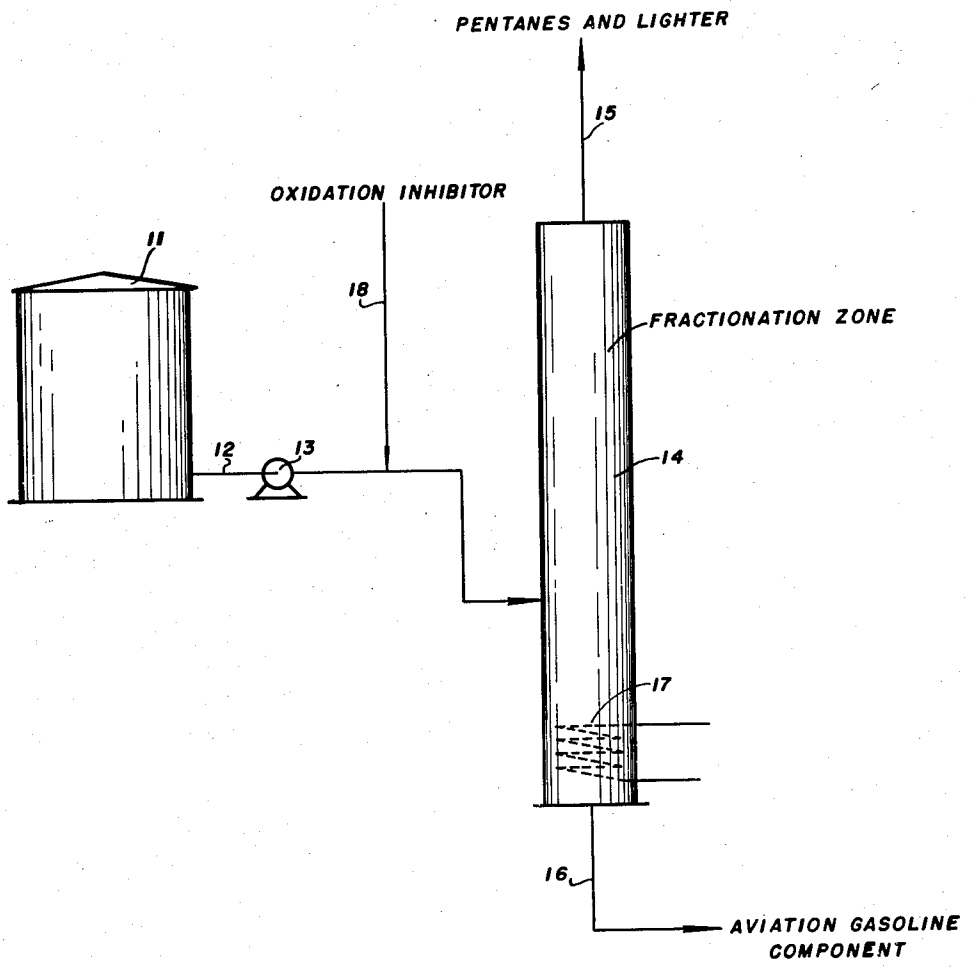
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DISTILLATION OF AVIATION GASOLINE COMPONENTS

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## DISTILLATION OF AVIATION GASOLINE COMPONENTS

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The present invention is directed to the distillation of aviation gasoline components. More particularly, the invention is concerned with the distillation of a hydrocarbon fraction containing olefins which is susceptible to formation of gum on exposure of the fraction to an elevated temperature such as encountered in distilling same.

The present invention may be briefly described as involving the recovery of a higher boiling fraction from a mixture of same with a lower boiling fraction which involves distilling an olefinic hydrocarbon fraction having a boiling point no greater than 300° F. and susceptible to formation of gum therein on exposure to elevated temperatures in the presence of at least 0.01 pound of an oxidation inhibitor per 1000 gallons of said fraction to remove as an overhead fraction hydrocarbons boiling below 100° F. and recovering as a bottoms fraction gum stable higher boiling fractions containing said inhibitor.

The feed stock of the present invention may be a paraffinic and aromatic fraction which is contaminated to a slight extent with olefins. This fraction has a boiling range from about 85° to about 300° F. The feed stock of the present invention may be recovered by distilling selected crude petroleum or it may be formed in certain catalytic conversion operations such as hydroforming operations. A preferred feed stock of the present invention is a fraction recovered from a hydroforming operation which boils in the range from about 85° to about 200° F. and which contains about 3.0% by volume of olefins. This fraction is predominantly paraffinic but may contain 20% by volume of aromatics. Ordinarily such a fraction will contain aromatics in the range from 10% to about 20% by volume.

The oxidation inhibitor which is added to the olefin-containing hydrocarbon fraction prior to distilling same is preferably an alkylated mono-hydroxy phenol. Suitable mono-hydroxy phenols have been disclosed in the patent literature and particularly in U. S. 2,202,877, issued to Stevens and Gruse. Particularly desirable alkylated mono-hydroxy phenols are the tri-alkylated mono-hydroxy phenols, such as 2,4,6-tri-tertiary-butyl-phenol, 2,4 - di - methyl - 6 - tertiary-amyl-4-methyl-phenol. Particularly useful as an oxidation inhibitor in the present invention is a 2,6 - di - tertiary - butyl - 4 - methyl - phenol. This latter compound is particularly useful when the recovered fraction is to be used as a component of aviation gasoline. Other suitable inhibitors in the practice of the present invention are the diamines such as illustrated by p-phenylene diamine and N,N'-di-sec. butyl-p-phenylene diamine.

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In the practice of the present invention it is to be emphasized that the oxidation inhibitor is added to the fraction to be distilled and not to the distilled fraction. If the inhibitor is added to the distilled fraction undesirable results are obtained.

The invention will be further illustrated by reference to the drawing in which the single figure is a flow diagram of the preferred mode. Referring now to the drawing, numeral 11 designates a charge tank in which a body of a hydrocarbon fraction having a boiling point no greater than 300° F. is maintained. Such fraction may be a hydroformed fraction boiling in the range from about 85° to 200° F. The feed stock is withdrawn from tank 11 by line 12 containing pump 13 and is discharged thereby into a fractionation zone 14. Fractionation zone 14 may be a single fractionation tower or a plurality of fractionating towers but for convenience of description is shown as a single tower. It is understood that fractionation zone 14 will be provided with suitable internal baffling equipment, such as bell cap trays and the like, to insure intimate contact between vapors and liquids to allow a sharp separation in the fractionation zone 14. Fractionation zone 14 is provided with line 15 for removal of an overhead fraction and line 16 for recovery of a bottoms fraction. Fractionation zone 14 is also provided with a heating means illustrated by a steam coil 17 for adjustment of temperatures and pressure therein.

The feed stock of the present invention prior to introduction in the fractionation zone 14 has injected thereinto by line 12 an inhibiting amount of an oxidation inhibitor by way of line 18. The oxidation inhibitor employed may suitably be one of the type illustrated before and is used in an amount in the range between 0.01 and 0.5 pound of oxidation inhibitor per 1000 gallons of feed stock.

In practicing the present invention, the inhibited feed stock is subjected to distillation conditions to remove overhead fractions boiling below about 120° F. which will include pentanes and lighter which may suitably be used for adjustment of vapor pressure in hydrocarbon fractions having a deficient volatility. The desired fraction containing the oxidation inhibitor is recovered by line 16 and may suitably be used as an aviation gasoline component. This fraction is gum stable and has not formed in it gum components as a result of the high temperatures pre-

vailing in fractionation zone 14. Such temperatures for distilling a stock, such as illustrated having a final boiling point of about 200° F., will be around about 145° F.

In order to illustrate the invention further a light fraction obtained from a hydroforming operation which boiled up to 200° F. was distilled. Pentane and lighter were removed and the bottom fraction which was recovered was inhibited by adding 0.1 pound of 2,3-di-tertiary-butyl-4-methyl-phenol thereto. A second portion of the same fraction from the hydroforming operation had added to it 0.1 pound of 2,6-di-tertiary-butyl-4-methyl-phenol and was then distilled under similar conditions to that of the first run, pentanes and lighter being discharged as an overhead and a bottoms containing the inhibitor recovered. The results of these runs are shown in the following table:

*Table*

| Stock | 16-Hr. Acc. Gum |
|---|---|
| Charge to Still | 0.0 |
| Bottoms from Still (Inhibitor added immediately after distillation) | 26.4 |
| Bottoms from Still (Inhibitor added to charge to still) | 1.4 |

It will be seen from the data that the 16-hour accelerated gum test of the bottoms fraction which was inhibited after distillation was 26.4, whereas in the practice of the present invention the 16-hour accelerated gum test was only 1.4. From the foregoing data it is believed apparent that the practice of the present invention allows markedly superior results to be obtained. In fact, the practice of inhibiting the bottoms product after distillation rather than before, due to the high accelerated gum values, which averaged from 10 to 50 milligrams per 100 milliliters of sample, had to be discontinued. These high values are unacceptable for components of aviation gasoline. On the other hand, the value of 1.4 milligrams per 100 milliliters of sample is entirely acceptable and the bottoms fraction so recovered in the practice of the present invention may suitably be used in aviation gasoline as a blending component thereof.

The accelerated gum test is determined in accordance with the A. S. T. M. Procedure D-873-49.

The amount of olefins in the feed stock of the present invention is small but apparently enough to contribute a susceptibility to formation of gum on activation by heat at the temperature prevailing during distillation. The bromine number of the stocks utilized ranged from about 1 to 6. The stock given in the foregoing examples had a bromine number of 5. A description of the bromine number test may be found in A. S. T. M. Procedure D-875-46T.

It is to be emphasized that the present invention is directed to the recovery of components which may be used in aviation gasoline and has nothing to do with the inhibition during distillation of polymerizable components, such as butadiene, styrene, and the like.



The nature and objects of the present invention having been completely described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A method for recovering a higher boiling fraction from a mixture of same with a lower boiling fraction which comprises adding an alkylated monohydroxy phenol oxidation inhibitor, in an amount in the range between 0.01 and 0.5 pound per thousand gallons, to a converted hydrocarbon fraction consisting of a predominant amount of saturated hydrocarbons, a lesser amount of aromatic hydrocarbons, and a still lesser amount of olefinic hydrocarbons and boiling in the range between 85° and 300° F. and susceptible to formation of gum therein on exposure to an elevated temperature within said boiling range, distilling, said inhibited hydrocarbon fraction to form an overhead fraction boiling below 120° F. and a gum stable bottoms fraction containing said inhibitor, and recovering said bottoms fraction as a component of aviation gasoline.

2. A method in accordance with claim 1 in which the oxidation inhibitor is 2,6-di-tertiary-butyl-4-methyl phenol.

3. A method in accordance with claim 1 in which the fraction susceptible to gum formation is a hydroformed fraction boiling in the range between 85° and 200° F.

4. A method for removing pentanes and lighter fractions from a hydrocarbon fraction susceptible to formation of gum on exposure of same to an elevated temperature which comprises distilling a hydroformed fraction consisting of a predominant amount of saturated hydrocarbons, a lesser amount of aromatic hydrocarbons, and a still lesser amount of olefinic hydrocarbons and boiling in the range between 85° and 200° F. in the presence of 0.1 pound of 2,6-di-tertiary-butyl-4-methyl phenol per thousand gallons of said hydroformed fraction at a temperature no greater than 145° F. to remove as an overhead fraction pentanes and lighter and recovering as a bottoms fraction gum stable higher boiling fractions containing said inhibitor as a component of aviation gasoline.

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