Patented June 30, 1942 2,287,898

UNITED STATES PATENT OFFICE

2,287,898

STABILIZATION OF GASOLINE AND THE LIKE

Jacque C. Morrell, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

No Drawing. Original application November 11, 1929, Serial No. 406,515. Divided and this application May 12, 1938, Serial No. 207,574. Renewed May 4, 1940

5 Claims. (Cl. 44—9)

This application is a division of my application Serial No. 406,515, filed November 11, 1929.

This invention relates to stabilization of gasolines, and more particularly to the prevention of color formation and gum forming substances in gasoline, and also to prevent the reduction in antiknock properties of said gasolines on storage.

It has been observed that when gasolines are stored, particularly cracked gasolines, and especially under the influence of light and oxygen, chemical changes occur which affect the color, increase the gum formation, and reduce the antiknock properties. In some cases all of these changes occur simultaneously, while in others they occur independently or in pairs. Although the chemistry of these changes is not thoroughly understood, I have discovered that certain compounds act as stabilizing or inhibiting agents and substantially prevent this undesirable chemical change from occurring.

Generally speaking, cracked gasolines are composed of mixtures of hydrocarbons, principal among which are the aromatic, unsaturated, naphthene, and paraffin hydrocarbons. While it has not been definitely proven, it is believed that color and gum formation and reduction in antiknock properties upon storage involve changes in the unsaturated compounds, more particularly in the highly unsaturated compounds such as diolefins, terpenes, and related compounds. Oxidation products of the various hydrocarbons present in the gasolines are apparently responsible also for the changes noted.

The formation of color in gasolines is undesirable mainly from a marketing viewpoint, for changes in color are usually accompanied by the formation of gum-like and polymer-like materials which affect not only the sale of the gasoline when dispensed from visible bowls, but also the operation of the motor owing to clogging of the gasoline feed lines, interference with the proper operation of the carburetor, and the sticking of valves in the motor. Gum formation is likewise objectionable for the same reasons.

The gum content of a gasoline is measured by a test which involves the gum formation. The present test is stated in terms of milligrams of gum formed upon the evaporation of a specific volume of the gasoline, namely, 100 cc. The presence of oxygen during evaporation increases the gum formation, but as this condition is one which is present in the use of the gasoline, it has a bearing upon its performance in the motor. The so-called gum content of the gasoline will also vary as a function of the material in which it is evaporated, for example, in the presence of copper, the resulting gum will be very much higher than in glass. These tests have a bearing upon the performance of the gasoline in the motor and its auxiliary feed system, and the beneficial effects of my invention will be indicated by such tests as well as by actual motor tests.

The antiknock property of a gasoline is among its most important and valuable characteristics. The higher the antiknock value or rating of a gasoline, the more efficient it is as a motor fuel. Knocking in a motor is an index of inefficient operation because energy which otherwise would be utilized in the operation of the motor must be dissipated by rapid cooling, and unless this remedy is resorted to, a condition will be set up where auto-ignition occurs, thus interfering with the normal functioning of the motor. It has been observed that the higher the compression pressure or compression ratio of a motor, the greater the tendency for a given fuel to knock, and inasmuch as the efficiency of a motor increases with compression pressure and compression ratio, it is desirable that a motor fuel possess sufficiently high antiknock properties to avoid knocking. The present tendency is to increase the compression pressure of motors in order to increase their efficiency or mileage per gallon of fuel consumed so that antiknock fuels are at a premium.

The change in antiknock rating during storage of a motor fuel is particularly embarrassing in that although the antiknock rating of a tank of motor fuel is established and found to be satisfactory, there is a complete uncertainty as to its antiknock value at the time of sale. The economic loss of restoring such gasolines to their original antiknock value can be realized from cases which have been observed where the antiknock value has dropped from approximately fifty per cent benzol equivalent to zero per cent over a period of several months standing.

I have discovered that when relatively small amounts, for example, from a trace up to two per cent, more or less, of the inhibiting or stabilizing agents which are the subject of this invention are added to a gasoline which shows a tendency to depreciate with respect to color, gum, and antiknock properties, that such gasolines will practically retain their original condition. I have found that these inhibitors or stabilizers are effective in preventing the changes which take place as a result of storage, exposure

to light, or oxidation naturally occurring or under accelerated conditions.

I have discovered that naphthalene and its derivatives and homologues when added to motor fuels, especially cracked gasoline, are capable of accomplishing the stabilizing and inhibiting effects above pointed out, and in the present invention I employ for the purposes set forth naphthalene and its derivatives, such as the naphthols, alpha and beta; the alkyl derivatives of naphthalene, for example, methyl and ethyl naphthalene, naphthylamines, both alpha and beta, tetralene or tetrahydro naphthalene, and other derivatives of naphthalene.

I am aware that certain of the above compounds possess antiknock properties but the present invention is to be distinguished from the mere addition of antiknock compounds to motor fuels in that my treatment prevents deterioration of the gasoline upon storage as above described. In my invention, the amount of reagent employed is materially less than that required in motor fuels to impart anti-knock properties thereto. For example, with naphthalene 0.1% will serve effectively to perform the purposes of my invention, whereas several hundred times this amount of naphthalene would be required to impart any appreciable degree of antiknock properties to a motor fuel.

As examples of the color stabilizing properties of naphthalene and its derivatives, I may cite as examples the following:

Starting with a gasoline of 18 Saybolt color which on exposure to diffused sunlight dropped to 14 color in three days with the addition of naphthalene or its derivatives, I have found that by the addition of approximately one-tenth per cent of naphthalene itself the color of the gasoline under the same conditions of exposure was 19 after three days. With beta-naphthol the color was 16 under the same conditions, and with tetralene or tetrahydronaphthalene the color was 21 after three days' exposure, and it will be observed that not only was there a stabilizing of the color, but there was actually an improvement with naphthalene and tetralene.

In regard to the stabilization of gums, starting with a gasoline showing 6 mgs. of gum per 100 cc. by the glass dish test, which on exposure for twenty-four hours to sunlight increased to a gum content of 16 mgs., the addition of one-tenth per cent by weight of naphthalene showed only 2.5 mgs. of gum after exposure. With a gasoline showing approximately 13 mgs. of gum, no increase in gum was shown when beta-naphthol or tetralene were used to the extent of approximately one-tenth per cent; whereas a blank sample without the addition of a stabilizer showed a marked increase in gum content. Similar results were obtained when the gasoline was subjected to accelerated oxidation by heating in the presence of oxygen, which promotes the gum formation without the addition of the stabilizer. The latter when added to the gasoline prevented increased gum on further exposure to light, and also prevented an increase in the gum during the accelerated oxidation test. For example, with a gasoline showing 25 mgs. of gum by the copper dish test after exposure to oxygen at elevated temperatures, the use of naphthalene and some of its derivatives during the oxidation will show a gum content of approximately one-half that of the gasoline where the stabilizer or inhibitors were not present.

Similar results were shown with regard to the antiknock properties, which in some cases without the use of my reagents dropped as low as zero benzol equivalent from a value of approximately 35 when stored for several months, but which drop in benzol equivalent or antiknock rating was prevented by the addition of small amounts of naphthalene and its derivatives.

It can be appreciated that the present invention is of prime economic importance to the oil refining industry since it assures a stable product after refining and at the same time avoids a large expenditure in bringing up the antiknock properties of depreciated gasoline by the addition of costly antiknock dopes or hydrocarbons possessing high antiknock properties, such as benzol. These inhibitors are not to be confused with antiknock dopes, because the amount added will give no antiknock properties per se, but simply acts to prevent the loss of antiknock and other desirable properties of the gasoline.

The above examples are given by way of illustration only and are not to be construed as limitations upon the spirit and broad scope of the invention.

I claim as my invention:

1. A motor fuel product consisting substantially entirely of cracked hydrocarbon distillates of the character of gasoline which tend to deteriorate and develop gums on storage, said product containing a small proportion of beta-naphthylamine such that its tendencies to deteriorate and develop gums are appreciably inhibited.

2. Motor fuel comprising gum-forming cracked gasoline containing, as a gum inhibitor, from a trace to about 2% of beta-naphthylamine.

3. The method of stabilizing cracked gasoline against gum formation which comprises adding thereto from a trace to about 2% of beta-naphthylamine.

4. A method for stabilizing cracked gasoline normally tending to form gums and depreciate in anti-knock value on storage, which comprises incorporating into said cracked gasoline a sufficient quantity of beta naphthylamine to substantially prevent said gum formation and depreciation in anti-knock value.

5. Motor fuel comprising cracked gasoline normally tending to form gum and depreciate in anti-knock value on storage and containing a sufficient quantity of beta naphthylamine to substantially prevent gum formation and depreciation of antiknock value in said cracked gasoline.

JACQUE C. MORRELL.