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PROCESS AND PRODUCT FOR THE STABILIZING OF UNSATURATED HYDROCARBONS

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6 Claims. (Cl. 44—9)

This invention relates to a method of preventing deterioration of oils, fats, and rubber, and is applicable to substances liable to oxidation. The process and product will be described more particularly in relation to inhibiting auto-oxidation of motor fuels resulting from pyrolysis of heavy oils or coal.

Color deterioration and gum formation are known to be the result of oxidation. Color deterioration does not render motor fuel or motor oil unfit for use, but lowers its market value. Gum formation is the result of oxidation of unsaturated hydrocarbons, and when present in motor fuel in small quantities renders the fuel unfit for use in an internal combustion engine. To obtain gum free and stable products, the usual practice is to remove a substantial quantity of the unsaturated hydrocarbons through treatment with sulfuric acid, or through the control of the cracking plant in such a manner as not to produce a high concentration of the unstable unsaturated hydrocarbons. Control of the cracking process in this way sometimes results in a lower percentage of cracked fuel, and the sulfuric acid treatment always results in a loss, which in many cases runs as high as 5% of the motor fuel produced. This treatment is costly and wasteful, and also results in a lowering of the anti-knock value of the motor fuel.

The primary object of the invention is the manufacture and use of an oxidation inhibitor which, when added in minute quantities, prevents deterioration of hydrocarbons and various oils liable to oxidation. It is particularly useful in the manufacture and marketing of motor fuel containing unsaturated hydrocarbons liable to oxidation, since it not only inhibits gum formation in storage, but actually reduces the gum yield when the cracked product to which the inhibitor has been added is tested for gum by the copper dish method. In the majority of cases only a minute quantity of the inhibitor, the cost of which is almost negligible, is required to reduce the result of the copper dish test to any desired specification. Results of tests made with identical cracked gasolines with and without the addition of the stabilizing compound are shown hereunder:

COPPER DISH TESTS

Sample 1

Amount of inhibitor added (gms. per 100 cc.)	Gum (gms. per 100 cc.)
Nil	0.103
0.002	0.048
0.005	0.008
0.018	0.025
Sample 2	
Nil	0.183
0.0007	0.101
0.0014	0.066
0.0035	0.008
0.007	0.011

I have found that the following substances are effective in preventing gum formation when added in minute quantities to oils:—Pyrogallol, catechol, hydroquinone, ortho-aminophenol, para-aminophenol, para-phenylenediamine, methylaminophenol, alpha-naphthol, ortho-phenylenediamine, para-amino-dimethylaniline, benzidene, and alpha-naphthylamine.

Numerous other compounds, such as cresol, dimethylaniline, etc., have a slight stabilizing effect, but my experience has been that as a general rule only aromatic compounds with two hydroxyl and/or amino groups in the ortho or para positions of the benzene ring will completely prevent oxidation, although it will be noted that alpha-naphthol, which has only one hydroxyl group, is an exception. The presence of other groups in the benzene ring in addition to the above mentioned does not destroy the inhibiting action.

All of the above mentioned substances except alpha-naphthol are more soluble in water than in oil, in which they are nearly insoluble, and they are not satisfactory for use in practice for the commercial stabilization of motor fuels on account of the fact that it is difficult to prevent the latter from coming into contact with water. Naphthol cannot be used, since it causes motor fuel to deteriorate in color, although it is satisfactory as regards solubility.

I have found that if an alkyl, aryl or terpenyl group is substituted for a hydrogen atom in these compounds, their solubility in water is decreased

and their solubility in oil is increased without an appreciable loss in their power to inhibit oxidation. The greater the number of alkyl, aryl or terpenyl groups which can be substituted in the compounds, the more soluble is the resulting product in the hydrocarbon to be stabilized and the less soluble in water.

The new and novel features of the present invention are: the production of oil soluble oxidation inhibitors from certain types of oil insoluble phenolic or amino compounds, by substitution of one or more alkyl, aryl or terpenyl groups for hydrogen atoms; an improved method of introducing an alkyl group into a phenol amine or aminophenol; and the utilization of turpentine, a liquid sulfur dioxide extract of an oil, or the unsaturated hydrocarbons derived from the pyrolysis of oil or coal, as the base or stock from which the substituted phenolic or amino compound is produced; oils containing mixed unsaturated hydrocarbons are very much cheaper than the pure unsaturated compounds, but are equally satisfactory for the preparation of the substituted compound.

The introduction of the substituted groups may be effected by a modification of the method of Koenigs (Ber. 23, 3144; 24,179; 3889; 25, 2649) who prepared alkyl substituted phenols by allowing a mixture of one part of the phenol with the equivalent amount of an unsaturated hydrocarbon to stand for several days in the presence of one part of concentrated sulfuric acid and nine parts of acetic acid. My improvements in this method that are new to the art are as follows:

1. The use of a mixture of a commercial unsaturated hydrocarbon oil, such as oil of turpentine, a liquid sulfur dioxide extract of an oil, or an oil derived from the pyrolysis of oil or coal. Such oils should preferably contain a large percentage of unsaturated hydrocarbons, as high concentrations of the latter cause the reaction to take place more readily.

2. The use of dilute sulfuric acid (about 50%) instead of concentrated acid. This prevents loss of the phenolic compound by eliminating side reactions such as the formation of acetates.

3. The use of a much smaller quantity of sulfuric and acetic acid, thus reducing the cost of manufacture.

4. Carrying out the reaction at an elevated temperature with agitation. This reduces the time required to a few hours.

5. The use of a considerable excess of unsaturated compounds, in order to avoid loss of the more costly phenol.

6. Incomplete removal of acetic acid from the solution of alkyl substituted phenol. A trace of acid present in the solution acts as a preservative, preventing oxidation of the compound itself before it is added to the oil to be stabilized.

7. The use of a dilute solution of a mineral acid for extracting the acetic acid instead of water or ammonium carbonate. Oxidation of the compound during the washing is thus prevented.

It will be noted that by alkylation of the various oil insoluble oxidation inhibitors, such as pyrogallol and aminophenol, in various ways, an almost infinite number of different compounds can be obtained which would be suitable for inhibiting the oxidation of oils. For the preparation of the various types of compounds, a number of different methods are available. For example, amyl pyrogallol may be prepared by the action of amyl alcohol on pyrogallol in the presence of anhydrous zinc chloride; and aminophenol can be alkylated by heating under pressure with alcohols; or the reaction between pyrogallol and unsaturated hydrocarbons will take place to some extent without a catalyst, or with aluminum chloride. I have, however, found that the cheapest and easiest compounds to manufacture are those prepared from pyrogallol by the method described above. Catechol also gives good results by this method, but is more expensive. Examples of the preferred method of the preparation of phenolic derivatives using cracked distillate and turpentine are given below:

Five parts by weight of powdered pyrogallol, ten parts of glacial acetic acid, one part of 50% sulfuric acid, and ten parts of cracked distillate are placed in an acid-resisting container fitted with a stirrer and a reflux condenser, and supplied with facilities for heating. The mixture is agitated violently, and heated to boiling. The agitation and heating are continued for two hours, 75 parts of cracked distillate being gradually added during this period. After two hours, when substantially all of the pyrogallol should have entered into combination with the unsaturated hydrocarbons present, the agitation is stopped and the product allowed to cool in an oxygen-free atmosphere.

The reaction which occurs is probably as follows:

$$\underset{\text{olefine}}{R.CH.CH_2} \text{ plus } \underset{\text{pyrogallol}}{C_6H_3(OH)_3} \text{ gives } \underset{\text{stabilizer}}{RCH_2.CH_2.C_6H_2(OH)_3}$$

The resulting mixture consists of a solution of the oxidation inhibitor and acetic acid in the oil which supplied the unsaturated hydrocarbons, and a layer of sludge on the bottom of the containing vessel. Twenty parts of 0.1% sulfuric acid are introduced, and the mixture is agitated for fifteen minutes for the purpose of removing excess acetic acid. The washing also causes any substituted compound contained in the sludge to return to the oil solution. The lower layer is drained off, and the extraction repeated twice. The solution of oxidation inhibitor thus prepared is then run into a storage vessel, preferably of copper or wood.

When turpentine is used, forty parts of pyrogallol are dissolved by heating and agitation in sixty parts of glacial acetic acid. One part of 50% sulfuric acid is added, and a hundred parts fresh turpentine introduced while the mixture is being agitated. Heat is evolved, and care must be taken that the temperature does not rise above 100° C. When all the turpentine has been added, the mixture is maintained at about 90° C. until the reaction is substantially complete. After cooling, it may be diluted by a suitable oil. It is then washed as in the previous example. The amount of the substituted compound formed is substantially twice the weight of pyrogallol used. I have found that acetic acid acts as a preservative of the compound, but most of it must be removed, as it would cause the motor fuel to which the above described inhibitor had been added to become corrosive. The acetic acid may be removed by extraction with any suitable solvent, such as water or a mineral acid, or by other suitable methods such as distillation, instead of by dilute sulfuric acid as described in the above examples.

In the preparation of the aromatic amino compounds, the same procedure, in general, may be used as described above for preparing the phenolic compounds. The following example will illustrate one method of preparing the amino compounds when using turpentine as the unsaturated hydrocarbon oil:

Twenty parts by weight of para-phenylene diamine are added to fifty parts of strong acetic acid and the mixture formed into a uniform mass using a small amount of heat if necessary. One part of 50% sulfuric acid and fifty parts of turpentine dissolved in fifty parts of cracked naphtha are then added, and the whole mixture agitated for about one hour under a reflux condenser, during which time 100 parts more of naphtha are gradually added. Substantially all of the para-phenylene diamine should go into solution and more acetic acid and naphtha may be added if necessary. The mixture is allowed to cool and then washed thoroughly with 0.1% sulfuric acid until practically all of the acetic acid is removed. The washings tend to hydrolyze any salts which may be formed between the amine and the acetic acid. The mixture is allowed to settle and any sludge remaining in the oil is separated and drawn off. The liquid product consists of a concentrated solution of the mixture in unsaturated naphtha. This solution may be stored in a suitable acid resistant container and utilized as a base stock for adding to the cracked gasoline to be stabilized.

When using turpentine it is advantageous to mix the turpentine with a diluent oil, such as cracked naphtha, although straight turpentine may be used. I have found, however, that the reaction with turpentine is rather vigorous and the proportions of reactants and catalysts should be adjusted to eliminate, as far as possible, undesirable polymerization reactions. Also, with high concentrates of turpentine or fairly elevated temperatures, the reaction takes place rapidly and the reaction time may be cut down to a few minutes.

While I have described the preparation of the compounds according to the modified Koenigs' reaction, the invention is not limited to such a method. It has been found that heat or heat and pressure without the use of a catalyst may often produce the desired results. I have found that by refluxing the phenol, amine or aminophenol with the unsaturated oil that substantial reaction may be effected to produce improved inhibitors. By using pressure and more elevated temperatures the reaction is faster and more extensive. Pressures of the order of upwards of 50 or 100 pounds and temperatures of about 300° to 600° F. are usually sufficient.

The reactions which take place are not fully understood but it is believed that there are formed mainly substituted derivatives, in which an alkyl, aryl or terpenyl group is substituted for a hydrogen on the benzene ring, or for hydrogen on the amino or hydroxyl group. In the case of the aromatic amines and lower reaction temperatures, it is believed a substantial amount of substitution takes place on the nitrogen of the amino group, while at higher temperatures the substitution in the benzene ring appears to predominate.

It has been found that the substituted compound when prepared as described above may be stored for a long period of time, at least as long as two years as shown by practical tests, without losing activity as a stabilizer.

I have found that a compound as thus prepared is acidic and that it can be removed or destroyed by shaking with alkalies, such as sodium carbonate or caustic soda. It is, therefore, necessary to prevent the motor fuel from coming into contact with alkaline substances after the addition of the inhibitor. The compound is also destroyed by organic peroxides, and to prevent this the motor fuel should be perfectly fresh and preferably free from peroxides when the compound is added.

The gum content of Samples 3 and 4 shown hereunder has been determined by the U. S. Bureau of Mines Steam Oven Method, in which a 20 cc. sample of motor fuel is evaporated in a steam oven from which oxygen is excluded. The gummy residue obtained in this manner is considered to represent the actual or inherent gum present in the fuel.

The gum content of Samples 1 and 2 hereinbefore described under "Copper dish tests" was determined by evaporating 100 cc. of cracked gasoline on a steam bath. In this test the gasoline is exposed to atmospheric oxygen during the evaporation and although a sample of cracked gasoline gives a considerable residue by this method, the same sample might be found to be entirely free from inherent gum as determined by the steam oven method.

Results of storage tests made on identical cracked gasolines, with and without addition of inhibitor, are given below. The samples consist of cracked gasoline stored in dark in glass bottles vented to atmosphere:

Sample No. 3

Time of storage (weeks)	Steam oven gum (gms. per 20 cc.)		Color, Saybolt chromometer	
	Without inhibitor	With 0.001% inhibitor	Without inhibitor	With 0.001% inhibitor
1	Nil	Nil	plus 25	plus 25
3	Nil	Nil	25	25
5	Nil	Nil	25	25
7	Nil	Nil	25	25
10	Nil	Nil	25	25
15	Nil	Nil	25	25
19	.003	Nil	25	25
23	.026	Nil	plus 17	25
29	----------	Nil	----------	25
35	----------	Nil	----------	25
41	----------	Nil	----------	plus 24
47	----------	Nil	----------	22
59	----------	Nil	----------	23
65	----------	Nil	----------	23
71	----------	Nil	----------	25
77	----------	.016	----------	----------
83	----------	.018	----------	23

Sample No. 4

(Weeks)	Without inhibitor	With 0.0005% inhibitor	Without inhibitor	With 0.0005% inhibitor
5	Nil.	Nil.	plus 25	plus 25
9	Trace.	Nil.	25	25
13	Trace.	Trace.	25	25
19	.001	Nil.	25	25
24	.006	Nil.	25	25
30	----------	Nil.	plus 22	25
36	----------	Nil.	21	25
42	----------	Nil.	----------	plus 24
48	----------	Nil.	----------	24
54	----------	Nil.	----------	23
60	----------	Nil.	----------	21
77	----------	Nil.	----------	----------
83	----------	.001	----------	19

This application is a continuation-in-part of my co-pending application, Serial No. 730,728, filed June 15, 1934, which in turn is a continuation of Serial No. 503,095, filed December 17, 1930.

From the above description it will be evident that while I have described and claimed the preferred embodiment of the invention, it is to be understood that I reserve the right to make all changes properly falling within the spirit of the invention and without the ambit of the prior art.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of treating cracked hydrocarbon distillates of the class of gasoline and kerosene, normally tending to deteriorate and form gum on storage, which comprises subjecting the distillate to the action of a small amount of a mixture of substituted aromatic amines, said amines being oil soluble and containing constituents of turpentine as substituents, whereby said deterioration and gum formation are substantially retarded.

2. The method of treating cracked hydrocarbon distillates of the class of gasoline and kerosene, normally tending to deteriorate and form gum on storage, which comprises adding to the distillate, in sufficient amount to retard such deterioration and gum formation, a mixture of oil soluble substituted phenylene diamines, said diamines containing components of turpentine as substituted groups.

3. The method of treating cracked hydrocarbon distillates, particularly cracked gasoline, normally tending to deteriorate and form gum on storage, which comprises incorporating in the distillate, in sufficient amount to retard such deterioration and gum formation, a mixture of oil soluble substituted phenylene diamines of the class of ortho and para phenylene diamines containing components of turpentine as substituted groups.

4. A cracked hydrocarbon distillate of the class of gasoline and kerosene, normally tending to deteriorate and form gum on storage, and containing, in sufficient amount to substantially retard such deterioration and gum formation, a mixture of substituted aromatic amines, said amines being oil soluble and having components of turpentine as substituted groups.

5. A cracked hydrocarbon distillate of the class of gasoline and kerosene, normally tending to deteriorate and form gum on storage, and containing a mixture of oil-soluble substituted phenylene diamines in sufficient amount to substantially retard such deterioration and gum formation, said diamines containing components of turpentine as substituted groups.

6. A cracked hydrocarbon distillate, particularly cracked gasoline, normally tending to deteriorate and form gum on storage, and having incorporated therein in sufficient amount to substantially retard such deterioration and gum formation, a mixture of oil-soluble phenylene diamines of the class having amino groups in the ortho and para positions, said amines containing hydrocarbon components of turpentine as substituted groups.

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