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LOW BOILING HYDROCARBON OILS

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The present invention relates to improved hydrocarbon oils which have been made stable against gum formation by the addition of small amounts of para diamino aryl compounds or para amino phenolic compounds, and it will be fully understood from the following description:

It has long been well known in the petroleum industry that low boiling hydrocarbon oils such as gasoline and naphtha, especially cracked gasoline and naphtha, often contain gum or gum forming constituents in harmful quantity. In the following description, the oil to be treated will be referred to as low boiling hydrocarbon oil or naphtha. It is to be understod, however, that the principles of the invention may be applied to other oils of analogous character.

Naphthas containing large quantities of gum, or constituents tending to form gum during storage, are objectionable for many purposes, such as for motor fuels, light solvents, etc. Recently a careful study of gum formation has been made by petroleum chemists, and several organic compounds have been found which, when added in small quantities to low boiling hydrocarbon oil, will retard or inhibit gum formation for periods of time varying with the nature of the compound, the oil, and other conditions.

The usual test for such gum forming constituents is known as the copper dish method and is described on page 96 of the United States Bureau of Mines Technical Paper No. 323 D, revised October 21, 1927. The result of this test is expressed in milligrams of gum left in the dish on evaporation of 100 cc. of naphtha.

Another testing method consists of adding oxygen under pressure to the sample of the low boiling hydrocarbon oil to be tested in a closed vessel, and then keeping the oil at elevated temperature of say 100° C. under a pressure of oxygen of say 100 lbs. per square inch. For a certain time the pressure remains practically constant, then it begins to drop suddenly. This drop is observed on a pressure gage. The period of time during which no pressure drop is observed is called the induction period. The longer this induction period, the better is the particular oil tested, and the less likely it is to form gum during storage.

An approximate quantitative relation for the gum inhibiting power of a certain inhibitor may be expressed by the following equation:

$$I.\ P. = \frac{S-B}{B} \times \frac{1}{C}$$

where I. P.=inhibiting power
S=induction period of solution
B=induction period of blank or solvent
C=concentration of the inhibitor in % by weight.

The test just described is quicker and more reliable and gives more readily reproducible data, than the copper dish method. The I. P. number of an inhibitor will accordingly be used herein as a measure of its value. It will be understood, however, that the inhibitors of the present invention may be rated according to the copper dish method, or other suitable method, and will show a corresponding value. Moreover, these inhibitors are effective in actual storage tests, that is, when added to naphtha stored in the tanks of refineries or distributors. The oxidation test described herein gives an accelerated indication of the performance to be expected during storage.

I have discovered that compounds having a benzene ring containing two amino groups, or an amino and a hydroxyl group, in the para position, are powerful gum inhibitors. The simplest types of such compounds are para phenylene diamine, para amino phenol, and their homologues in which one or more hydrogen atoms of the benzene ring are substituted by an alkyl, an aryl or a cycloparaffinic group.

One or both hydrogen atoms of the amino group or groups may be substituted, for example, by the introduction of a hydrocarbon group such as alkyl or aryl group. Such alkylation increases the solubility of the compound in oils according to the number of carbon atoms in the alkyl radical, and the alkylated products often have a preference over the non-alkylated products due to this increase of solubility.

Compounds of the class described above will give an efficient protection against gum formation in a gasoline during ordinary storage for a long period of time when added in amounts of from 0.0005 to 0.1% by weight of the oil. The necessary amounts are best determined empirically. Compounds of the type described are in general sufficiently oil soluble and may be readily distributed uniformly throughout even large bodies of oil by simple mixing. If desirable they may be dissolved in benzene or other suitable solvent from which they will not be readily precipitated by access of moisture. The solution so prepared may be mixed with the oil.

In the following are given the names of some individual members of the type of compounds which are comprised in the present invention together with their I. P. numbers: para phenylene diamine with an I. P. number of 2,000, para amino phenol with an I. P. number of 1,000, amylated (secondary) para amino phenol with an I. P. number of over 1,000.

My invention is not to be limited by any theory nor by the examples given as illustrations but only by the following claims in which it is my intention to claim all novelty inherent in my invention:

I claim:

1. A low-boiling hydrocarbon oil normally tending to deteriorate and form gum during storage, containing a small amount of an amino phenol in which at least one of the amino hydrogens has been substituted by an alkyl radical and the substituted amino group contains at least five carbon atoms, said gum inhibitor having solubility and inhibiting power of the order of those of an amylated amino phenol, in quantity sufficient to retard such gum formation.

2. Product according to claim 1 in which only one amino hydrogen has been substituted by an alkyl radical.

3. A cracked gasoline normally tending to deteriorate and form gum during storage, containing about .0005 to 0.1% by weight of a para amino phenol in which one of the amino hydrogens has been substituted by an amyl group.

4. Product according to claim 3, in which the amino phenol contains a secondary amyl group.

5. A method of stabilizing a low-boiling hydrocarbon oil tending to deteriorate and form a gum during storage, which comprises adding thereto a small amount of an amino phenol in which at least one of the amino hydrogens has been substituted by an alkyl radical and the substituted amino group contains at least five carbon atoms, said gum inhibitor having solubility and inhibiting power of the order of those of an amylated amino phenol, in quantity sufficient to retard such gum formation.

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