

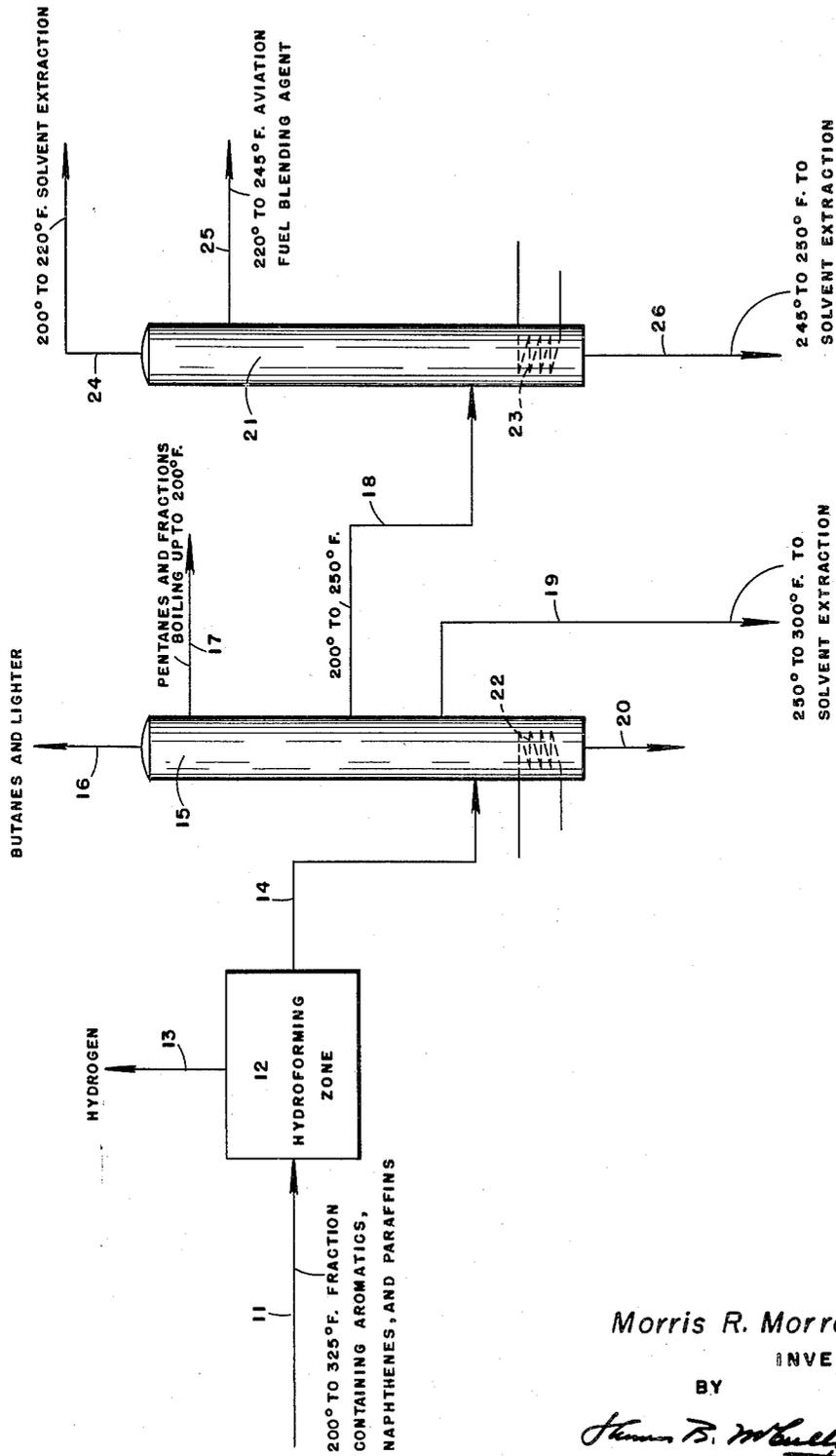
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AVIATION FUEL BLENDING AGENT AND METHOD FOR PRODUCING SAME

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# UNITED STATES PATENT OFFICE

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## AVIATION FUEL BLENDING AGENT AND METHOD FOR PRODUCING SAME

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The present invention is directed to a method for producing an aviation fuel blending agent. More particularly, the invention is directed to a method for forming a fraction comprising aromatic and paraffinic hydrocarbons having enhanced anti-knock qualities.

Prior to the present invention it has been known that aromatic hydrocarbons have desirable characteristics which make them suitable for inclusion in aviation fuels. It has also been known that aromatic hydrocarbons are very good solvents for employment in the paint and lacquer industry and in many other services where aromatic hydrocarbons find usage. It has been customary prior to the present invention, in obtaining aromatic hydrocarbon fractions for employment in aviation fuels, to resort to expensive procedures to concentrate the aromatic hydrocarbons. Thus, for example, it has been known to subject selected hydrocarbon fractions containing naphthenes to hydroforming conditions wherein the naphthenes are converted to the corresponding aromatics. The resulting product from the hydroforming operation is then subjected to distillation to recover fractions having desirable boiling ranges which are then subjected to solvent extraction to obtain aromatic hydrocarbons or concentrates which can be included in aviation gasolines. Such procedures are disadvantageous in that it is necessary to subject the aromatic containing hydrocarbon fractions to expensive solvent extraction procedures to recover a substantially purified product.

It is, therefore, the main object of the present invention to prepare an aromatic fraction suitable for inclusion in aviation fuels without resort to solvent extraction.

Another object of the present invention is to provide a method for recovering a fraction including aromatics and paraffins which has substantially improved anti-knock qualities.

A still further object of the present invention is to prepare by distillation a fraction comprising paraffinic and aromatic hydrocarbons of improved octane number characteristics.

The objects of the present invention are obtained by forming a fraction consisting substantially of aromatic, paraffinic, naphthenic and olefinic hydrocarbons boiling in the range between 200 and 250° F. and distilling said fraction to obtain a fraction boiling in the range between 220° and 245° F. The fraction boiling in the range between 220° and 245° F. has substantially improved octane number characteristics and its anti-knock qualities make it suitable for inclusion in aviation gasoline.

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The present invention, therefore, may be described briefly as involving the formation of a hydrocarbon fraction boiling in the range between 200° and 250° F. and containing substantially aromatic, paraffinic, naphthenic and olefinic hydrocarbons. Such a fraction may be formed, for example, by hydroforming a fraction boiling in the range between 200 to 325° F. and containing aromatic, naphthenic and paraffinic hydrocarbons and if desired, olefinic hydrocarbons. Hydroforming is a well known technique and details of the hydroforming procedures may be found in U. S. 2,400,363 issued May 14, 1946, in the name of Herbert H. Meier. From the hydroformed product a fraction boiling in the range between 200 and 250° F. may be separated, for example, by distillation, which has the desired characteristics as a feed stock for the process of the present invention. The fraction having the characteristics enumerated and containing substantially aromatic, paraffinic, naphthenic and olefinic hydrocarbons is subjected to a distillation operation in efficient fractionating equipment to separate a fraction boiling in the range between 220 and 245°. Such a fraction has enhanced octane number or anti-knock qualities which make it suitable for inclusion in an aviation fuel. This fraction consists substantially of aromatics and other hydrocarbons having good octane number characteristics.

The invention will be further illustrated by reference to the drawing in which the single figure is a flow diagram of a preferred mode of practicing my invention. Referring now to the drawing, numeral 11 designates a charge line by which a fraction boiling in the range between 200° and 325° F. containing aromatics, naphthenes and paraffins and if desired, olefins, is charged into hydroforming zone 12 which is indicated as a block in the diagram. It will be understood that hydroforming zone 12 will include a suitable catalyst such as that described in the aforesaid patent to Meier and that the conditions in the hydroforming zone will be similar to the conditions given in the Meier patent supra. Zone 12 is provided with a line 13 through which hydrogen may be discharged therefrom. Conditions in zone 12 are adjusted to cause conversion of naphthenes to aromatics, the aromatics originally present in the feed stock and the paraffins being substantially inert to the reaction and passing through hydroforming zone 12 substantially unaffected. The product leaving hydroforming zone 12 by line 14 is discharged thereby into a first distillation zone 15 which is provided respectively with lines 16, 17, 18, 19, and 20. An

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overhead fraction comprising butanes and lighter hydrocarbons is removed from distillation zone 15 by line 16, whereas pentanes and fractions boiling up to 200° F. are removed from zone 15 by line 17 for use as a gasoline blending agent or as desired. A fraction boiling in the range between 200° and 250° F. consisting substantially of aromatic, naphthenic, paraffinic, and olefinic hydrocarbons is withdrawn from zone 15 by line 18 and discharged into second distillation zone 21 wherein it is distilled in a manner which will be described. A fraction boiling in the range between 250° and 300° F. is withdrawn from zone 15 by line 19 and may be introduced into a solvent extraction zone such as one employing liquefied sulfur dioxide as a solvent at a low temperature in the range between -20° F. and -60° F. in order to recover the desired aromatics therefrom in a substantially purified condition. The heavier fractions may be withdrawn by line 20 and may find use in motor gasoline or as a cracking stock. It will be noted that distillation zone 15 is provided with a heating means 22 which is illustrated as an internal steam coil. It is also understood that distillation zone 15 is equipped with internal baffle equipment such as bell cap trays, packing and other means for insuring intimate contact between vapors and liquids in order to cause separation of the desirable fractions.

Distillation zone 21 is similar to distillation zone 15, but is operated under conditions conducive to more precise fractionation. Zone 21 is provided with a heating means illustrated by coil 23 for adjustment of temperature and pressure therein. Distillation zone 21, like distillation zone 15, is provided with suitable internal equipment such as bell cap trays, packing and other means to insure intimate contact between vapors and liquids and to allow separation of the desirable fractions as will be described. Distillation zone 21 is also provided with lines 24, 25, and 26. After conditions have been adjusted properly in zone 21 there is removed overhead therefrom by line 24 a fraction boiling in the range between 200° and 220° F. containing aromatics which may be routed to a solvent extraction zone not shown for separation of desirable aromatics therefrom. There is recovered from zone 21 by line 26 a fraction boiling in the range between 245° and 250° F. which may also be routed to a solvent extraction zone not shown for recovery of desirable aromatics therefrom. Line 25 is provided whereby the desirable fraction boiling in the range between 220° and 245° F. which comprises aviation fuel blending agent produced in the present invention. This fraction consists predominantly of aromatic and paraffinic hydrocarbons and has improved octane number characteristics. The concentration of aromatics in this fraction is between 60% and 80% by volume. By virtue of concentrating the aromatic, paraffinic, naphthenic and olefinic fractions boiling in the range between 200° and 250° F., it is possible to distill therefrom a fraction boiling in the range between 220° and 245° F. which is eminently suitable as an aviation fuel blending agent.

The reason for the peculiar enhanced properties of the fuel boiling in the range between 220° and 245° F. produced by distillation of the 200°-250° fraction is not entirely understood and may not be predicted from the composition of the feed stock charged to hydroforming zone 12. This hydroformer feed ordinarily boils in the range between 200° and 325° F. and may com-

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prise approximately 10% by volume aromatic hydrocarbons, 43% by volume naphthenic hydrocarbons, 47% by volume paraffinic hydrocarbons and a trace of olefins. Neither is it predictable from the composition of the fraction obtained by line 18 from distillation zone 15 boiling in the range between 200° and 250° F. which may contain approximately 50% by volume aromatic hydrocarbons, 12% by volume naphthenic hydrocarbons, 35% by volume paraffinic hydrocarbons and 3% by volume olefinic hydrocarbons.

In an effort to characterize the components present in the 200°-250° F. boiling range fraction, a raffinate was examined, which had been produced from this fraction by solvent extraction with liquid sulfur dioxide at a low temperature of about -30° F. under conditions which allowed the recovery of aromatics from the mixture in substantially pure form. The raffinate or non-aromatic portion of this fraction was then tested for antiknock characteristics. The Supercharge rich rating of the 220°-245° portion of this raffinate with 4 cc. tetraethyl lead (T. E. L.) per gallon added thereto was 104 I. M. E. P. (This method of quality characterization is known as the Supercharge method for determining the knock characteristics of aviation fuels and is described in the "A. S. T. M. Standards on Petroleum Products and Lubricants," Committee D-2, 1938, Test D909-48T.) The rating of the same 220 to 245° F. boiling range fraction produced by distillation alone from the 200°-250° F. boiling range hydroformate fraction was 242 I. M. E. P. This fraction contained approximately 60% toluene, and, therefore, it was possible to calculate the octane quality of the non-aromatic portion of this fraction by subtracting the effect of the toluene (which was the only aromatic present) from the octane rating of the fraction. The value so calculated was 138 I. M. E. P., or approximately 34 points higher than the rating of the non-aromatic portion of the raffinate described heretofore. Octane ratings of this order of magnitude are not characteristic of components boiling in this range. To confirm this calculated rating of 138 I. M. E. P., a sample of the distillate 220°-245° F. fraction containing 60% toluene was solvent extracted at about -90° F. with liquid sulfur dioxide to obtain great selectivity and thus remove substantially completely the aromatic portion of the distillate. The octane rating on the raffinate from this extraction was found to be in very good agreement with the value of 138 I. M. E. P. calculated as described above.

By adjusting the composition of the feed stock introduced by line 11 into the hydroformer 12, it will be possible to produce aromatic concentrates of 220°-245° F. boiling range containing more than 60% aromatics. As a further example, such a fraction containing approximately 80% aromatics (toluene) shows a similar advantage for producing this fraction by distillation rather than reblending the solvent extracted products of the same boiling range since the I. M. E. P. reference number of the non-aromatic portion so distilled is 128 as compared with 104 mentioned previously. This advantage also was confirmed by employing extremely low temperature extraction as described heretofore.

It is indeed surprising that the fraction produced by distillation should have such enhanced octane characteristics over one produced by solvent extraction. It is obvious that the octane rating of the combined aromatic and non-aro-

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matic components in the 220°-245° F. boiling range fraction produced in accordance with my invention is superior to that of a blend which could be made to the same aromatics concentration and boiling range from aromatics and non-aromatics produced by solvent extraction.

As mentioned previously, the reason for obtaining this surprising result is not entirely understood, but it is believed that the presence of aromatic hydrocarbons with the non-aromatic hydrocarbons boiling in the range between 200°-250° F. may result in the non-aromatic hydrocarbons of superior quality having abnormal behavior which allows them to be segregated by distillation with the aromatics.

In order to obtain the desirable results, as a general statement, it may be said that the aromatic and paraffinic hydrocarbon content of the fraction boiling in the range between 200° and 250° F. should comprise a major amount of the fraction, while minor amounts of the fraction will comprise naphthenic and olefinic hydrocarbons. Further, it may be stated that the aromatic hydrocarbons should be in excess of the paraffinic hydrocarbons and the naphthenic hydrocarbons should be present in lesser amounts than the paraffinic hydrocarbons and in greater amounts than the olefinic hydrocarbons. Apparently, an excess of aromatic hydrocarbons over paraffinic hydrocarbons allows the latter to be distilled to obtain a fraction boiling in the range between 220° to 245° F. having the unusual octane number characteristics.

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 obtaining an aviation fuel blending agent of improved anti-knock qualities which comprises forming a first fraction boiling in the range between 200° and 250° F. and consisting substantially of a major amount of aromatic and paraffinic hydrocarbons, said aromatic hydrocarbons being in excess of said paraffinic hydrocarbons, and minor amounts of naphthenic and olefinic hydrocarbons, said naphthenic hydrocarbons being in excess of said olefinic hydro-

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carbons, and distilling said first fraction under suitable conditions to obtain a second fraction boiling in the range between 220° and 245° F. having an I. M. E. P. of 242 and consisting of an amount of aromatic hydrocarbons in the range between 60% and 80% by volume and the remainder predominantly paraffinic hydrocarbons, said remainder having an I. M. E. P. of at least 128 on addition thereto of 4 cc. of tetraethyl lead per gallon suitable for use in aviation fuels.

2. A method in accordance with claim 1 in which the first fraction consists substantially of 50% by volume aromatic hydrocarbons, 35% by volume paraffinic hydrocarbons, 12% by volume naphthenic hydrocarbons, and 3% by volume olefinic hydrocarbons.

3. An aviation fuel blending agent boiling in the range between 220° and 245° F. consisting of aromatic hydrocarbons, in an amount in the range between 60% and 80% by volume, and the remainder predominantly paraffinic hydrocarbons, said remainder having an I. M. E. P. of at least 128 on addition thereto of 4 c. c. of tetraethyl lead per gallon.

4. An aviation fuel blending agent boiling in the range between 220° and 245° F. having an I. M. E. P. of 242 consisting of toluene in an amount in the range between 60% and 80% by volume and the remainder predominantly paraffinic hydrocarbons, said remainder having an I. M. E. P. of at least 128 on addition thereto of 4 cc. of tetraethyl lead per gallons.

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