## UNITED STATES PATENT OFFICE

2,004,094

## HYDROCARBON OIL AND METHOD OF MAKING THE SAME

Herbert G. M. Fischer, Westfield, and Clifford E. Gustafson, Elizabeth, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application September 21, 1928, Serial No. 307,545

12 Claims. (Cl. 44-9)

The present invention relates to improvements in low boiling non-viscous hydrocarbon oils such as naphtha and the like and will be fully understood from the following description.

Hydrocarbon oils such as naphtha, which include gasoline, and particularly such naphthas as are made by decomposition of heavier oils and the like, often contain gum or gum forming constituents which are objectionable in many respects. The exact nature of these objectionable impurities is at present unknown but gum content or more properly gum formation tendency is measured by the method No. 530.1 in the United States Bureau of Mines Technical Paper 323 B, entitled 15 "Specification for petroleum products and methods of testing", revised October 21, 1927, page 96. In brief, this method consists in placing 100 cc. of the naphtha to be tested in a  $3\frac{1}{2}$  inch diameter spun copper dish on a steam bath and evaporat-20 ing off the volatile material. The result is expressed in milligrams of gum left in the dish per 100 cc. of naphtha.

As noted above, naphthas containing relatively large quantities of gum are objectionable, particularly for motor fuels, cleaning naphtha, light solvents and the like. It is also well known that on standing the gum content of many naphthas steadily increases. We have discovered that the addition of certain organic materials to the naphtha even though in very small quantities greatly reduces the gum as indicated by the above described test and also prevents an increase of gum for prolonged, if not for indefinite periods.

In general, aromatic hydrocarbons with condensed rings (polycyclic compounds) are suitable for our process such as naphthalene, anthracene, phenanthrene and the like and certain derivatives of these compounds are also useful for our purpose. The substitution of certain groups, particularly those of a basic character, in the alpha position greatly increases the effect of the addition agents, for example, alpha-naphthol appears to be better than naphthalene as also are alphanaphthylamine and phenyl alpha-naphthylamine.

The quantity of the addition agent is very small, not being greater in any case than 5 gr. per litre of the naphtha and generally between the approximate limits of .01 to 1.0 gr. per litre. There appears to be an optimum quantity of the agent which will give the best results and it is a simple matter to make up samples of the different strengths and empirically select the most suitable concentration. This behavior appears to be characteristic of all suitable addition agents including those disclosed in our copending application

Serial No. 307,546, filed Sept. 21, 1928. As an illustration, the following example is given, alphanaphthol being added in different quantities as indicated and opposite the number of milligrams of gum per 100 cc. of naphtha is given as determined by the above described test.

Gum	
Original cracked naphtha280 mg./100 cc.	
Naphtha + .5 gr. C <sub>10</sub> H <sub>7</sub> .OH/litre_ 12	
.29	10
.18	
.056	
.0370	
.01260	
	15

The reagent may be dissolved directly in the oil or may be added in the form of a more concentrated solution in naphtha, benzol or other suitable solvents. The agent should be added to the gasoline, which is preferably slightly alkaline or neutral and no treatment which will remove the agent should thereafter be given the oil.

We have observed that mixtures of addition agents such as alpha-naphthol and naphthylamine may be added to gasoline with good results and that volatile metal compounds such as metal carbonyls, metallo-organic substances, which are useful for their anti-detonation effects, may be present in the naphtha without any adverse action.

As examples of other materials the following tests are given:

Original cracked naphtha Original naphtha+alpha-naphthol	VIg. 231	35
Original naphtha+phenyl alpha-		
naphthylamine Original naphtha+naphthylamine	22 24	

The agents are in proportion of .1/gr. per litre of 40 naphtha.

In other tests it has been found that in addition to reducing general gum formation, these agents also reduce acid formation on standing and in one such test the original gasoline is found to have a gum test of 1227 mg./100 cc. after 3 weeks' storage while a comparative sample which contained an addition agent shows only 7.2 mg. The acidity of the first sample is 28.95 as against 0.0 of the second after 3 weeks. The acidity is given in grams of NaOH per barrel of oil and it should be noted that both samples were of the same oil and both were neutral at the beginning of the test.

In the following claims the term "naphthalene

compounds" having certain substituted groups is used and by this term we wish to include the substituted naphthalene itself, and the substituted homologues, of which phenyl naphthalene 5 may be taken as an example.

Our invention is not to be limited by any theory of the mechanism of the process nor by any example given merely by way of illustration but only by the following claims in which we wish to claim all novelty inherent in the invention. We do not claim herein the use of alphanaphthol or alphanaphthylamine alone as gum inhibitors in gasoline nor the use of the class of substances composed of alpha hydroxyl and amino compounds of naphthalene hydroxyl and since those inventions are claimed in application Serial No. 652,420 filed January 18, 1933 by Herbert G. M. Fischer.

We claim:

20 1. A composition of matter comprising a low boiling hydrocarbon oil containing unsaturated constituents of the type normally tending to form gum and produced by pyrolysis of heavy hydrocarbons, to which has been added an alphanaphthylamine having one hydrogen of the amino group substituted by a benzene hydrocarbon radical, in quantity sufficient to retard such deterioration.

2. A composition of matter comprising a low boiling hydrocarbon oil containing unsaturated constituents of the type normally tending to form gum and produced by pyrolysis of heavy hydrocarbons, to which has been added a phenyl alpha-naphthylamine in quantity sufficient to

35 retard such gum formation.

3. The method of preserving low boiling hydrocarbon oils containing unsaturated constituents of the type normally tending to form gum and produced by pyrolysis of heavy hydrocarbons, which comprises incorporating therein a small amount of an alpha-naphthylamine having one hydrogen of the amino group substituted by a benzene hydrocarbon radical, in quantity sufficient to retard such deterioration.

4. The method of preserving low boiling hydrocarbon oils containing unsaturated constituents

of the type normally tending to form gum and produced by pyrolysis of heavy hydrocarbons, which comprises incorporating therein a small proportion of a phenyl alpha-naphthylamine.

5. The method of preserving cracked naphtha normally tending to deteriorate and form gums on storage, which comprises incorporating therewith 0.1 to 5 grams per litre of phenyl alphanaphthylamine.

6. A motor fuel comprising cracked gasoline 10 normally tending to deteriorate upon storage to which has been added a phenylalpha naphthylamine in quantity sufficient to retard such deteri-

oration.

7. A motor fuel comprising cracked gasoline 15 normally tending to deteriorate upon storage to which has been added phenyl alpha naphthylamine in quantity sufficient to retard such deteri-

8. A motor fuel comprising cracked gasoline 20 normally tending to develop gum on storage to which has been added phenyl alpha naphthylamine in quantity sufficient to retard the formation of gum.

9. A cracked gasoline normally tending to de- 25 velop gum to which has been added phenyl alpha naphthylamine in quantity sufficient to retard

the formation of gum.

10. A motor fuel comprising a gasoline normally tending to deteriorate upon storage to 30 which has been added phenyl alpha naphthylamine in quantity sufficient to retard such deterioration.

11. A composition of matter comprising a low boiling hydrocarbon oil of the class produced by 35 thermal decomposition of hydrocarbon of higher molecular weight normally tending to form gum, and 0.01–5 grams per liter of phenyl alpha naphthylamine.

12. A composition of matter comprising 40 cracked naphtha normally tending to form gum, and 0.01-1 gram per liter of phenyl alpha naphthylamine.

HERBERT G. M. FISCHER. CLIFFORD E. GUSTAFSON.