Patented May 26, 1942 2,284,267

UNITED STATES PATENT OFFICE

2,284,267

STABILIZATION OF NONVISCOUS CRACKED PETROLEUM DISTILLATES

Frederick B. Downing and Charles J. Pedersen, Penns Grove, N. J., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application August 3, 1940, Serial No. 351,118

21 Claims. (Cl. 44—9)

This invention relates to improvements in the stabilization of non-viscous cracked petroleum distillates and more particularly to the stabilization of cracked gasoline against the formation of gummy products and the loss of anti-knock value resulting from aging in the presence of air and traces of vanadium.

It is well known that the non-viscous cracked petroleum distillates, such as fuel oils and cracked gasoline, tend to deteriorate in the presence of air with the formation of gummy substances. The aging of cracked gasoline in the presence of air results in the formation of gum and the development of color. When the gum content exceeds a certain value (approximately 10 mg./100 c. c. by the A. S. T. M. air jet method) the gasoline is considered unfit for use in gasoline motors. The deterioration of gasoline caused by the action of atmospheric oxygen can be retarded by the addition of compounds called "gasoline antioxidants" or "gum inhibitors." "Inhibitors in cracked gasoline" Egloff, Morrell, Lowry, Jr. and Dryer, J. I. E. C. 24 1375 (1932); "Inhibitors in cracked gasoline" Lowry, Jr., Egloff, Morrell and Dryer, J. I. E. C. 25 804 (1933); "Gum formation in gasoline" Rogers and Voorhees, J. I. E. C. 25 520 (1933).

Copper and its compounds accelerate the rate of oxidation of cracked gasoline and most of the commonly used organic antioxidants. Hence copper and antioxidants are antagonistic in action, and the normal inhibiting effect of the latter is greatly reduced in the presence of the former. Compounds capable of effectively suppressing the catalytic activity of copper and its compounds in gasoline and methods of utilizing them are described in U. S. Patents 2,181,121 and 2,181,122.

It has also been found that vanadium and its compounds increase the rate of deterioration of the non-viscous cracked petroleum distillates, even when they are stabilized with antioxidants. Vanadium occurs naturally in some crude petroleums, particularly in the crudes found in Venezuela and Iran, and see "The Science of Petroleum" Thomas, vol. II, p. 1053 (1937).

An object of the present invention is to retard the deterioration of non-viscous cracked petroleum distillates caused by the action of molecular oxygen and promoted by the presence of vanadium and its compounds. Another object is to provide a class of organic compounds which, when added to a non-viscous cracked petroleum distillate normally subject to deterioration by oxygen in the presence of vanadium and its compounds, will suppress the activity of the vanadium or its compounds. A further object is to provide a method for rendering antioxidants more effective for the preservation of non-viscous cracked petroleum distillates in the presence of vanadium and its compounds. A still further object is to provide a class of organic compounds which, when added to cracked gasoline in the presence of an antioxidant and in the presence of vanadium or its compounds, increases the efficiency of the antioxidant. Still further objects are to inhibit the formation of color, acids, gum, sludge and the like in mineral hydrocarbons containing or in contact with vanadium or its compounds. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accordance with our invention which comprises incorporating, in non-viscous cracked petroleum distillates, which are subject to deterioration normally caused by oxygen in the presence of vanadium and its compounds, aldehyde-amine condensation products of the type of arylidene amines or Schiff's bases, identical with those obtained by condensing one mol of an aliphatic polyamine, containing at least two primary amino groups capable of reacting with aromatic aldehydes to form arylidene amines, with at least two mols of an ortho-hydroxy substituted aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

The polyamine may be an aliphatic amine containing at least two primary amino groups directly attached to different carbon atoms of the same open chain and which amine may contain aromatic or other cyclic groups substituted on the chain. The term "aliphatic polyamine," as employed hereinafter and in the claims, will be understood to have the foregoing meaning. The preferred polyamines are the alkylene polyamines, consisting of carbon, hydrogen and nitrogen, those in which at least two primary amino groups are directly attached to adjacent carbon atoms, and particularly the diamines. By "adjacent atoms," we mean atoms directly bonded together.

By an "ortho-hydroxy substituted aldehyde," we mean one in which the hydroxy group and the aldehyde, or —CHO, group are directly bonded to adjacent benzene ring carbon atoms. The aldehyde is preferably devoid of substituents other than hydrocarbon and hydroxy groups. However, such aldehyde may contain, as sub-

stituents, alkoxy, aryloxy, halogen, heterocyclic, amino, cyano, carboxyl and sulfonic groups, as well as hydroxy, alkyl and aryl radicals. The polyamine may be likewise substituted but is preferably unsubstituted.

The quantity of vanadium deactivator added will be dependent upon the amount of vanadium present in the non-viscous cracked petroleum distillates. At least one mol of vanadium deactivator must be added for each gram atom of vanadium in the distillate. Preferably, from about 1.5 to 100 mols of vanadium deactivator is used for each gram atom of vanadium in the distillate. From about 0.0002 to about 0.01% of vanadium deactivator, based on the cracked distillate, will generally be satisfactory in most cases where the vanadium or vanadium compound is accidentally present. Higher ratios of vanadium deactivator may be used, particularly when the cracked distillate is in contact with metallic vanadium in bulk which forms a reservoir of vanadium ions.

By "non-viscous cracked petroleum distillates," we mean distillates obtained by the cracking of petroleum and which are in the boiling range of motor fuels and fuel oils and intend to include furnace oils and Diesel fuels, as well as cracked gasoline.

In order to illustrate our invention, the results of some of the experimental tests are given:

These results were obtained by means of the induction period method developed by Voorhees and Eisinger (S. A. E. J. 24, 584 (1929)), and consists in shaking 100 c. c. of gasoline at 100° C. in a 1 liter Pyrex flask containing pure oxygen. The internal pressure is observed every ten minutes by means of a manometer attached to the system. The elapsed time, from the start of the test until the gasoline begins to absorb oxygen at the rate of 10 c. c. per 10 minutes as shown by the fall in internal pressure, is taken as the induction period. It has been found that the induction period, obtained by this method, although greatly shortened, is a fairly accurate measure of the relative stability of gasoline under normal storage conditions.

The gasoline used was a blend of straight run and cracked gasoline and had an initial induction period (not inhibited with antioxidant) of 160 minutes. Para-benzylaminophenol, a well known commercial product, was selected as a representative antioxidant. Vanadium was added in the form of vanadium dibutyl dithiocarbamate dissolved in benzene. Disalicylal ethylenediamine, obtained by condensing 2 mols of salicylaldehyde with 1 mol of ethylenediamine, was chosen as the representative vanadium deactivator.

TABLE I

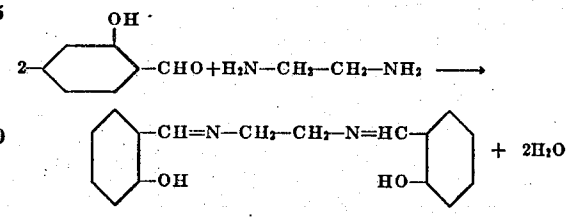
The effect of dissolved vanadium

[Gasoline inhibited with 0.002% by weight of p-benzylaminophenol]

No.	Conc. deactivators, weight percent	Induction period in minutes	
		No added V	1 P. P. M. V
1	None	330	180
2	0.005	460	390

It will be observed that the addition of 1 part per million of dissolved vanadium decreased the induction period of the gasoline containing 0.002% p-benzylaminophenol from 330 to 180 minutes. This effect was overcome by the addition of 0.005% disalicylal ethylenediamine.

The vanadium deactivators of the class of the present invention are well known compounds and the methods of preparing the same are described in the literature. They are readily prepared by reacting the required molal proportions of aldehyde and polyamine with or without the use of a suitable solvent such as water, methanol or ethanol. The reactions are exothermic and water is formed. Nearly theoretical yields of the compounds are obtained. The chemical equation for the formation of di-(2-hydroxybenzal)-ethylenediamine may be represented as follows:



The solubility of our compounds in the organic substances is dependent upon their constitution. For example, with a given polyamine, a ring-alkylated 2-hydroxybenzaldehyde yields a more soluble product than 2-hydroxybenzaldehyde. With a given aldehyde, hexamethylenediamine forms a more soluble deactivator than ethylene diamine. Our compounds are only slightly soluble in water except when they are solubilized with certain groups such as the sulfonic acid and carboxyl groups, or when the hydrogen atoms of the hydroxyl groups are replaced by suitable cations such as sodium or potassium ions.

Unlike antioxidants, our compounds are resistant to the action of molecular oxygen and solutions of our compounds may be kept in the presence of air for years without any apparent change. They are thermally stable at temperatures appreciably above their melting points, but are destroyed by strong mineral acids or hot dilute mineral acids. They are generally colored yellow of varying shade and intensity, and form copper compounds which are greenish in color and not bluish or purplish. Our vanadium deactivators may be added to the petroleum distillates to be treated in any desirable form and manner. They may be in solid or liquid form, mixed with other addition agents or dissolved in a solvent. Liquid phenolic mixtures, such as commercial xylenols or cresylic acids, and liquid aromatic amines, such as aniline, are particularly good solvents for this class of deactivators.

While the non-viscous cracked petroleum distillates treated in accordance with our invention will contain or be in contact with vanadium, they may also contain other contaminants and additives such as copper and iron and their derivatives, tetraethyl lead, dyes, color stabilizers, gum solvents and overhead lubricants.

Mixtures of deactivators may be used, as well as the condensation products of a given polyamine with a mixture of aldehydes or a given aldehyde with a mixture of polyamines. Besides many others, the compounds, obtained by condensing each of the following aldehydes with each of the following polyamines, are vanadium deactivators:

Aldehydes:
- 2-hydroxybenzaldehyde
- 2-hydroxy-5-chlorobenzaldehyde
- 2-hydroxy-6-methylbenzaldehyde
- 2-hydroxy-3-methoxybenzaldehyde
- 2-hydroxynaphthaldehyde-1

Polyamines:
- ethylenediamine
- 1,2-propylenediamine
- 2,3-butylenediamine
- 3,4-diaminohexane
- trimethylenediamine
- triethylenetetramine

Di - (2 - hydroxybenzal) 1,2 - propylenediamine, obtained by condensing 2 mols of salicylaldehyde with 1 mol of 1,2-propylenediamine, is a preferred compound. It is a yellow crystalline substance melting at 45° C. The addition of 10 to 20% of an aromatic hydrocarbon, such as benzene, toluene or xylene, will produce a liquid composition which resists crystallization at even relatively low temperatures. The solubility of the pure product in cracked gasoline exceeds 10% by weight at room temperature.

Other deactivators may be obtained by condensing each of the following aldehydes with each of the following polyamines:

Aldehydes:	Polyamines:
2-hydroxybenzaldehyde	methylenediamine
2-hydroxy-5-chlorobenzaldehyde	ethylenediamine
2-hydroxy-3:5-dibromobenzaldehyde	1:2-propylenediamine
2-hydroxy-6-methylbenzaldehyde	1:3-propylenediamine
2-hydroxy-3-methoxybenzaldehyde	1:10-decylenediamine
2:4-dihydroxybenzaldehyde	diethylenetriamine
2:6-dihydroxybenzaldehyde	triethylenetetramine
2-hydroxy-3-cyanobenzaldehyde	
2-hydroxy-3-carboxybenzaldehyde	
2-hydroxybenzaldehyde-3-sulfonic acid	
2-hydroxynaphthaldehyde-1	
1-hydroxynaphthaldehyde-2	
anthrol-2-aldehyde-1	
2-hydroxyfluorene-aldehyde-1	
4-hydroxydiphenyl-aldehyde-3	
3-hydroxyphenanthrene-aldehyde-4	
1:3-dihydroxy-2:4-dialdehydobenzene	

It will be apparent that by this invention, we have made it possible to effect the stabilization of non-viscous cracked petroleum distillates, particularly cracked gasoline, when contaminated with vanadium and its derivatives. It is generally unfeasible to remove the vanadium by other methods and it is usually not economical to counteract the catalytic action of vanadium by means of an antioxidant alone. We believe that the vanadium deactivators form very stable complex chemical compounds with the vanadium, which complex chemical compounds possess little or no pro-oxidant catalytic properties.

While we have disclosed the preferred embodiments of our invention and the preferred modes of carrying the same into effect, it will be readily apparent to those skilled in the art that such disclosures are given for illustrative purposes and that many variations and modifications may be made therein without departing from the spirit of our invention. Accordingly, we propose to claim our invention broadly as in the appended claims and not be limited by the specific embodiments particularly disclosed.

We claim:

1. The method of inhibiting the catalytic deterioration of a non-viscous cracked petroleum distillate normally caused by vanadium and its compounds in the presence of oxygen which comprises incorporating in the said distillate a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an aliphatic polyamine containing at least two primary amino groups directly attached to different carbon atoms of the same open chain with at least 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

2. The method of inhibiting the catalytic deterioration of a non-viscous cracked petroleum distillate, normally caused by vanadium and its compounds in the presence of oxygen which comprises incorporating in the said distillate a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an aliphatic polyamine containing exactly two primary amino groups directly attached to different carbon atoms of the same open chain with 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

3. The method of inhibiting the catalytic deterioration of a non-viscous cracked petroleum distillate normally caused by vanadium and its compounds in the presence of oxygen which comprises incorporating in the said distillate a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an aliphatic diamine in which the amino groups are primary amino groups directly attached to adjacent carbon atoms of the same open chain with 2 mols of an ortho-hydroxy substit. ed aromatic aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

4. The method of inhibiting the catalytic deterioration of a non-viscous cracked petroleum distillate normally caused by vanadium and its compounds in the presence of oxygen which comprises incorporating in the said distillate a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an alkyl diamine in which the amino groups are primary amino groups directly attached to different carbon atoms of the same open chain with 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

5. The method of inhibiting the catalytic deterioration of a non-viscous cracked petroleum distillate normally caused by vanadium and its compounds in the presence of oxygen which comprises incorporating in the said distillate a small proportion of an antioxidant normally effective to prevent deterioration of the said distillate in the absence of vanadium and its compounds but which is less effective in the presence of vanadium and its compounds and a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an aliphatic polyamine containing at least two primary amino groups directly attached to different carbon atoms of the same open chain with at least 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

6. The method of inhibiting the catalytic deterioration of cracked gasoline normally caused by vanadium and its compounds in the presence of oxygen which comprises incorporating in the cracked gasoline a small proportion of an antioxidant normally effective to prevent deterioration of the cracked gasoline in the absence of vanadium and its compounds but which is less effective in the presence of vanadium and its compounds and a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an aliphatic polyamine containing at least two primary amino groups directly attached to different carbon atoms of the same open chain with at least 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so

that not more than one mol of aldehyde reacts for each primary amino group of the amine.

7. A non-viscous cracked petroleum distillate normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an aliphatic polyamine containing at least two primary amino groups directly attached to different carbon atoms of the same open chain with at least 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

8. A non-viscous cracked petroleum distillate normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of an aldehye-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an aliphatic polyamine containing only two primary amino groups directly attached to different carbon atoms of the same open chain with 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

9. A non-viscous cracked petroleum distillate normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an aliphatic diamine in which the two amino groups are primary amino groups directly attached to different adjacent carbon atoms of the same open chain with 2 mols of an ortho-hydroxy substituted aromatic aldehyde which, except for the OH and CHO groups, consists of carbon and hydrogen, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

10. A non-viscous cracked petroleum distillate normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an alkylene diamine in which the two amino groups are primary amino groups directly attached to different carbon atoms of the same open chain with 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

11. A non-viscous cracked petroleum distillate normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an alkylene diamine in which the amino groups are primary amino groups directly attached to different carbon atoms of the same open chain with 2 mols of an ortho-hydroxy substituted aromatic aldehyde which, except for the hydroxy group and the —CHO group consists of carbon and hydrogen, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

12. A non-viscous cracked petroleum distillate normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an alkylene diamine in which the amino groups are primary amino groups directly attached to different carbon atoms of the same open chain with 2 mols of an orthohydroxy substituted aromatic aldehyde of the benzene series, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

13. A non-viscous cracked petroleum distillate normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of disalicylal 1,2-propylenediamine.

14. A non-viscous cracked petroleum distillate normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of an antioxidant normally effective to materially retard deterioration of the said distillate in the absence of vanadium and its compounds but which is less effective in the presence of vanadium and its compounds and a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an aliphatic polyamine containing at least two primary amino groups directly attached to different carbon atoms of the same open chain with at least 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

15. A non-viscous cracked petroleum distillate normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of an antioxidant normally effective to materially retard deterioration of the said distillate in the absence of vanadium and its compounds but which is less effective in the presence of vanadium and its compounds and a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an aliphatic polyamine containing only two primary amino groups directly attached to different carbon atoms of the same open chain with 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

16. A cracked gasoline normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an aliphatic polyamine containing at least two primary amino groups directly attached to different carbon atoms of the same open chain with at least 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

17. A cracked gasoline normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol

of an aliphatic polyamine containing only two primary amino groups directly attached to different carbon atoms of the same open chain with 2 mols of an ortho-hydroxy substituted aromatic aldehyde, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

18. A cracked gasoline normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of an aldehyde-amine condensation product of the Schiff's base type identical with that obtained by condensing 1 mol of an alkylene diamine in which the amino groups are primary amino groups directly attached to different carbon atoms of the same open chain with 2 mols of an ortho-hydroxy substituted aromatic aldehyde which, except for the hydroxy group and the —CHO group consists of carbon and hydrogen, so that not more than one mol of aldehyde reacts for each primary amino group of the amine.

19. A cracked gasoline normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of disalicylal 1,2-propylenediamine.

20. A non-viscous cracked petroleum distillate normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of di-(2-hydroxy-3-methoxybenzal) propylenediamine.

21. A non-viscous cracked petroleum distillate normally subject to deterioration caused by oxygen and catalyzed by vanadium or its compounds having incorporated therein a small proportion of disalicylal triethylenetetramine.

FREDERICK B. DOWNING.
CHARLES J. PEDERSEN.