United States Patent Office 2,747,979 Patented May 29, 1956



2,747,979

# MONO-ESTERS OF CITRIC ACID AS METAL DEACTIVATORS FOR MOTOR FUELS

John W. Thompson, Kingsport, Tenn., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application November 14, 1952, Serial No. 320,607

6 Claims. (Cl. 44—70)

This invention relates to a method of improving the quality of petroleum hydrocarbons, and more particularly, to improving the quality of hydrocarbons which have been treated with copper-containing and/or other metal-containing reagents for the removal or conversion of sulfur compounds.

It is well known to remove sulfur compounds, such as mercaptans, from petroleum hydrocarbons, such as gasoline motor fuels, or to convert such mercaptans into less objectionable compounds by appropriate chemical treatment, generally referred to as a sweetening operation. One quite common method of sweetening involves the use of a doctor solution made from sodium hydroxide and lead oxide. Treatment of the sour gasoline with this solution and added sulfur converts the mercaptants to alkyl disulfides. The amount of sulfur used must be very carefully controlled since excess sulfur in the gasoline is harmful with respect to corrosiveness, lead susceptibility and inhibitor susceptibility. On the other hand, the use of insufficient sulfur causes lead mercaptides to be left in the fuel.

Instead of using the doctor solution method, it has been previously proposed to substitute other sweetening operations employing copper salts for the purpose of removing the sulfur compounds or converting them into less objectionable substances. This operation is widely used for the treatment of petroleum motor fuels, such as gasoline. Frequently in the copper sweetening process various copper compounds may be carried over into the treated gasoline where they are very objectionable since even in trace concentrations they catalyze oxidative deterioration of the treated hydrocarbon. This difficulty is somewhat alleviated through the use of the known antioxidants, although the amount of improvement is not great enough to completely overcome the objections noted above. It is, therefore, desirable to provide some method which would substantially completely remove all heavy metal compounds from the petroleum hydrocarbon, thus allowing the antioxidant to function at its fullest efficiency.

It is, therefore, an object of my invention to provide an improved method of deactivating metals, such as copper, contained in petroleum hydrocarbons. Another object is to render petroleum hydrocarbons, such as cracked gasoline, more stable to oxidative deterioration catalyzed by metals and to permit more effective use of gasoline antioxidants.

Still another object is to provide a class of new and effective treating agents for deactivating such metals in petroleum hydrocarbons, such as cracked gasoline. Other objects will become apparent from a consideration of the following description and examples.

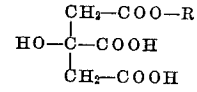
In the prior art the employment of aliphatic esters, such as esters of citric acid, has been suggested for the stabilization of motor fuels containing gum-forming unsaturated compounds (e. g. cracked gasoline) and also for stabilizing mineral wax compositions; however, no partial esters of citric acid have been suggested for such purposes. The prior art discloses the employment of



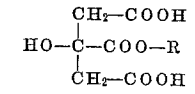
partial esters of citric acid in the stabilizing of edible oils such as various glyceridic oils, e. g. soyabean oil, etc.

According to my invention I have found that the monoesters of citric acid are superior metal deactivators in organic compositions such as gasoline. Such monoesters can be employed to deactivate metals such as copper, cobalt, manganese, etc. in organic compositions such as cracked gasoline whereby the product obtained is of greatly improved stability. By employing the monoesters of citric acid as metal deactivators, the more economical use of gasoline antioxidants is facilitated, since excessive quantities of antioxidants are required to properly stabilize gasoline containing catalytically-active metals.

Thus, I have discovered that the catalytic effects of metals, such as copper on the oxidative deterioration of organic substances, such as cracked gasoline, can be extensively suppressed by adding to such organic substances a small amount of a monoester of citric acid. These monoesters can be represented by the following general formulas:



and



wherein R represents a substituent selected from the group consisting of an alkyl radical containing from 1 to 18 carbon atoms and an aryl radical of the benzene series containing from 6 to 10 carbon atoms. Examples of suitable radicals that can be employed include: ethyl, isopropyl, n-butyl, 2-ethylhexyl, cyclohexyl, octadecyl, benzyl, phenyl, tolyl, etc. Thus, the term alkyl includes alicyclic radicals. It is generally rather difficult as a practical matter to obtain the pure monoesters of citric acid. Consequently, this invention also contemplates the employment of citric esters which are mixtures comprising mono-, di- and triesters of citric acids even though the pure triesters by themselves have been found to be practically ineffective as metal deactivators.

From about 0.0001 to about 0.1% by weight of a monoester of citric acid is generally required to deactivate any catalytically-active metal that may be present depending on the concentration of metal which exists in the gasoline or other similar organic material being treated. Higher and lower concentrations can also be employed depending upon the circumstances.

The metal deactivators of this invention can be added alone or in admixture with other additives which are to be incorporated into the material being treated. Such other additives include antioxidants, dyes, antiknock compounds, etc. It is advantageous to employ the metal deactivators of this invention in the form of a concentrated solution in a suitable solvent such as a lower aliphatic alcohol (1 to 10 carbon atoms), e. g. isopropanol.

The metal deactivators of this invention possess an advantage over known metal deactivators such as N,N'-disalicylidene-1,2-propylenediamine in that they will deactivate metals other than copper, e. g. cobalt, iron, manganese, etc.

The efficiency of the citric acid monoesters in deactivating copper and other metals can be demonstrated by oxygen bomb stability tests on cracked gasoline containing various combinations of antioxidants, catalytically-active metals, and the subject deactivators. The metal used in one series of tests was copper which was added in the form of a benzene solution of cupric oleate. In another series of tests cobalt and manganese were added as toluene solutions of the stearate and oleate respectively. The

antioxidant used was N-n-butyl-p-aminophenol. The oxygen bomb stability test used to determine the induction periods of the various samples was that described in Industrial and Engineering Chemistry (Ind. Ed.), vol. 24, p. 1375 (1932).

*Example 1.—Mono isopropyl citrate deactivating copper*

A Pennsylvania reformed gasoline was employed which had an induction period of 45 minutes, which was raised to 522 minutes upon addition of 0.0048 weight per cent of N-n-butyl-p-aminophenol which is a very effective gasoline antioxidant known in the art. Upon addition of 1.0 mg. of copper/liter to this inhibited fuel the induction period was reduced to 155 minutes, illustrating the harmful effect of copper upon gasoline stability. However, the addition of 0.0010 weight per cent of mono isopropyl citrate to this inhibited, copper-containing fuel gave an induction period of 490 minutes, indicating practically complete restoration of the stability loss due to copper.

*Example 2.—Mono cyclohexyl citrate deactivating copper*

The same inhibited, copper-containing gasoline described in Example 1 was treated with 0.001 weight per cent of another deactivator, mono cyclohexyl citrate. The induction period was raised from 145 to 347 minutes.

*Example 3.—Mono isopropyl citrate deactivating cobalt*

This example illustrates the effectiveness of the monoesters of citric acid in deactivating another catalytically-harmful metal, viz cobalt. A Pennsylvania reformed gasoline containing 0.0048 weight per cent of the antioxidant N-n-butyl-p-aminophenol had an induction period of 470 minutes. Upon addition of 1.0 mg. of cobalt/liter to this inhibited sample the induction period was reduced to 282 minutes. However, the addition of 0.0005 weight per cent of mono isopropyl citrate to this inhibited, cobalt-containing fuel raised the induction period to 447 minutes, indicating almost complete deactivation of the metal.

*Example 4.—Mono isopropyl citrate deactivating manganese*

The deactivation of still another catalytically-harmful metal is shown in this example. The addition of 1.0 mg. of manganese per liter to the inhibited gasoline described in Example 3 reduced the induction period from 467 to 370 minutes. Upon the addition of 0.0005 per cent by weight of mono isopropyl citrate to the inhibited fuel containing manganese, the induction period was raised to 440 minutes indicating substantial improvement in the gasoline stability.

In a like manner a number of other citric acid monoesters were found to be effective deactivators for copper in gasoline. The results obtained are shown in the table. It is clearly apparent that any of the monoesters covered by the general formula set forth above can be employed to deactivate the various catalytically-active metals.

*Example 5.—Mono lauryl citrate deactivating copper*

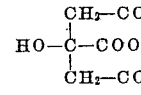
A Pennsylvania cracked gasoline containing 0.0048 weight per cent of the antioxidant N-n-butyl-p-aminophenol had an induction period of 555 minutes. Upon addition of 1.0 mg. of copper per liter to this inhibited sample, the induction period was reduced to 130 minutes. However, the addition of 0.005 weight per cent of an esterification product of citric acid and lauryl alcohol containing a substantial proposition of the mono ester raised the induction period to 360 minutes.

TABLE.—EFFECTIVENESS OF CITRIC ACID MONESTERS AS METAL DEACTIVATORS FOR GASOLINE

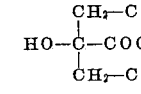
| Test No. | Antioxidant Conc., Wt. Percent (N-n-Butyl-p-aminophenol) | Metal Present, 1 Mg./Liter | Deactivator Compound | Deactivator Conc., Wt. Percent | Induction Period, Min. (Oxygen Bomb Stab. Test) |
|---|---|---|---|---|---|
| 1 | None | None | None | None | 45 |
| 2 | 0.0048 | do | do | None | 522 |
| 3 | 0.0048 | Copper | do | None | 155 |
| 4 | 0.0048 | do | Mono isopropyl citrate | 0.001 | 490 |
| 5 | 0.0048 | do | Mono-n-butyl citrate | 0.001 | 457 |
| 6 | 0.0048 | do | Mono-2-ethylhexyl citrate | 0.001 | 312 |
| 7 | 0.0048 | do | Monocyclohexyl citrate | 0.001 | 347 |
| 8 | 0.0048 | Cobalt | None | None | 282 |
| 9 | 0.0048 | do | Mono isopropyl citrate | 0.0005 | 447 |
| 10 | 0.0048 | Manganese | None | None | 370 |
| 11 | 0.0048 | do | Mono isopropyl citrate | 0.0005 | 440 |

What I claim as my invention and desire to secure by Letters Patent of the United States is:

1. A motor fuel comprising a cracked gasoline containing a harmful catalytically-active metal reagent intimately admixed with from about 0.0001 to about 0.01 per cent based on the weight of the gasoline of a monoester of citric acid having one of the following formulas:



and



wherein R represents a substituent selected from the group consisting of an alkyl radical containing from 1 to 18 carbon atoms and an aryl radical of the benzene series containing from 6 to 10 carbon atoms.

2. A motor fuel as defined in claim 1 wherein the monoester of citric acid is mono-isopropyl citrate.

3. A motor fuel as defined in claim 1 wherein the monoester of citric acid is mono-n-butyl citrate.

4. A motor fuel as defined in claim 1 wherein the monoester of citric acid is mono-cyclohexyl citrate.

5. A motor fuel as defined in claim 1 wherein the monoester of citric acid is mono-2-ethylhexyl citrate.

6. A motor fuel as defined in claim 1 wherein the monoester of citric acid is monolauryl citrate.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,081,407 | Minnick | May 25, 1937 |
| 2,493,717 | Christ | Jan. 3, 1950 |
| 2,523,792 | Vahlteich et al. | Sept. 26, 1950 |
| 2,578,649 | Vahlteich et al. | Dec. 11, 1951 |
| 2,641,539 | Thompson et al. | June 9, 1953 |

FOREIGN PATENTS

| | | |
|---|---|---|
| 790,041 | France | Nov. 12, 1935 |