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STABILIZING AND SWEETENING ADDITIVE FOR HYDROCARBONS

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ABSTRACT OF THE DISCLOSURE

A composition for stabilizing and sweetening hydrocarbons boiling in the range of about 50° F. to about 750° F. comprising about 25–50 parts by weight N,N'-di-sec-lower-alkyl-o-phenylenediamine and about 50–75 parts by weight N,N'-di-sec-lower-alkyl-p-phenylenediamine.

This is a continuation-in-part of application Ser. No. 423,357, filed Jan. 4, 1965, and now abandoned.

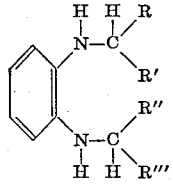
This invention relates to the chemical arts. In particular, it relates to the sweetening of sour, unsaturated, hydrocarbon distillates, such as, for example, sour, cracked gasoline and the like.

The inhibitor sweetening of sour, cracked gasoline and the like is a well known process. The basic process is described in the U.S. Patent No. 2,508,817, to Devol et al. As generally practiced, it comprises admixing the sour, unsaturated, hydrocarbon distillate with a p-phenylenediamine, an alkaline material such as, for example 10–40° Bé. caustic, and oxygen which is usually already present in the sour distillate. The mixture that results is stored preferably at 80–100° F., although higher and lower temperatures can be employed, until the desired extent of sweetening has taken place. The sweetened hydrocarbon distillate and alkaline material are then separated. The p-phenylenediamine which is soluble in the distillate, remains with it and subsequently functions to inhibit gum formation in the distillate.

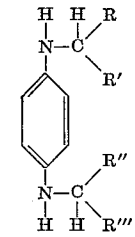
While p-phenylenediamines have been quite effective as sweetening agents, there is a need for faster sweetening or higher sweetening rates, particularly at temperatures lower than about 80° F.

This invention is based upon the discovery that mixtures of certain N,N'-di-sec-alkyl-(ortho and para)-phenylenediamines generally give substantially higher sweetening rates than p-phenylenediamines, particularly at 40–80° F.

In summary, this invention comprises an inhibitor sweetening process which comprises contacting sour, unsaturated hydrocarbon distillate with oxygen, alkaline material and a sweetening agent consisting essentially of a mixture of at least one N,N'-di-sec-alkyl-o-phenylenediamine represented by the formula



and at least one N,N'-di-sec-alkyl-p-phenylenediamine represented by the formula



wherein R and R'' are radicals independently selected from the group consisting of methyl and ethyl radicals and R' and R''' are radicals independently selected from the group consisting of straight chain and branched alkyl radicals, the number of carbon atoms in R and R' totaling 2–12 and the number of carbon atoms in R'' and R''' totaling 2–12. The R and R'' radicals can be the same or different and the R' and R''' radicals can be the same or different.

In this connection, mixed alkyl derivatives of o- and p-phenylenediamines, such as N-sec-butyl-N'-isopropyl-(o- and p-)-phenylenediamines and the like, can be made by various processes including the reductive alkylation of the corresponding o- and p-phenylenediamine with a mixture of corresponding ketones. The R' and R''' radicals include: isopropyl, secondary butyl, 1-methylbutyl, 1-methylpentyl, 1-methylhexyl, 1-methylheptyl, 1-ethylpropyl, 1-ethylbutyl, 1-ethylpentyl, 1-ethylhexyl, 1-ethyl-3-methylpentyl, 1,2-dimethylpropyl, 1,3-dimethylbutyl, 1,4-dimethylpentyl, and the like. Preferred specific N,N'-di-sec-alkyl-o- and p-phenylenediamines of this invention include: N,N'-di-isopropyl-o- and p-phenylenediamine, N,N'-di-sec-butyl-o- and p-phenylenediamine and N,N'-bis(1,4-dimethylpentyl)-o- and p-phenylenediamine.

In this mixture the weight ratio of all said N,N'-di-sec-alkyl-o-phenylenediamine to all said N,N'-di-sec-alkyl-p-phenylenediamine is generally in a range from about 9:1 to about 1:9 and preferably from about 1:1 to about 1:3. A feature of advantage of this mixture is that in general it has a low freezing point. For example a mixture of N,N' - di-sec-butyl-o-phenylenediamine and N,N'-di-sec-butyl-p-phenylenediamine at a weight ratio of the o-phenylenediamine to the p-phenylenediamine of 35:65 has a freezing point of 32° F. Another feature of advantage of this mixture is that in the ASTM gum test it appears to have good gum inhibition activity in gasoline.

The sweetening agent of this invention is employed in the inhibitor sweetening process by admixing it with the sour, unsaturated hydrocarbon distillate to be sweetened. It can be added as such or as a concentrate wherein it is dissolved in an appropriate solvent such as alcohol, xylene or a gasoline fraction. In addition, it is within the concepts of this invention to add the N,N'-di-sec-alkyl-p-phenylenediamine separately from the N,N'-di-sec-alkyl-o-phenylenediamine either before, after or at the same time as the addition of N,N'-di-sec-alkyl-o-phenylenediamine.

In the sweetening process of this invention the quantity of sweetening agent added to the sour, unsaturated hydrocarbon distillate to be sweetened depends on the size of the R' and R''' radicals as well as on the particular hydrocarbon distillate being treated. Generally, the sweetening agent concentration is in a range from about 0.0005 to about 0.02% by weight of the sour, unsaturated hydrocarbon distillate to give satisfactory results. A preferred range is about from 0.001 to about 0.01% by weight of

the sour, unsaturated hydrocarbon distillate. The quantity of sweetening agent added to sour, unsaturated hydrocarbon distillate to give a concentration in these ranges is generally in a range from about 1.3 to about 52 pounds per 1000 barrels (U.S.) of sour, unsaturated, hydrocarbon distillate and preferably in a range from about 2.6 to about 26 pounds per 1000 barrels (U.S.) of sour, unsaturated, hydrocarbon distillate.

Unsaturated hydrocarbon distillate under the concepts of this invention is a liquid hydrocarbon having an unsaturated hydrocarbon content. It covers an unsaturated hydrocarbon distillate boiling generally in a range from about 50 to about 750° F. and usually in a range from about 90 to about 490° F. It includes cracked gasoline including thermally cracked gasoline, catalytically cracked gasoline, reformed gasoline, polyform gasoline and the like, and substantially saturated gasoline such as, for example, straight run gasoline, natural gasoline and the like blended with olefinic or other unsaturated hydrocarbons, and cracked or blends of cracked and straight run, higher boiling distillates including jet fuel, kerosene, diesel fuel, burner oil, lubricating oil, gas oil and the like.

This invention is further illustrated by the following examples of various aspects of the invention including specific embodiments thereof. This invention is not limited to the specific embodiments unless otherwise indicated.

Example 1

The following table illustrates specific embodiments of the sweetening agent of this invention.

TABLE 1

Components	Concentration in parts by wt.		
	1	2	3
N,N′-di-sec-butyl-o-phenylenediamine	25	35	50
N,N′-di-sec-butyl-p-phenylenediamine	75	65	50

These specific embodiments are made by physically mixing together the components at 20–25° C.

Example 2

This example illustrates the outstanding efficacy of one embodiment of the sweetening agent of this invention.

Three samples of a cracked gasoline containing 0.007% by weight of mercaptan sulfur were made up by placing 300 milliliters of the gasoline in three one pint amber bottles. To one sample was added N,N′-di-sec-butyl-o-phenylenediamine, to another sample was added a mixture consisting essentially of N,N′-di-sec-butyl-o-phenylenediamine and N,N′-di-sec-butyl-p-phenylenediamine at a weight ratio of the o-phenylenediamine to the p-phenylenediamine of 35:65, and to the third sample was added N,N′-di-sec-butyl-p-phenylenediamine. The quantity of additive in each sample, the mixture in the second sample being considered as the additive, was about 8 pounds per 1000 barrels (U.S.) of the gasoline. This gave an additive concentration in each sample of about 0.005% by weight of the gasoline. 5% by volume of the sample of 10° Bé. aqueous caustic (NaOH) solution was added to each sample and each sample was shaken for one minute. Thereafter the mercaptan sulfur content of each sample was periodically determined by potentiometric titration. The results are summarized in the following tables.

TABLE 2A

Additive	Percent reduction in mercaptan sulfur after indicated hours				
	0	4	8	12	16
N,N′-di-sec-butyl-p-phenylenediamine	21.4	39.3	50.0	60.7	
N,N′-di-sec-butyl-o-phenylenediamine	35.7	60.7	75.0	89.3	

Based upon the results summarized in Table 2A, the expected or predicted percent reduction in mercaptan sulfur after the same indicated hours for a mixture of N,N′-di-sec-butyl-p-phenylenediamine and N,N′-di-sec-butyl-o-phenylenediamine (65:35 weight ratio) is set forth below in Table 2B.

TABLE 2B

Additive	Expected percent reduction in mercaptan sulfur after indicated hours				
	0	4	8	12	16
Mixture of N,N′-di-sec-butyl-p-phenylenediamine and N,N′-di-sec-butyl-o-phenylenediamine (65:35 weight ratio)	25.7	47.1	58.6	71.4	

However, as shown in Table 2C below, the actual percent reduction in mercaptan sulfur for a mixture of N,N′-di-sec-butyl-p-phenylenediamine and N,N′-di-sec-butyl-o-phenylenediamine indicates that synergistic effect is obtained from the combination.

TABLE 2C

Additive	Actual percent reduction in mercaptan sulfur after indicated hours				
	0	4	8	12	16
Mixture of N,N′-di-sec-butyl-p-phenylenediamine and N,N′-di-sec-butyl-o-phenylenediamine (65:35 weight ratio)	28.6	50.0	71.4	78.6	

Example 3

This example illustrates the good gum inhibition properties which are possessed by specific embodiments of the mixture type sweetening agent of this invention.

Gasoline samples containing the additives indicated in the following table were stored in one quart bottles in an oven at 110° F. While so stored they were periodically inspected for ASTM gum as determined by ASTM Method D381. When the ASTM gum concentration reached 10 milligrams per 100 milliliters of gasoline, the oven storage time of the sample was determined. This time is referred to as the gasoline life. The results are summarized in the following table.

Sample No.	Additive	Concentration in pounds per 1,000 barrels (U.S.)	Gasoline life (in weeks)
1	None		10.3
2	Mixture of N,N′-di-sec-butyl-o-phenylenediamine and N,N′-di-sec-butyl-p-phenylenediamine at a weight ratio of 25:75.	3	28.5
3	Mixture of N,N′-di-sec-butyl-o-phenylenediamine and N,N′-di-sec-butyl-p-phenylenediamine at a weight ratio of 50:50.	3	28
4	Mixture of N,N′-di-sec-butyl-o-phenylenediamine and N,N′-di-sec-butyl-p-phenylenediamine at a weight ratio of 25:75.	6	39
5	Mixture of N,N′-di-sec-butyl-o-phenylenediamine and N,N′-di-sec-butyl-p-phenylenediamine at a weight ratio of 50:50.	6	34.6

Other features, advantages and embodiments will be apparent to those in the exercise of ordinary skill in the art after reading the foregoing disclosures. In this regard, while specific embodiments of this invention have been disclosed in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as described and claimed.

We claim:

1. An additive composition for hydrocarbons having an unsaturated hydrocarbon content and boiling in the range of about 50° F. to about 750° F. consisting essentially of N,N′-di-sec-lower-alkyl-o-phenylenediamine and

N,N'-di-sec-lower-alkyl-p-phenylenediamine in the weight ratio of 25/75 to 50/50.

2. The additive composition of claim 1 wherein the N,N'-di-sec-lower-alkyl-o-phenylenediamine is N,N'-di-sec-butyl-o-phenylenediamine and the N,N'-di-sec-lower-alkyl-p-phenylenediamine is N,N'-di-sec-butyl-p-phenylenediamine.

3. A process for stabilizing and sweetening hydrocarbons having an unsaturated hydrocarbon content and boiling in the range of about 50° F. to about 750° F. comprising admixing with said hydrocarbons from about 0.0005% to about 0.02% by weight of said hydrocarbons of the additive composition of claim 1.

4. A composition comprising:

(A) hydrocarbons having an unsaturated hydrocarbon content and boiling in the range of about 50° F. to about 750° F., and

(B) about 0.0005% to about 0.02% by weight of said hydrocarbons of the additive composition of claim 1.

5. A composition comprising:

(A) hydrocarbons having an unsaturated hydrocarbon content and boiling in the range of about 50° F. to about 750° F., and

(B) about 0.0005% to about 0.02% by weight of said hydrocarbons of the additive composition of claim 2.

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