

UNITED STATES PATENT OFFICE

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TREATING HYDROCARBON OILS

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16 Claims. (Cl. 196—39)

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This invention relates to the treatment of light hydrocarbon oils and more particularly relates to the stabilization of light petroleum oils which have been sweetened with a copper compound.

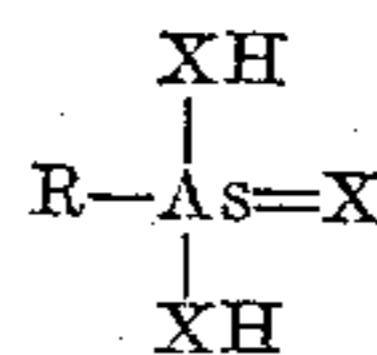
Hydrocarbon oils, particularly light petroleum oils, such as kerosene, gasoline, naphtha and similar petroleum distillates, usually contain a variety of sulfur compounds which are undesirable from the viewpoint that they impart an unpleasant odor and corrosive properties to the petroleum oil. A number of methods are employed to remove these undesirable sulfur compounds or to convert the sulfur compounds to form which do not impart undesirable properties to the oil. One of the methods employed is the so-called copper sweetening method wherein the sour petroleum oil is treated with copper chloride and/or other copper salts for the purpose of removing the offensive sulfur compounds or converting the same into a harmless and unobjectionable form. Oils treated with such copper reagents are susceptible to oxidative deterioration, as evidenced by a marked decrease in the so-called induction periods, by a loss of color stability, and by the formation of gum.

It is an object of the present invention to provide a method of stabilizing petroleum oils which have been subjected to treatment with a copper-containing reagent. Another object of the invention is to provide a method of stabilizing copper-sweetened petroleum distillates. A further object of the invention is to provide an improved method of inhibiting the oxidative deterioration of copper-sweetened petroleum distillates. Still another object of the invention is to provide a method of treating copper-sweetened petroleum distillates to remove therefrom copper and/or copper compounds which promote the oxidative deterioration of such petroleum distillates. Other objects and advantages of the herein described invention will become apparent as the description thereof proceeds.

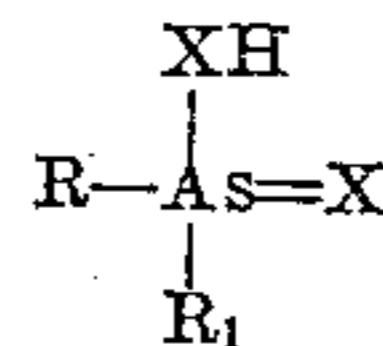
In accordance with the present invention hydrocarbon oils, particularly petroleum oils, such as gasoline, kerosene, fuel oils, naphthas, and the like, whether obtained from straight run or cracking processes which have been subjected to treatment with a copper reagent to remove undesirable constituents therefrom or to convert such undesirable constituents to unobjectionable forms, and which are normally susceptible to oxidative deterioration because of the presence of copper and/or copper compounds therein, can be stabilized against such oxidative deterioration by treatment with a water-soluble organo-substituted acid of arsenic selected from the class consisting

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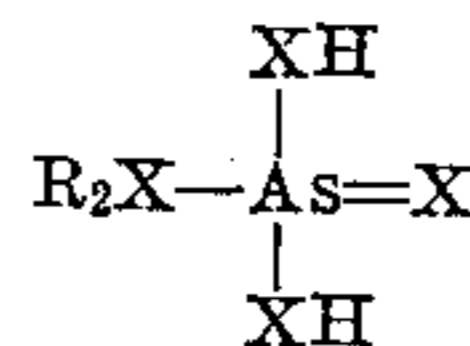
of an organo-arsenic acid having the general formula



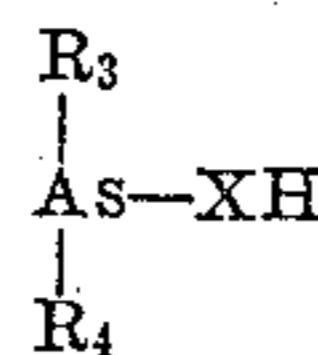
an organo-arsinic acid having the general formula



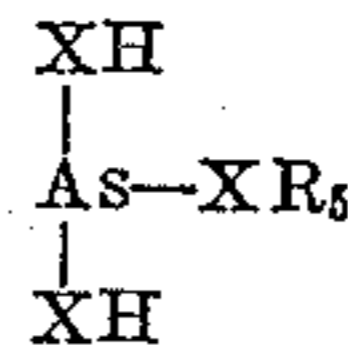
an organo-arsenic acid having the general formula



an organo-arsinous acid having the general formula



an organo-arsenous acid having the general formula



and mixtures thereof, in which R, R₁, R₂, R₃, R₄ and R₅ are organo radicals selected from the group consisting of aliphatic, cycloaliphatic, aromatic, heterocyclic radicals and mixtures thereof, and X is at least one element selected from the class consisting of oxygen and sulfur.

The term "organo-radical" as used herein and in the appended claims includes organo radicals which may contain substituent groups, such as for example, oxy, hydroxyl, thio, amino, mercapto, halogen, or other groups.

Specific examples of compounds falling within the above-named arsenic compounds are the following:

Organo arsonic acids, e. g.—

Benzylarsonic acid

Butylarsonic acid

Phenylarsonic acid

Allylarsonic acid

Octylarsonic acid

Phenylthioarsonic acid

Allylthioarsonic acid

Butylthioarsonic acid

Cetylarsenic acid

Tolylarsonic acid

Hydroxyphenylarsonic acid

Terphenylarsonic acid

Ethoxyphenylarsonic acid

3-amyl-4-hydroxyphenyl-arsonic acid, etc.

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- Organo thion-arsonic acid, e. g.—
 Hexyl thion-arsonic acid
 Phenyl thion-arsonic acid, etc.
 Organo thion-thiol-arsonic acid, e. g.—
 Lauryl thion-thiol-arsonic acid
 Xylyl thion-thiol-arsonic acid, etc.
 Organo-trithio-arsonic acid, e. g.—
 Butyl-trithio-arsonic acid
 Phenyl trithio-arsonic acid, etc.
 Organo-monothiol-arsonic acid, e. g.—
 Phenyl monothiol-arsonic acid
 Decyl monothiol-arsonic acid
 Xylyl monothiol-arsonic acid, etc.
 Organo dithiol-arsonic acid, e. g.—
 Lauryl dithiol-arsonic acid
 Isoamyl dithiol-arsonic acid

and similar organo derivatives of arsinic and thio-arsinic acid, arsenic and thio-arsenic acid, arsinous and thio-arsinous acid, arsenous and thio-arsenous acid. While all of the organo arsenic compounds of the above type are effective for the herein described purpose, it is not to be implied that all are equivalent since the specific gravity of the various compounds varies to some extent.

The treatment with the organo-substituted acid of arsenic is carried out by contacting the hydrocarbon oil with the oil-immiscible solution of the organo-substituted acid of arsenic, at a temperature of from about 35° F. to about 210° F., and preferably from about 60° F. to about 100° F., for a period sufficient to remove the objectionable copper compounds. Usually, contact times of from about 0.5 minute to about 15 minutes will be found sufficient, contact times being dependent on the means employed to obtain most intimate contacts between the immiscible liquids. Solutions of from about 0.01% to about 10%, preferably from about 0.5% to about 5.0% concentration can suitably be used in accordance with the present invention. Oil-immiscible solutions of the organo-substituted acids of arsenic are, for example, solutions of the acid in water, alcohols, e. g. methanol, ethanol, etc., acetone-water mixtures, glycol-water mixture and other substantially oil-insoluble solvents.

The effectiveness of organo arsenic acids in stabilizing light petroleum oils which have been sweetened with a copper compound, is illustrated by the data in Table I, obtained by subjecting the following petroleum distillate to oxidation stability tests, as determined by the A.S.T.M. Method D-525-46.

(A) A catalytically cracked naphtha having a distillation range of from about 155° F. to about 400° F., sweetened by vigorously stirring and bubbling oxygen through a slurry of one liter of the naphtha and 8 grams of copper chloride-clay catalyst, consisting of 72% Attapulugus clay fines, 8% copper chloride and 20% water for 30 minutes, and filtering.

(B) A thermally cracked naphtha having a distillation range of from about 150° F. to about 385° F., sweetened in the same manner as sample A; and

(C) A thermally cracked naphtha having a distillation range of from about 145° F. to about 400° F., sweetened by contacting the naphtha with the copper-clay catalyst in the presence of oxygen with vigorous stirring for two and one-half hours at room temperatures.

Before subjecting each of the above-described copper sweetened naphthas to the oxidation stability test, 4 parts of each sample were shaken with 1 part of a 1% aqueous solution of various

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- organo arsenic compounds for five minutes, the aqueous phase separated from the upper layer, and the latter filtered. Each of the treated sweetened samples was stored under a nitrogen atmosphere until tested.

Table I

10	Stock	Induction Period, Minutes		
		A	B	C
15	Unwashed.....	35	248	85
	Washed with 1% Solution p-OH-phenylarsonic acid.....	235	675	-----
	Washed with 1% Solution allylarsonic acid.....	175	600	-----
	Washed with 1% Solution n-propylarsonic acid.....	-----	-----	220
	Washed with 1% Solution phenylarsonic acid.....	-----	-----	185

- 20 The effectiveness of the organo arsenic compounds in increasing the oxidation stability of copper chloride sweetened light petroleum distillates is indicated by the increase in the induction period.

- 25 The effectiveness of the organo arsenic acids in stabilizing copper sweetened light petroleum distillates against color and gum forming bodies is illustrated by the data in Table II. These data were obtained by treating a heater oil having a distillation range of from about 340° F. to about 575° F. with a copper chloride clay catalyst and with an organo arsenic compound in the manner above described and determining the color of the treated heater oil before and after aging at 200° F. for twenty hours. The gum reported in Table II was obtained according to A.S.T.M. Method D-381, modified by the use of preheated steam as a substitute for air and 500° F. operating temperature instead of 320° F.

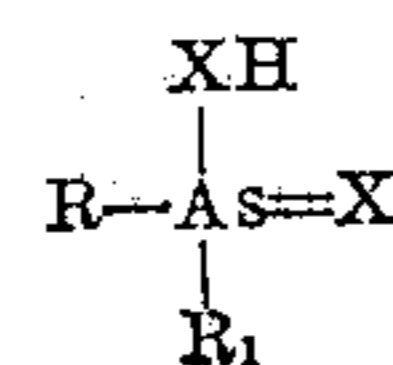
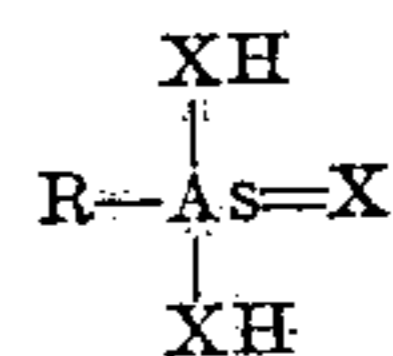
Table II

45	Original Color, Saybolt	After 20 Hrs. Aging at 200° F.		
		NPA Color	500° F. Steam-Gum; mg./100 ml.	
50	Unwashed.....	+12	7	33.6
	Washed with 1% Solution p-OH-phenylarsonic Acid.....	+12	1-1½	1.8
	Washed with 1% Allylarsonic Acid.....	+12	1+	3.1

- 55 While I have described my invention by reference to specific embodiments thereof, the invention is not to be limited thereby, but includes within its scope such modifications as come within the spirit of the appended claims.

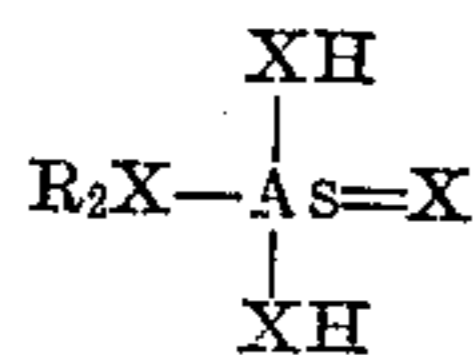
- 60 1. The method of stabilizing a copper-contaminated hydrocarbon oil comprising mixing said oil with an oil-immiscible solution of an organo-substituted acid of arsenic selected from the class consisting of an organo arsonic acid having the general formula

- 65 an organo-arsinic acid having the general formula

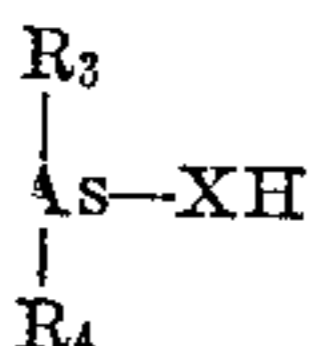


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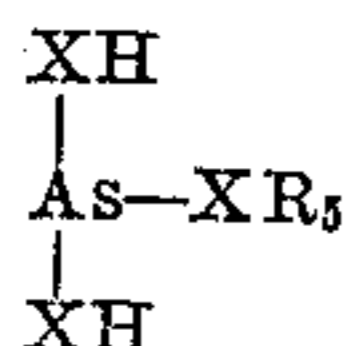
an organo-arsenic acid having the general formula



an organo-arsinous acid having the general formula



an organo-arsenous acid having the general formula



and mixtures thereof, in which R, R₁, R₂, R₃, R₄ and R₅ are organo radicals selected from the group consisting of aliphatic, cyclo-aliphatic, aromatic, heterocyclic radicals and mixtures thereof, and X is an element selected from the group consisting of oxygen and sulfur, and separating the oil-immiscible solution from the treated oil.

2. The method of stabilizing a copper-contaminated hydrocarbon oil comprising agitating a mixture of said oil and an oil-immiscible solution of an organo-substituted arsonic acid and separating the oil-immiscible solution from the treated oil.

3. The method of claim 2 in which the organo-substituted arsonic acid is an aliphatic-substituted arsonic acid.

4. The method of claim 3 in which the aliphatic-substituted arsonic acid is propylarsonic acid.

5. The method of claim 3 in which the aliphatic-substituted arsonic acid is allylarsonic acid.

6. The method of claim 2 in which the organo-substituted arsonic acid is an aromatic-substituted arsonic acid.

7. The method of claim 6 in which the aromatic-substituted arsonic acid is a phenylarsonic acid.

8. The method of claim 6 in which the aromatic-substituted arsonic acid is para-hydroxy phenylarsonic acid.

9. The method of claim 2 in which the organo-substituted arsonic acid is a cyclo-aliphatic-substituted arsonic acid.

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10. The method of stabilizing a copper-containing hydrocarbon oil comprising agitating a mixture of said oil and an aqueous solution of organo substituted arsonic acid having a concentration of from about 0.01% to about 10% at a temperature of from about 35° F. to about 210° F., permitting the mixture to separate into an aqueous layer and an oil layer, and separating the aqueous solution from the treated oil.

11. The method of stabilizing a light petroleum distillate sweetened by treatment with a copper compound, comprising contacting said copper-sweetened hydrocarbon petroleum distillate with an aqueous solution of an organo-substituted arsonic acid of from about 0.01% to about 10% concentration at a temperature of from about 35° F. to about 210° F., and separating the treated petroleum distillate from the aqueous solution.

12. The method of claim 11 in which the organo-substituted arsonic acid is propylarsonic acid.

13. The method of claim 11 in which the organo-substituted arsonic acid is allylarsonic acid.

14. The method of claim 11 in which the organo-substituted arsonic acid is a phenylarsonic acid.

15. The method of claim 11 in which the organo-substituted arsonic acid is para-hydroxy phenylarsonic acid.

16. The method of stabilizing a copper chloride sweetened petroleum distillate comprising contacting said copper chloride sweetened petroleum distillate with an aqueous solution of an organo-substituted arsonic acid having a concentration within the range of from about 0.01% to about 10%, at a temperature of from about 60° F. to about 100° F., and separating the treated petroleum distillate from the aqueous solution.

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