Patented Oct. 27, 1942

2,300,246

UNITED STATES PATENT OFFICE

2,300,246

INHIBITOR FOR GASOLINE

Joseph A. Chenicek and Robert H. Rosenwald, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

No Drawing. Application October 27, 1939, Serial No. 301,636

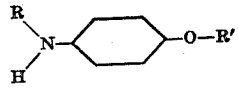
5 Claims. (Cl. 44—75)

This invention relates to a method for stabilizing olefin-containing hydrocarbon oils and more particularly cracked gasoline of petroleum origin against deterioration and loss of valuable properties on storage. Gasolines from other sources may also be treated according to the present invention, as may other hydrocarbon fractions such as those produced by the polymerization of normally gaseous olefins, the reforming of naphthas, etc.

More particularly the invention concerns a method for stabilizing olefin-containing gasoline during storage in respect to valuable properties such as color, antiknock value and low gum content which tend to depreciate because of the action of oxygen upon the olefins in said gasoline.

The cracking and reforming of petroleum oils to produce additional yields of valuable motor fuel or to improve the antiknock characteristics of straight-run gasolines and naphthas has been practiced to a large extent during recent years. Furthermore, processes have been developed for polymerizing the normally gaseous olefins contained in cracking plant gases to produce substantial yields of high octane number blending fluid. All of the products thus produced, whether by cracking, reforming or polymerization, contain substantial amounts of olefinic hydrocarbons which tend to form peroxides and gums and to depreciate in antiknock quality, color, odor, etc. when stored in the presence of even minor amounts of oxygen. The use of inhibitors has been practiced to prevent such reactions and many types of compounds have been suggested for this purpose, including aminophenols, fractions of wood tar, polyhydroxyphenols, etc.

In one specific embodiment the present invention comprises a method for treating unstable olefin-containing gasolines to preserve their valuable properties in respect to gum content, color and antiknock properties by adding thereto minor quantities of alkyl ethers of aminophenols of the general structure:



wherein R is either a hydrogen atom or an alkyl group, and R′ is an alkyl group.

The properties desirable in a gasoline gum inhibitor are as follows:

(a) Solubility in the gasoline to a degree in excess of the maximum concentration in which it is likely to be used.

(b) High degree of potency so that relatively small concentrations can be used.

(c) Insolubility or relatively low solubility in water or aqueous alkaline or acidic solutions with which the gasoline is likely to come in contact.

(d) Either normally liquid or having a high degree of solubility in a non-aqueous, gasoline-miscible solvent thus increasing the ease of handling and addition to the gasoline.

(e) Non-reactive with tanks, fittings, lines, engine parts, etc., with which the gasoline is likely to come in contact.

(f) Of light color, and imparting or developing no objectionable color or odor to the gasoline when added, or during storage.

The inhibitors of the present invention to a large extent fulfill these requirements.

A representative group of the compounds which are useful are given in the example.

The alkoxy group and the N-substituted alkyl group may contain any suitable alkyl group such as normal, secondary, or tertiary alkyl groups, and may be either the same or different in molecular weight and structure.

The compounds may be prepared by reacting the sodium salt of nitrophenol with an alkyl halide of the desired molecular weight and structure followed by reducing the nitro ether thus formed to the amino ether. The amino ether may then be reacted with an alkyl halide to produce the N-substituted amino ether. Another method of preparing the compounds is to react the sodium salt of an N-substituted aminophenol with an alkyl halide to produce the N-substituted amino ether.

The following examples are given to illustrate the usefulness and practicability of the compounds characterizing the invention but should not be construed as limiting it to the exact compounds given therein.

The inhibitor effectiveness of the compounds was measured by means of the oxygen bomb induction period. In this test a sample of gasoline with and without 0.01% by weight of the added

compound was heated under oxygen pressure in a bomb equipped with a pressure recording device whereby the interval of time between the initiation of heating and the point at which substantial oxygen absorption by the gasoline occurred was measured. This interval is known as the induction period.

TABLE I

Inhibitor ratios of various p-alkylaminophenyl ethers

No.	Compound	Induction period
		Minutes
	Blank gasoline	85
1	p-(n-Butylamino)-phenyl t-butyl ether	410
2	p-(Isoamylamino)-phenyl t-butyl ether	375
3	p-Aminophenyl isobutyl ether	205
4	p-(n-Butylamino)-phenyl n-butyl ether	180
5	p-(n-Butylamino)-phenyl allyl ether	175
6	p-(Methylamino)-phenyl isobutyl ether	170
7	p-Aminophenyl isopropyl ether	165
8	p-(Isoamylamino)-phenyl sec-butyl ether	165
9	p-(Isopropylamino)-phenyl isopropyl ether	165
10	p-(Isopropylamino)-phenyl t-butyl ether	165
11	p-(n-Butylamino)-phenyl isobutyl ether	155
12	p-(n-Butylamino)-phenyl sec-butyl ether	155
13	p-(n-Butylamino)-phenyl isoamyl ether	155
14	p-(Isopropylamino)-phenyl isobutyl ether	150
15	p-(Isoamylamino)-phenyl n-butyl ether	150
16	p-Aminophenyl n-propyl ether	145
17	p-(Isopropylamino)-phenyl sec-butyl ether	145
18	p-(n-Butylamino)-phenyl ethel ether	145
19	p-(n-Butylamino)-phenyl isopropyl ether	140
20	p-(Isoamylamino)-phenyl isobutyl ether	140
21	p-(Isopropylamino)-phenyl isoamyl ether	140
22	p-Aminophenyl methyl ether	135
23	p-Aminophenyl n-amyl ether	135
24	p-(Isoamylamino)-phenyl isopropyl ether	135
25	p-(Isoamylamino)-phenyl isoamyl ether	135
26	p-Aminophenyl ethyl ether	130
27	p-Aminophenyl sec-butyl ether	130

As further evidence of the usefulness of the compounds of the present invention, several representative compounds were compared with two commercial inhibitors. Sufficient amounts of the various compounds were added to a gasoline to give an induction period of the same order of figure. The copper dish gum and induction periods were determined before and after shaking the samples with water and with dilute (1%) sodium hydroxide solution. The data obtained are shown in Table II.

TABLE II

Effect of caustic and water on aminophenyl ethers

Inhibitor	Cu dish gum, mg./100 cc.			Induction period, minutes			Per cent removed by—	
	Original	Water wash	Caustic wash	Original	Water wash	Caustic wash	Water wash	Caustic wash
Blank gasoline	99	113	19	80	70	50		
Commercial inhibitor A	7	12	80	340	285	105	17	79
Commercial inhibitor B	5	9	14	300	305	210	0	27
p-Aminophenyl isobutyl ether	49	18	19	360	325	280	9	18
p-Aminophenyl isopropyl ether	25	25	25	305	280	260	7	7
p-(n-Butylamino)-phenyl t-butyl ether	10	12	10	350	310	310	11	4
p-(n-Butylamino)-phenyl n-butyl ether	21	35	23	310	310	305	0	0
p-(Isopropylamino)-phenyl isopropyl ether	10	17	10	280	265	240	3	5
p-(Isoamylamino)-phenyl t-butyl ether	8	9	11	315	295	285	4	0

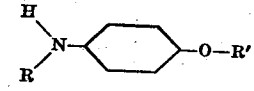
The per cent inhibitor removed by water and by caustic respectively were determined by the amount of decrease in the induction period which was obtained as a result of the treatment. The results indicate that the compounds of this invention are relatively insoluble in water and sodium hydroxide, being superior in this respect to the commercial inhibitors with which they are compared. Translated into terms of commercial practice, these data indicate that the inhibitors when present in gasoline stored in tanks containing water or alkaline aqueous solutions will not be removed thereby, but will continue to protect the gasoline from the deleterious effects of oxidation.

We claim as our invention:

1. An inhibitor for cracked gasoline comprising essentially p-(n-butylamino)-phenyl t-butyl ether.

2. An inhibitor for cracked gasoline comprising essentially p-(n-butylamino)-phenyl n-butyl ether.

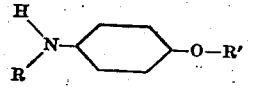
3. A process for stabilizing olefin-containing hydrocarbon oil against deterioration of its valuable properties which comprises adding to said oil a minor portion of a compound of the following general structure:



wherein R and R' are alkyl groups selected from the group consisting of normal butyl, isobutyl, secondary butyl and tertiary butyl groups.

4. An inhibitor for cracked gasoline comprising essentially p(n-butylamino)-phenyl-secondary-butyl ether.

5. An inhibitor for cracked gasoline which comprises essentially a compound having the general formula:



wherein R and R' are alkyl groups selected from the group consisting of normal butyl, isobutyl, secondary butyl and tertiary butyl groups.

JOSEPH A. CHENICEK.
ROBERT H. ROSENWALD.