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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	Para-aminophenol
Catechol	Para-phenylenediamine
Hydroquinone	Methylaminophenol
Ortho-aminophenol	Alpha-naphthol

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 or aryl group

is substituted for a hydrogen atom in these compounds, their solubility in water is decreased and their solubility in oil is increased wthout an appreciable loss in their power to inhibit oxidation. The greater the number of alkyl or aryl groups which can be substituted in the benzene ring, the more soluble is the resulting compound 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 or aryl groups for hydrogen atoms; an improved method of introducing an alkyl group into a phenol; 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 alkyl groups is 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 that are new to the art are as follows:

1. The use of a mixture of unsaturated hydrocarbons, such as 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 preparation 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:

$R.CH:CH_2$	plus	$C_6H_3(OH)_3$	gives	$RCH_2.CH_2.C_6H_2(OH)_3$
olefine		pyrogallol		stabilizer

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 has 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.

Referring more particularly to the use of a

sulfur dioxide extract of an oil, mentioned heretofore, I have found it advantageous to use an extract of cracked distillates, such as cracked gasoline, naphtha or kerosene. The distillate may be from an asphaltic, mixed or paraffin base crude. I have obtained good results with a cracked distillate obtained by cracking a gas oil from a mixed base crude. The cracking may be done in the liquid or vapor phase, but the invention may find best application in treating a distillate that is not extensively cracked, such as that from a liquid or semi-liquid phase cracking operation wherein the unsaturated content may vary from 10–30%, since the highly cracked vapor phase distillates containing 40–60% unsaturation may be used as such without further concentration of the unsaturated constituents. While I have mentioned specifically the extraction with liquid sulfur dioxide, I may use other solvents, such as furfural, nitrobenzene, phenol or mixtures thereof with modifying solvents, which function in a substantially equivalent manner to sulfur dioxide, i. e. which effect a separation of constituents useful in my invention from the distillate extracted.

In the extraction of the cracked distillate the procedure may be the same as ordinarily followed in the prior art for treating such distillates. The extraction is usually carried out at a low temperature, say around zero, in the case of liquid sulfur dioxide or at a somewhat higher temperature with a correspondingly higher pressure in order to maintain the solvent in the liquid phase. The ratio of solvent to oil may be adjusted to effect the required separation and this will readily be done by the skilled operator. The extraction should be conducted so that a large proportion of the unsaturated constituents of the oil is extracted by the solvent. Aromatic hydrocarbons and a substantial amount of sulfur compounds, if present, will also be extracted but these are usually not objectionable. In case the amount of sulfur compounds is large, it may be reduced by treating with sulfuric acid or other suitable desulfurizing operation.

The extract is readily recovered from the solvent by vaporization of the solvent; for example, in the case of sulfur dioxide the solvent readily volatilizes on release of the pressure. The quantity of extract will vary with the oil treated but usually runs from about 15–30% of the distillate. It is highly unsaturated and normally of slightly higher gravity and boiling point than the original distillate. The unsaturation of the extract will be high and will vary according to the selectivity of the solvent. It is not necessary to obtain a product consisting entirely of unsaturated compounds since such a material might even be too reactive; accordingly, it is often advantageous to have present a substantial amount of aromatics, naphthenes or paraffins as diluents.

As an example of the operation of this modification of the invention the following may be cited:

A mixed base cracked distillate from a commercial cracking operation, such as the Holmes-Manley, was treated with liquid sulfur dioxide and the oil separated into an upper layer, comprising about 80% of the distillate treated, and a lower layer, containing about 20% of the original oil dissolved in liquid sulfur dioxide. The lower layer was separated from the upper layer and the sulfur dioxide removed by distillation. The remaining oil was washed with caustic soda to remove the remainder of the sulfur dioxid , and some of the other sulfur compounds. Five parts of pyrogallol, ten parts of glacial acetic acid, one part of 50% sulfuric acid were mixed with ten parts of the extract and the mixture refluxed for about two hours during which time 40 parts more of the extract were gradually added. The mixture was then cooled and the excess acids washed out with 0.1% sulfuric acid. The product was then ready for use as a gum inhibitor.

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 it is advantageous that the motor fuel be fresh and 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 percent inhibitor	Without inhibitor	With 0.001 percent 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		25

Sample No. 4

Time of storage (weeks)	Steam over gum (gms. per 20 cc.)		Color, Saybolt chromometer	
	Without inhibitor	With 0.0005 percent inhibitor	Without inhibitor	With 0.0005 percent 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	Plus 21	25
42		Nil		Plus 24
48		Nil		24
54		Nil		23
60		Nil		21
77		Nil		
83		.001		19

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.

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

I claim:

1. The method of inhibiting gum formation in low boiling liquid cracked hydrocarbon distillates, which comprises incorporating in the distillate a small amount of polyhydric phenol derivatives, said derivatives containing, as substituted groups, unsaturated constituents extracted from cracked naphtha by sulfur dioxide.

2. A low boiling liquid cracked hydrocarbon distillate, normally tending to deteriorate and form gum on storage, and containing a small amount of polyhydric phenol derivatives, whereby such deterioration and gum formation are substantially retarded, said derivatives containing, as substituted groups, unsaturated constituents extracted from a cracked naphtha by sulfur dioxide.

3. The method of inhibiting gum formation in cracked hydrocarbon distillates of the class of gasoline and kerosene, which comprises adding to the distillate a small proportion of a condensation product of a sulfur dioxide extract of a cracked naphtha and a polyhydric phenol of the class having hydroxyl groups in the ortho and para position, said condensation product consisting essentially of a mixture of substituted polyhydric phenols containing components of said extract as substituted groups.

4. The method of inhibiting gum formation in cracked gasoline, which comprises adding to the gasoline a small amount of a condensation product of pyrogallol and a sulfur dioxide extract of cracked hydrocarbon distillate, said condensation product consisting essentially of a mixture of pyrogallol derivatives containing hydrocarbon components of said extract as substituted groups.

5. A cracked gasoline, normally tending to deteriorate and form gum on storage, and containing, in sufficient amount to substantially retard such deterioration and gum formation, a condensation product of a sulfur dioxide extract of a cracked hydrocarbon distillate and a polyhydric phenol of the class having hydroxyl groups in the ortho and para positions, said condensation product consisting essentially of a mixture of substituted polyhydric phenols carrying as substituted group hydrocarbon components of said extract.

6. A cracked gasoline, normally tending to deteriorate and form gum on storage, and containing a small proportion of a condensation product of pyrogallol and a solvent extract of a cracked naphtha to retard said deterioration and gum formation, said condensation product consisting essentially of a mixture of pyrogallol derivatives carrying components of said extract as substituted groups.

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