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FUEL COMPOSITION

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This invention has to do particularly with protecting hydrocarbon motor fuel compositions from objectionable influences of corrosive impurities and sunlight by the addition of small but effective quantities of organic compounds characterized by ammonium derivatives of alkyl phenol-formaldehyde-hydrogen halide condensation products.

Liquid hydrocarbon fuels employed in internal combustion engines and burners, even though highly refined, are apt to be contaminated with some corrosive impurities such as sulfur- or oxygen-containing compounds, which give rise to a number of difficulties. These impurities are nuisance factors in the corrosion of metal containers, fuel supply lines and engine parts; they lead to bad engine conditions, to lowering of anti-knock value in a spark ignition engine motor fuel and to certain forms of deterioration in the appearance of the fuel.

The undesirable changes in motor fuel compositions arise from a number of different causes, and it is difficult to correct for the effects of all causes by any single stabilizing agent. For example, antioxidants have been used to increase the resistance of a fuel to oxidation, which causes change of color and formation of gum. But this correction by itself is not always sufficient, for it has been found that low boiling hydrocarbon liquids free from gum-forming bodies are subject to discoloration by sunlight and even many of the well-known antioxidants become discolored by sunlight and tend to make the oil cloudy.

Another form of undesirable change occurring particularly in spark ignition motor fuels is due to the instability of metallo-organic anti-knock addition agents, as for example, lead alkyl anti-knock agents, for these compounds have a tendency to decompose and form a precipitate in the fuel, especially when exposed to sunlight or when stored in contact with various metals commonly used in fuel containers.

Still another type of deterioration encountered with hydrocarbon fuel distillates is their discoloration by the action of metals, which action is accentuated when the oils are at elevated temperatures.

An object of the present invention is to provide fuel compositions in which the undesirable effects of corrosive impurities and sunlight are satisfactorily suppressed.

A more specific object is to preserve the clarity and stability of motor fuels containing metallo-organic anti-knock agents with improvement and preservation of the effectiveness of these agents. A further specific object is to confer on the fuel distillates an inertness to metals so as to prevent discoloration or contamination of the fuel, the surface of the metal contacted by the fuel

being made passive at the same time to corrosion by impurities in the fuel.

The type of agent utilized for the purpose of this invention is characterized by ammonium derivatives of alkyl phenol-formaldehyde-hydrogen halide condensation products. These compounds are obtained with satisfactory oil-solubility and effectiveness for the objects of this invention by condensing an alkyl phenol with formaldehyde in the presence of a hydrogen halide acid, then reacting the resulting phenolic condensation product with liquid ammonia or an equivalent strong base, e. g., an amino compound, an organic nitrogen base, or other organic bases, which may contain other metalloids, such as phosphorus. Liquid ammonia is the highly preferred base reactant. Next in order of importance come the aliphatic amines and aromatic amines, primary, secondary, and tertiary.

A very important factor in the preparation and use of these agents is that their effectiveness and oil-solubility increases with the length of the alkyl substituent in the phenol nucleus.

Even though the initial phenolic compound contains a long alkyl or aliphatic substituent group, which in ordinary types of reaction lowers the reactivity of the phenolic compounds, the reaction for preparing the desired agent goes with great ease. The complete reaction may be considered as involving two stages: first, a substitution of a halogenated aliphatic radical in the phenolic compound; and second, a splitting out of the halogen by condensation of the substituted phenolic compound with the base. Very little halogen, and preferably none, is left in the final product. The preparation of the preferred agents is illustrated by the following:

Procedure

Into a solution of 18 parts by weight of para-formaldehyde and 100 parts by weight of strong hydrochloric acid, hydrogen chloride gas was introduced until the solution was saturated. To this mixture, 41 parts by weight of para-isooctyl phenol (para tetramethylbutyl phenol) in benzol solution (50% by weight) were added in the course of one half hour, while stirring well, the temperature increasing from about 15° C. to 50° C. The stirring was continued at 50° C. for an hour after the phenol had been added, and during this time a feeble current of hydrogen chloride was conducted into the solution. The alkyl phenol-formaldehyde-hydrogen chloride condensation product formed remained in solution in the benzol and was separated from the aqueous hydrochloric acid mother liquid. For the second stage of treatment, the separated benzol solution of the condensation product was placed in a beaker, and a dilute liquid ammonia solution in isopropyl alcohol was added to this

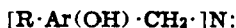
solution while stirring until a fair excess, about 10%, of ammonia was present. The mixture was then transferred to a bomb and heated therein for 16 to 20 hours at 110° C. without further agitation. The pressure developed during heating ranged from about 20 lbs. to 40 lbs. per square inch. The material in the bomb reacted vigorously with considerable evolution of heat. After the reaction was complete in the bomb, the reaction mixture comprising ammonium chloride, an ammonium derivative of the phenol-formaldehyde-hydrogen chloride condensation product, and isopropyl alcohol, was transferred to an open vessel wherein it was diluted with naphtha and water, stirred until the ammonium derivative of the alkyl phenol-formaldehyde-hydrogen chloride condensation product went into solution in the naphtha, while ammonium chloride, excess ammonia, and the isopropyl alcohol were removed by the water. The naphtha solution was washed several times with water to free it of all soluble chlorides after which, to obtain a concentrate of the product, the naphtha solution was distilled to leave a brittle resinous material.

As in the case of many resin preparations, the exact mechanism of the reaction is not entirely understood. In the first stage the alkyl phenol may be regarded as condensing with the reaction product of the hydrogen halide and aldehyde, i. e., with chloromethyl alcohol; or, as condensing with formaldehyde, and the condensation product thereof being condensed with the hydrogen halide. Either way, the resulting product of this reaction may be considered as being a hydroxy alkyl benzyl chloride, or chloromethyl alkyl phenol, with the formula:

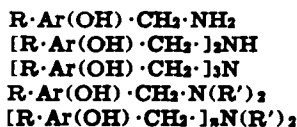


wherein the chlorine analysis of this product shows introduction of approximately one chloromethyl group into one alkaryl-hydroxy or alkyl phenol group, $R \cdot Ar(OH)$, R representing one and more alkyl substituents in the aromatic nucleus Ar .

In the second stage of reaction, the condensation product of the alkyl phenol, the formaldehyde, and the hydrogen halide acid, or the hydroxy alkyl benzyl chloride, splits off the halogen in undergoing a further condensation with the organic base, and thus, the alkyl phenol radical becomes united with the base radical through the methylene ($\cdot CH_2 \cdot$) group, thereby forming compounds containing the following characteristic group:



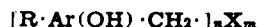
wherein, as before, $R \cdot Ar(OH) \cdot$ represents the alkyl phenol group and the nitrogen atom N , has valences which may be satisfied by hydrogen or organic radicals, (R') e. g. alkyl, cycloalkyl, aryl, or by more than one hydroxy alkyl benzyl radical, as for example, in the following types of compounds:



In the simplest reaction with ammonia the primary amine would be formed, but from analysis of the components of the product, which is a resinous mixture of the amines, it is found that more complex compounds, i. e., the secondary and tertiary amines, are more probably present. Analysis of separated fractions of the

product obtained by solvent extraction shows that one and more of the phenolic groups are combined with one nitrogen atom in the base radical, and principally the product is indicated to have the compositional formula corresponding to that of the secondary amines. However, fractionation is not necessary to obtain, the desired effects of the product as a blending agent; but if so desired, the fractions may be separated to be used as blending agents for the objects set forth.

The base derivatives of the alkyl phenol-aldehyde-hydrogen halide condensation products, which in the broad sense are to be used as stabilizing agents in accordance with the present invention, may be represented by the generalized formula:



wherein n is an integer denoting the number of hydroxy alkyl benzyl groups attached to one or more (m) base radicals X , which is an amino group or an equivalent base radical.

The stabilizing agents herein described, may be blended in small weight proportions of 0.01% to 0.1% or 0.5% with gasoline, naphthas, kerosene, Diesel fuels, heating oils, and similar hydrocarbon distillates boiling within the range of about 100° F. to about 700° F., depending upon the inherent stability of the fuel, its content of corrosive impurities, the particular effectiveness of the stabilizing substances added, the presence of other addition agents in the oil, and the conditions to which the composition is to be subjected.

For example, a gasoline rich in cracked products, e. g., unsaturated and cyclic hydrocarbons, such as are formed in a vapor phase catalytic cracking of gas oil, was satisfactorily stabilized in color; and with tetraethyl lead blended in the gasoline not only was the color in the gasoline kept from changing, but the tetraethyl lead was prevented from decomposing and precipitating.

Example

A cracked gasoline was blended with 0.1% of the ammonium derivative formed from iso-octyl phenol in accordance with the procedure described, and exposed to diffused sunlight in glass sample bottles, as were samples of the same gasoline unblended with the stabilizing agent. The gasoline samples which were not blended with the stabilizing agent underwent discoloration; and with the tetraethyl lead present, within a short period of about 2 days began to show a formation of a cloudy precipitate, which deposited on the sides and bottoms of the bottles as a fairly thick sediment within a few days. The sample containing the stabilizing agent did not change in color and showed no appreciable cloudiness or deposits of lead alkyl anti-knock agent even after standing in the diffused sunlight for a period of 3 months. These tests show the exceptional power of the described agents for preserving the color of the gasoline and for preventing decomposition of the lead alkyl anti-knock agent.

Samples of a light petroleum distillate oil containing immersed polished strips of copper were heated in an oven. In some of these samples were blended small amounts of the stabilizing agent. Examination of these samples, after they were thus treated, showed that those which did not contain the stabilizing agent became greatly discolored, turning grayish brown and murky, while the strips of metal became discolored and

corroded; whereas the oil samples blended with the stabilizing agent remained substantially unchanged, except for a slight coloring, but remained clear and otherwise unchanged, while the polished metal immersed in the blend remained unchanged.

The stabilizing agent blended in a fuel composition appears to render the surfaces of metals in contact with the fuel composition passive and resistant to corrosion when the fuel contains moisture and sulfur impurities. The inhibiting of corrosion has been particularly obtained with iron, copper, and aluminum metals or their alloys. The stabilizing agent may be added to a hydrocarbon fuel distillate to prevent corrosion while the fuel is undergoing processing, fractionation, or refining in order to retard corrosion of the metal apparatus in which the fuel is being treated; or it may be employed in the fuel to overcome corrosion of pipe lines through which the fuel is passed. Also, it is very beneficial in a fuel during storage in metal containers, particularly when there is a tendency for moisture to collect within the containers.

Unlike well-known classes of compounds, including certain phenols and amino phenols, such as amino phenol, alkyl amino phenol, benzyl amino phenol, naphthyl amines, naphthols, etc., which have been extensively investigated as oxidation and gum inhibitors, the stabilizing agents characterized by ammonium derivatives of alkyl phenol-formaldehyde-hydrogen chloride condensation products have relatively little effect in inhibiting oxidation, even though they have exceptionally high effectiveness in stabilizing leaded fuels and in stabilizing the oils against discoloration by sunlight and deterioration in the presence of metals. This does not mean that they are entirely devoid of ability to lower oxidation of the hydrocarbon oil, for even by themselves, they retard oxidation to some extent as illustrated in the following example:

Blends of cracked naphtha blended with 0.02% of the ammonium derivative resin were subjected to gum tests, as were samples of the unblended cracked naphtha, under comparable conditions using the procedure known as the Army gum breakdown tests. The results obtained are tabulated as follows:

	Breakdown
Blank (gasoline unblended).....	minutes.. 35
Blank +0.02% ammonium derivative of chloromethyl alkyl phenol.....	minutes.. 50

From these results it can be observed that the stabilizing agent increases the induction period in accelerated oxidation tests, in which the material tested is heated in a bomb with oxygen under pressure.

The stabilizing agents of the present invention serve a several-fold function; in preventing deterioration of metallo organic anti-knock agents, in retarding catalytic action of metals on the oils, in preserving the color of the oils, and in increasing the effectiveness of an added anti-oxidant or added metallo organic agent.

The substances described as ammonium derivatives of a phenol-formaldehyde-hydrogen chloride condensation reaction are apparently formed in a manner which prevents the reactants from condensing to an infusible and insoluble stage, as occurs in ordinary phenol and formaldehyde condensation reactions. This may be accounted for by the action of hydrogen halide, which evidently prevents many phenol groups from becoming in-

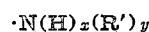
terlinked by methylene groups; and for the objects of this invention it has been found preferable to have the phenol groups contain alkyl or aliphatic substituents having at least 3 or 4 carbon atoms. The alkyl phenols having isoalkyl substituents containing from 4 to about 12 carbon atoms are more particularly preferred. Satisfactory products have been obtained with the aliphatic radical substituent ranging up to 18 or more carbon atoms, as with an octa-decyl group.

Although a very satisfactory procedure for preparing the stabilizing agent has been described with reference to the condensation of a base with a condensation product of an alkyl phenol, formaldehyde, and hydrogen chloride, it is to be understood that other procedures may be employed for obtaining fuel blending agents of similar character though the described procedure is preferred. In these procedures the order of the reaction steps may be changed and equivalent reactants may be used. For example, it may be desired to alkylate the intermediate or final condensation product to introduce alkyl substituents into the phenol nucleus; it may be desired to first react the formaldehyde or other aldehyde with ammonia, or with a primary, secondary, or tertiary amine to form alkyl-alkylol amines for condensation with the phenol or alkyl phenol; or it may be desired to alkylate the base or the base derivative of the phenol condensation product, e. g., with an alkylating agent such as di-ethyl sulfate, an alkyl halide, an alcohol, or ketone, by known alkylating methods, and with reduction by hydrogen, if needed or desired.

As stated before, the more complex resinous type of the agents herein disclosed have been found more particularly effective as stabilizing agents in hydrocarbon fuels. Hence to improve a monomeric agent having, for example, a compositional formula represented by



wherein R and R' represent hydrocarbon radicals, heat polymerization or condensation of such a monomer may be used to convert it into a more complex polymeric type compound, such as represented by the general compositional formula $[R \cdot Ar(OH) \cdot CH_2]_n [N(R')_2]_m$, wherein several of the units $[R \cdot Ar(OH) \cdot CH_2]$ may be linked to one another and be terminally linked to one or more of the structural units $[N(R')_2]$. The amino radical, $\cdot N(R')_2$, in these compounds may be represented more generally by the formula



wherein the y hydrocarbon radicals R' and the x hydrogen atoms attached directly to the nitrogen add up to two, e. g., $\cdot NH_2$, $\cdot N(H)(R')$, or $\cdot N(R')_2$; and of course, the hydrocarbon radicals in each instance may be similar or dissimilar.

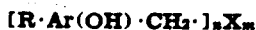
Together with the small amounts of the described blending agents, various other agents may be added to the hydrocarbon fuel distillates. For example, thickening agents, dyes, gum fluxes, ignition promoting agents, oiliness agents, other corrosion inhibitors, various anti-oxidants, and various other anti-knock agents, such as iron carbonyl tin tetraethyl, metallic chelated compounds, etc.

The present invention is not to be limited to any theory of reaction in the formation of the stabilizing agent, nor to any theory on the mechanism by which the agent functions. Although there have been shown and described certain

specific embodiments in this invention, many modifications thereof are possible.

We claim:

1. A fuel composition of matter comprising a hydrocarbon fuel distillate and a small quantity of a resinous condensation product having the general compositional formula:



wherein R represents at least one alkyl group substituent in the aromatic nucleus Ar, the subscripts n and m are integers, and X represents a base radical selected from the group consisting of nitrogen base radicals and phosphorus base radicals.

2. A fuel composition as described in claim 1, in which the subscript n is an integer from 1 to 3, and in which X is a nitrogen base radical in which the nitrogen is linked to the aryl nucleus, Ar, through carbon in a methylene group, $\cdot CH_2 \cdot$.

3. A fuel composition of matter comprising a hydrocarbon fuel distillate boiling within the range of about 100° F. to about 700° F., and a small amount of an ammonium derivative of an alkyl phenol-formaldehyde-hydrogen halide resinous condensation product containing a nitrogen base radical attached to the aryl nucleus of an alkyl phenol group through a methylene group.

4. A motor fuel comprising a gasoline base blended with a small proportion of an ammonium derivative of an alkyl phenol-formaldehyde-hydrogen chloride resinous condensation product, in which the alkyl substituent of the phenol contains at least 4 carbon atoms and in which nitrogen is linked through a methylene group to the cyclic carbon nucleus of the alkyl phenol.

5. A composition as described in claim 4, in which the alkyl phenol is para-iso-octyl phenol.

6. A composition as described in claim 4, in which a metallo-organic anti-knock agent is present in the fuel.

7. A composition as described in claim 4, in which a lead alkyl anti-knock agent is present in the said fuel.

8. A stabilized hydrocarbon fuel composition comprising a hydrocarbon liquid boiling in the range of about 100° F. to 700° F. blended with a small amount of a hydroxy alkyl benzyl chloride chemically condensed with a nitrogen base.

9. A composition as described in claim 8, in which said hydrocarbon liquid is a petroleum naphtha fraction.

10. A composition as described in claim 8, in which said hydrocarbon liquid is a Diesel fuel.

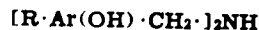
11. A composition as described in claim 8, in which said liquid is a heating oil.

12. The method of stabilizing a gasoline motor fuel composition against deterioration by action of sunlight, heat, and metals with suppression of objectionable influences of corrosive impurities in the fuel, which comprises adding to the fuel approximately 0.01% to 0.5% by weight of a resinous compound containing a nitrogen base radical attached to the aromatic nucleus of an alkyl phenol radical through a methylene group.

13. The method of enhancing and preserving the effectiveness of a lead alkyl anti-knock agent in a motor fuel blend, which comprises adding to said blend approximately 0.01% to 0.5% by weight of a resinous compound containing a nitrogen base radical attached to the aromatic nucleus of an alkyl phenol radical through a methylene group.

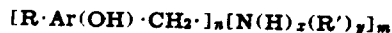
14. The method of suppressing objectionable influences of corrosive sulfur- and oxygen-containing compounds present as corrosive impurities in a hydrocarbon distillate fuel boiling within the range of about 100° F. to about 700° F., and inhibiting corrosion of metals contacted by said distillate, which comprises adding to said fuel approximately 0.01% to 0.5% by weight of a resinous mixture of amino compounds containing a nitrogen base radical attached to the aromatic nucleus of an alkyl phenol radical through a methylene group.

15. The method as described in claim 14, in which said resinous mixture includes principally an amino compound having the compositional formula:



wherein R represents one and more alkyl substituents, containing 4 to 12 carbon atoms, Ar represents a substituted benzene nucleus containing also a hydroxyl group, (OH), substituent, and attached through the methylene group, $\cdot CH_2 \cdot$, to the nitrogen of the secondary amino radical, NH.

16. The method as described in claim 14, in which said resinous mixture includes principally amino compounds having the general compositional formula:



wherein R represents at least one alkyl substituent containing 4 to 12 carbon atoms in a benzene nucleus, Ar, containing also a hydroxy group, (OH), substituent and attached through the methylene group, $\cdot CH_2 \cdot$, to the nitrogen of an amino group, $\cdot N(H)_x (R')_y$, in which the number x plus y of hydrocarbon radicals, R' , and hydrogen atoms, H, respectively, attached directly to the nitrogen add up to 2, and wherein the subscripts n and m are integers indicating the number of bracketed structural units combined in said compounds.

17. A stabilized hydrocarbon fuel composition comprising a hydrocarbon liquid boiling in the range of about 100° F. to 700° F. blended with a small amount of an oil-soluble resinous product of the reaction with excess ammonia of the reaction product of an alkyl phenol with formaldehyde in the presence of hydrogen chloride.

18. Fuel composition according to claim 17 in which said alkyl phenol contains an alkyl group of at least 3 carbon atoms.

19. Fuel composition according to claim 17 in which said alkyl phenol contains an alkyl group of 4 to 12 carbon atoms.

20. Fuel composition according to claim 17 in which said alkyl phenol is iso-octyl phenol.

21. Fuel composition according to claim 17 in which said hydrocarbon liquid is a gasoline.

22. Fuel composition according to claim 17 in which said hydrocarbon liquid is a gasoline containing a metallo-organic anti-knock agent.

23. Fuel composition according to claim 17 in which said hydrocarbon liquid is a gasoline containing lead tetraethyl.

24. Fuel composition according to claim 17 in which said hydrocarbon liquid is a Diesel fuel.

25. Fuel composition according to claim 17 in which said hydrocarbon liquid is a heating oil.

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