenols, one of which is 2,4-dimethyl-6-tertiary butyl phenol and the other being a different diortho para poly alkyl phenol having a maximum of about 18 carbon atoms and in which the para substituent is selected from the group consisting of hydrogen atoms and methyl and ethyl radicals, one ortho radical being selected from the group consisting of primary, secondary and tertiary alkyl radicals, the other ortho radical being selected from the group consisting of primary and secondary alkyl radicals.

6. A composition comprising gasoline hydrocarbons containing up to about 6 cc. tetraethyl lead per gallon of said composition, about 0.25% to 3% (by volume) of xylidine and about 0.001% to 0.1% (by weight) of a mixture of 2,4-dimethyl-6-tertiary butyl phenol and 2,4,6-trimethyl phenol.

7. A composition suitable for addition to a mixture of gasoline hydrocarbons containing a tetraalkyl lead compounds, which comprises a xylidine and a total of about 0.01%–1% (based on the xylidine weight) of 2,4-dimethyl-6-tertiary butyl phenol and 2,4,6-trimethyl phenol.

8. A composition comprising gasoline hydrocarbons containing a metal carbonyl, stabilized by an aromatic amine and a diortho para polyalkyl phenol in which the para substituent is selected from the group consisting of hydrogen atoms and methyl and ethyl radicals, one ortho radical being selected from the group consisting of primary, secondary and tertiary alkyl radicals, the other ortho radical being selected from the group consisting of primary and secondary alkyl radicals.

9. A composition comprising gasoline hydrocarbons containing iron carbonyl and tetraalkyl lead which composition is stabilized by a mono nuclear aromatic amine in which the total number of carbon atoms in all alkyl radicals is less than 7, 2,4-dimethyl-6-tertiary butyl phenol and another diortho para polyalkyl phenol having a maximum of about 12 carbon atoms in all alkyl radicals and in which the para substituent is selected from the group consisting of hydrogen atoms and methyl and ethyl radicals, one ortho radical being selected from the group consisting of primary, secondary and tertiary alkyl radicals, the other ortho radical being selected from the group consisting of primary and secondary alkyl radicals.

10. A composition consisting essentially of a mixture of normally stable saturated gasoline-type fuel hydrocarbons containing a knock-reducing amount of a mononuclear aromatic amine in which the total number of carbon atoms in all alkyl radicals is less than 7 and a stabilizing amount of a diortho para polyalkyl phenol in which the para substituent is selected from the group consisting of hydrogen atoms and methyl and ethyl radicals, one ortho radical being selected from the group consisting of primary, secondary and tertiary alkyl radicals, the other ortho radical being selected from the group consisting of primary and secondary alkyl radicals.

11. A composition consisting essentially of a mixture of normally stable saturated gasoline-type fuel hydrocarbons containing an amount of tetraalkyl lead sufficient to render it relatively unstable on storage, about 0.25% to 3% (by volume) of a mononuclear aromatic amine in which the total number of carbon atoms in all alkyl radicals is less than 7 and a total of about 0.001% to 0.1% (by weight) of two phenols, one of which is 2,4-dimethyl-6-tertiary butyl phenol and the other being a different diortho para polyalkyl phenol having a maximum of about 18 carbon atoms and in which the para substituent is selected from the group consisting of hydrogen atoms and methyl and ethyl radicals, one ortho radical being selected from the group consisting of primary, secondary and tertiary alkyl radicals, the other alkyl substituent being selected from the group consisting of primary and secondary alkyl radicals.

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