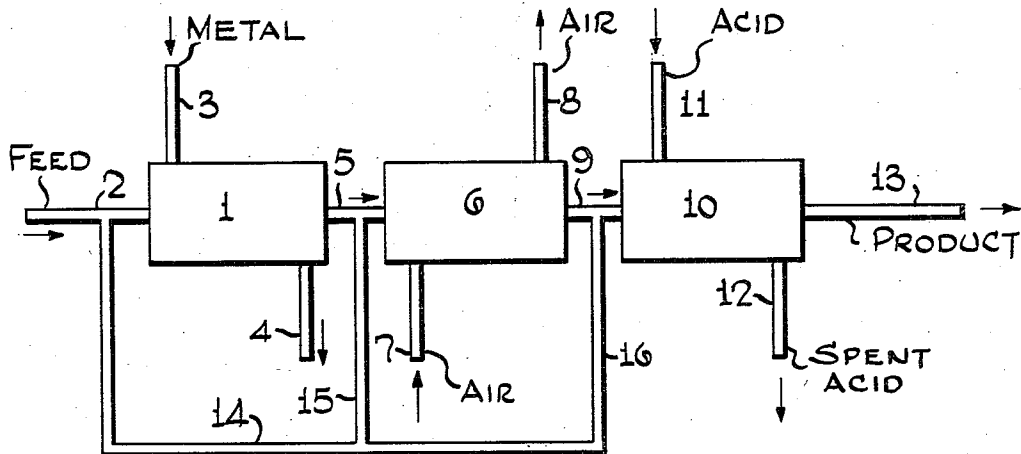


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BY FORMING PEROXIDES IN GASOLINE AND THEN TREATING
WITH AN ORGANIC HYDROXY CARBOXYLIC ACID
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TREATMENT OF GASOLINE FOR IMPROVING OXIDATION STABILITY BY FORMING PEROXIDES IN GASOLINE AND THEN TREATING WITH AN ORGANIC HYDROXY CARBOXYLIC ACID

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5 Claims. (Cl. 196-42)

The present invention is concerned with an improved process for producing stable gasoline. The invention is concerned with an operation wherein peroxides and other deleterious constituents present in a hydrocarbon mixture boiling in the motor fuel or gasoline boiling range are selectively removed by treating the hydrocarbon mixture with an acid. Among the deleterious constituents are small amounts of copper and iron introduced into the gasoline during ordinary refining processes. The copper may enter the gasoline as a result of corrosion of admiralty-metal tubes in heat-exchangers or as a result of reaction in the so-called copper sweetening processes of refining gasoline. The iron may also come from the corrosion of iron or steel pipes and vessels in which the gasoline is processed, conveyed or stored.

In accordance with the present invention, improved, stable, motor fuels are produced by treating hydrocarbon mixtures, containing constituents which form peroxides, with an acid selective for the removal of the peroxides and of the copper and iron impurities, which promote the formation of peroxides. In a preferred embodiment of the invention the formation of peroxides from easily oxidizable hydrocarbons present in the gasoline is first promoted and then the peroxides and the promoters are removed by the selective acid treatment.

Various types of hydrocarbons present in gasoline are susceptible of forming peroxides in varying degree. Naphthenes, isoparaffins, iso-alkyl-aromatics, olefins and di-olefins can form peroxides which tend to lower the antiknock rating of gasoline. All types of peroxides are not equally deleterious, however. Whenever they occur in a gasoline they can be removed selectively by an acid treatment according to the process of the present invention; but in the preferred modification of the process, the formation of the most easily formed and most objectionable peroxides is purposely promoted prior to their removal, so that thereafter the treated gasoline has improved stability in storage. The peroxides of diolefins and particularly of those with conjugated double-bonds are easily formed and are quite deleterious because they not only lower the anti-knock rating of gasoline, but also contribute to the formation of gum in gasoline.

It has been known in the prior art to treat gasolines, and particularly their thermally or catalytically cracked naphtha components, with acid to improve their stability in storage. In general, concentrated sulfuric acid and sometimes even oleum has been used for that purpose. Acid strength of at least 70% and usually of 90% to 95% has been employed. Acid of this concentration is not very selective and it removes not only deleterious constituents but also the desirable olefins of high anti-knock value or Octane Number. Acid of this concentration also tends to act as a polymerization catalyst and to promote the formation of high boiling polymers which have to be removed from the gasoline by re-running in a distillation step. Ordinarily, concentrated sulfuric acid is used in proportions of 5 to 20 lbs. per barrel of gasoline.

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Approximately, the percentages of acid by volume of gasoline being treated are in the range of 1 to 5% of acid of 95% strength.

In accordance with the preferred modification of the present invention, improved, stable, motor fuels are produced by treating hydrocarbon mixtures or naphthas with organic, hydroxy-carboxylic acids, as for example, lactic acid, glycolic acid, malic acid, tartaric acid and citric acid. In the manufacture of highly refined motor fuels by various operations it is well known, as mentioned hereinbefore, that those hydrocarbon compositions, due to the presence of various deleterious substances, tend in the course of time to go "off specification" by the formation of gum or various complex, polymerized or oxidized products.

In order to prevent or at least to retard that deterioration, various inhibitors, anti-oxidants or other addition agents are utilized. It has now been discovered that if hydrocarbon mixtures boiling in the range of motor fuel are treated with an aqueous solution of organic, hydroxy-carboxylic acid, various substances such as peroxides and metal-containing impurities are removed and thus the storage stability of the treated product is improved markedly.

The process of the present invention may be more fully understood by reference to the drawing illustrating a preferred embodiment of the same. Referring specifically to the drawing, a hydrocarbon mixture boiling in the motor fuel boiling range is introduced into zone 1 by means of feed line 2 wherein it is contacted with finely divided copper or iron, or with a naphtha-soluble organic compound containing iron or copper, that is introduced into zone 1 by means of line 3. Excess copper and iron may be removed from zone 1 by means of line 4. The hydrocarbon mixture introduced into zone 1 by means of line 2 is a finished, refined product having a relatively low sulfur content and is of satisfactory motor fuel quality. This contacting of the motor fuel favors the formation of the most easily formed and most objectionable peroxides. The treated oil is withdrawn from zone 1 by means of line 5 and passed into oxidation zone 6 wherein the same is contacted with an oxygen-containing gas introduced by means of line 7 and withdrawn by means of line 8. The treated oil is withdrawn from zone 6 by means of line 9 and passed to an acid contacting zone 10 wherein the same is contacted with acid which is introduced by means of line 11 and removed by means of line 12. This acid treatment removes from the gasoline or motor fuel the objectionable copper and iron as well as the peroxides. A motor fuel of increased stability having a high anti-oxidant characteristic is removed from zone 10 by means of line 13. It is to be understood that anti-oxidants may be added to the treated oil if needed.

While the invention has been described specifically with respect to the deliberate addition of either iron or copper, and in the treatment of oil with an oxygen-containing gas, it is to be understood that the motor fuel may have sufficient copper and iron dissolved therein. Under these conditions the feed oil is passed directly to zone 6 by means of lines 14 and 15. Furthermore, it may not be necessary to add oxygen in which case the feed oil is passed directly to treating zone 10 by means of lines 14 and 16.

The preferred acids used are selected from organic aliphatic or aromatic hydroxy-carboxylic acids. Examples of suitable mono-carboxylic aliphatic acids are lactic (CH₃.CH(OH).COOH) and glycolic (CH₂OH. COOH) acids. Suitable di-carboxylic acids are, for example, malic (HOOC.CH₂.CH(OH).COOH) and tartaric (HOOC.CH(OH).CH(OH).COOH) acids. An example of a suitable tricarboxylic acid is citric (HOOC.CH₂.C(OH)(COOH).CH₂.COOH)

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acid. Among the aromatic carboxylic acids are the three hydroxy-benzoic acids ($\text{HO.C}_6\text{H}_4\text{.COOH}$), the ortho-isomer also known as salicylic acid being preferred among them. The coumaric or hydroxy-cinnamic acids ($\text{HO.C}_6\text{H}_4\text{.CH:CH.COOH}$) can also be used. However, the hydroxy-carboxylic acids wherein the hydroxy-radical is attached to the same carbon atom as the carboxyl radical are particularly preferred. Next preference is given to the hydroxy-carboxylic acids, like the ortho-substituted aromatic acids, for example, salicylic acid, wherein the two functional groups are on adjacent carbon atoms. A very desirable acid comprises lactic acid.

The organic acids used in accordance with the instant invention are conveniently applied in aqueous solution. The concentration of acid in water can be varied greatly, from about 1% to 95% or higher or to the value of saturation at the operating temperature. When the acid solution is to be used only once, a low concentration is adequate to remove or to react with the deleterious materials present in the gasoline being treated. However, it is generally desirable to have the concentration at about 10%, or higher, in order to facilitate the solution of the deleterious materials in the excess reagent. The motor fuel is treated with about 0.1% to 10% by volume of the acid solution, preferably with from about 1% to 5% by volume. The time of treating depends on the quantity of material to be reacted and on the efficiency of contact with the reagent. The time of treating is usually between 1 and 60 minutes and preferably in the range from about 4 to 8 minutes. The temperature of treating can be varied from 0° F. to 220° F. and is preferably in the range of 70° F. to 130° F.

The process of the present invention may be more fully understood by the following illustrative examples:

Example I

Samples of 9 commercial motor gasolines were analyzed for copper content. All were found to contain traces of copper and, in spite of the presence of anti-oxidants, the gasolines with the highest copper contents had the least stability against oxidation as measured by the ASTM accelerated oxidation test for "Breakdown time" (ASTM-D-525-49).

Gasoline	Parts of Copper per 100 MM parts	Lbs. of Anti-oxidant per 5,000 gals.	Minutes to Breakdown
A-----	5.2	0.9	140
B-----	4.7	0	230
C-----	3.8	0.4	210
D-----	3.6	0.8	350
E-----	1.5	0.1	435
F-----	1.0	0.4	730
G-----	0.8	0.4	370
H-----	0.2	0.3	440
I-----	0.2	0.1	1,440+

Example II

A sample of motor gasoline originally containing no copper was tested for breakdown time, with and without antioxidant; and the tests were repeated after the addition of 10 parts of copper per 100 million parts of gasoline. The anti-oxidant was N,N'-di-butyl-para-phenylene-diamine used in concentration of 0.5 lb. per 5,000 gallons of gasoline. The test results were as follows:

Minutes to breakdown	
Uninhibited gasoline, copper-free-----	350
Inhibited gasoline, copper-free-----	580
Uninhibited gasoline, with cu 0.1 p. p. m-----	240
Inhibited gasoline, with Cu 0.1 p. p. m-----	270

From the foregoing results, it is apparent that the anti-oxidant, in concentration of 0.5 lb per 5,000 gals., and the copper in concentration of 0.1 p. p. m., were mutually and about equally antagonistic.

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Example III

Since it is known in the art to offset the deleterious effect of copper in gasoline by adding chelate-forming compounds known as metal-deactivators, gasoline samples B and H were tested for breakdown time after adding 2 lbs. of the commercial deactivator, N,N'-di-salicylal-ethylene-diamine, per 5,000 gals.

Gasoline	Parts Cu/100 MM	Minutes to Breakdown		
		Without Deacti-vator	With Deacti-vator	Increase
B-----	4.7	230	390	160
H-----	0.2	440	445	5

The results show that the deactivator has no significant effect on the stability of the gasoline when the copper content is negligibly low. Thus, the present invention is particularly directed toward the stabilizing of motor fuels having low concentrations of Cu and Fe; less than about 2.0 parts per 100 MM parts of oil.

Example IV

To a sample of commercial motor gasoline containing no additive, there were added successively 2 parts of iron, in the form of iron naphthenate, per million parts of gasoline and 2 lbs. of either of two metal deactivators per 5,000 gals. of gasoline. The results were:

Minutes to breakdown	
Gasoline, free of any additive-----	350
Gasoline with Fe, 2 p. p. m-----	250
Gasoline with Fe, 2 p. p. m. plus:	
2 lbs./5000 gals. "ethylene diamine" deacti-vator -----	40
or	
2 lbs./5000 gals. "propylene diamine" deacti-vator -----	50

The two deactivators were condensation products of salicylaldehyde with aliphatic diamines. The results clearly showed that in the presence of soluble iron the ease of oxidation of the gasoline was promoted by the deactivators.

Example V

A thermally reformed naphtha having ASTM boiling-range of 250° F. to 430° F. was oxidized with air under the following conditions in a continuous-flow reactor: Temperature, 700° F.; Reactor-pressure, 100 lbs./sq. in.; 50 percent oxygen introduced as air, 1%; throughput of naphtha, 0.85 volume per volume of reactor-space per hour. The feedstock re-run to 430° F. end-point had 119 minutes in breakdown time; the oxidized product at the same end-point had 401 minutes in breakdown time.

Example VI

Two samples of commercial, 91-Octane Number, premium-grade gasoline, containing about 50% catalytic cracked naphtha and having about 350° F. end-point, were inhibited respectively with 1.0 and 0.5 lb. of N,N'-di-butyl-para-phenylene-diamine and subjected to atmospheric oxidation at about 90° F. until respectively 0.18 and 1.2 gm. equivalents of active oxygen in the form of peroxides were formed per 1000 liters of gasoline. The samples were then treated with 85% lactic acid in proportions of 1% to 5% by volume at normal room temperature, decanted and tested for peroxide content.

Peroxidized Gasoline Sample-----	J		K		
	0	5	0	1	5
Vol. percent of aqueous lactic acid used-----					
Peroxide Number-----	0.18	0.08	1.20	0.56	0.32
Inhibitor content left, lb./5,000 gals-----	0.9	0	0.5	0	0
Minutes to Breakdown-----	452	152	103	95	80

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The lactic acid treatment removed 50% to 75% of the peroxides and also removed the inhibitor, as a result of which de-inhibition, the breakdown time in the accelerated oxidation test was decreased; but, since other deleterious constituents were simultaneously removed by the lactic acid, which has an affinity for ions of copper or iron, the actual stability of the gasoline in normal storage was improved, as shown by the following example.

Example VII

Gasoline sample K, before peroxidation as in Example VI, had 9.0 mgs. of gum per 100 ml. It was treated with 5% by volume of 85% lactic acid, which removed its inhibitor content completely and its gum content was found to be 8.2 mgs./100 ml. Then after two months of normal storage, without having been re-inhibited, its gum content was found to be still only 8.0 mgs. per 100 ml.

In the process of the present invention a gasoline or naphtha containing peroxides and/or substances which promote the formation of peroxides is treated with an organic hydroxycarboxylic acid, for example, lactic acid, to remove the peroxides and the promoters if any and thereby to improve the stability of the gasoline or naphtha in storage.

In a preferred embodiment of the process, the least stable peroxide-forming hydrocarbon constituents of the naphtha are oxidized in the presence of minute proportions of copper and/or iron in the form of naphtha-soluble compounds tending to promote oxidation. When the proportion of copper is below about 2 parts per 100 million of gasoline and the proportion of iron is higher, the oxidation is further promoted by adding from about 0.5 to about 5.0, preferably about 2.0, pounds of metal-deactivator per 5000 gallons of gasoline. Typical metal-deactivators are diamines and their derivatives having the property of forming chelates or Werner complex compounds with copper or iron. After oxidation in the presence of the promoters, the gasoline is treated with an equal volume or less, preferably about 5% to 10% by volume, of an aqueous solution of an organic hydroxy carboxylic acid, preferably lactic acid.

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What is claimed is:

1. A process for improving the oxidation stability of a hydrocarbon motor fuel which comprises treating the said fuel with a small quantity of metal-comprising material selected from the class consisting of iron, copper, naphtha-soluble compounds of iron, and naphtha-soluble compounds of copper, contacting the thus treated fuel with an oxygen-containing gas under conditions forming peroxides in said fuel, and thereafter contacting the fuel with an organic hydroxy carboxylic acid.
2. Process as defined by claim 1 wherein said organic acid comprises lactic acid.
3. Process as defined by claim 1 wherein said organic acid is characterized by having a hydroxyl radical attached to the same carbon atom as a carboxyl radical.
4. Process as defined by claim 1 wherein said organic acid is employed as an aqueous solution of from 10 to 95 per cent concentration, said solution being used in the proportion of about 0.1% to 10% by volume based on the volume of motor fuel treated.
5. Process as defined by claim 1 wherein said organic acid comprises an aqueous solution of lactic acid in about 85 percent concentration, said solution being used in the proportion of from about 1 to 5 percent by volume based on the volume of motor fuel treated.

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