July 19, 1932. L. M. HENDERSON ET AL 1,868,102

MOTOR FUEL AND ITS PRODUCTION

Filed Dec. 24, 1928

Fig. 1.

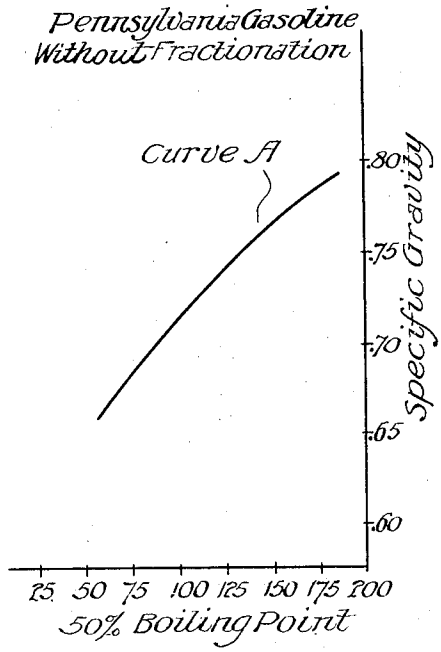
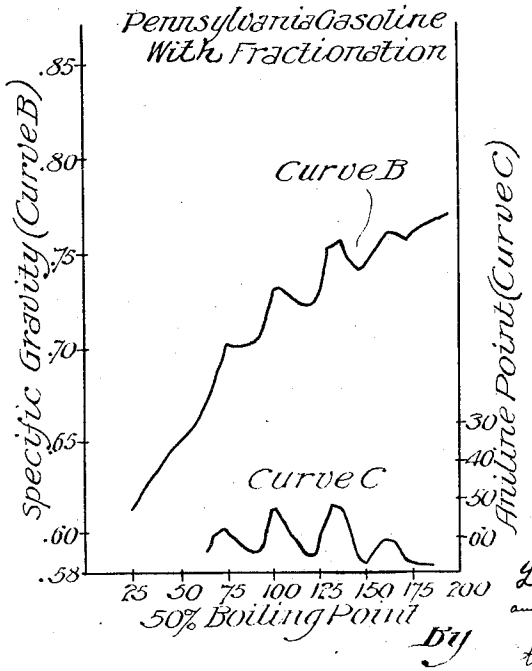


Fig. 2.



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By

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UNITED STATES PATENT OFFICE

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MOTOR FUEL AND ITS PRODUCTION

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Our invention relates to a motor fuel of relatively high antidetonating properties and a process for producing it.

In accordance with our invention crude petroleum or a product thereof is subjected to highly efficient fractionation whereby there are separated fractions of narrow ranges of boiling points within the boiling range of gasoline, some of which have a lower content of paraffine hydrocarbons than the gasoline obtained by the usual distillation of a similar petroleum product while other fractions have a higher content of paraffine hydrocarbons.

Petroleum is a mixture of various series of hydrocarbons containing within each series individual hydrocarbons of different boiling points. The relative percentages of the different series vary in different crudes; for example, the so-called paraffine base crudes, as those from Pennsylvania, have a high percentage of compounds of the paraffine series, while the naphthene base crudes of the Gulf Coast have a relatively high percentage of members of the naphthene series and correspondingly lower percentage of paraffines.

There are certain characteristic relationships between the properties of the hydrocarbons of the various series; for example, for a given boiling point the paraffines have the lowest specific gravity, the olefines, naphthenes and aromatics having specific gravities increasing in the order named. Similarly the aniline point, i. e., the critical temperature of solution of aniline in the hydrocarbons, is relatively high for the paraffines as compared to the other series. By comparison of these properties an approximation of the nature of a petroleum fraction may be obtained.

The tendency of a gasoline to detonate when used in an internal combustion engine is dependent to a large extent upon the relative percentages of the various series of hydrocarbons present. For the same boiling range the straight chain paraffines detonate most readily, the olefines next, followed by the naphthenes and aromatics. From the standpoint of antiknock value, those gasolines relatively low in content of the straight-chain paraffine hydrocarbons and relatively high in olefines, naphthenes and particularly aromatics are most desirable. For this reason California gasoline having a high naphthene content is more effective as an antidetonating fuel than gasoline from Pennsylvania crude.

Gasoline as produced by straight-run distillation, or by cracking or conversion of higher into lower boiling oils, is a mixture of the lower boiling hydrocarbons of the various series. When such liquid is distilled without close fractionation of the vapors, i. e., with no special provision for bringing reflux liquid into heat interchange relation therewith, and a series of cuts of increasing boiling points is collected, a relatively smooth curve is obtained if the specific gravity of the individual cuts be plotted against the 50% boiling point of the respective cuts. The general form of such a curve for a typical gasoline is shown in Curve A, Fig. 1. Practically all gasolines give a curve of substantially this shape although the location of the curves may vary somewhat according to the source, for example, the curve for Pennsylvania gasoline of low specific gravity for a given volatility will lie below the curve for a Gulf Coast gasoline of higher specific gravity of the same volatility.

When, however, a gasoline is subjected to efficient fractional distillation, as by bringing it into heat interchange relation with suitably controlled quantities of reflux liquid and it is separated into a series of small cuts, as for example, those representing 2.5% of the original gasoline, and the specific gravity of these fractions is plotted against the corresponding 50% boiling point, the curve will take the form of Curve B, Fig. 2, which is that of a Pennsylvania gasoline subjected to efficient fractional distillation.

Curve B shows that Pennsylvania gasoline when subjected to efficient fractional distillation is separated into a series of fractions or cuts of decreasing volatility and varying paraffine content, the peaks in the curve representing high specific gravity cuts and the troughs low specific gravity cuts which, as indicated by the relationship between the

50% boiling point and specific gravity are of low and high paraffine hydrocarbon content respectively. The relative paraffine content of these fractions is further shown by reference to the Curve C of Fig. 2, in which the aniline point, i. e., the critical temperature of solution of aniline, is plotted against the 50% boiling point of the 2.5% fractions. It will be observed that in Curve B the troughs and peaks, the latter indicating high specific gravity, correspond respectively, as to 50% boiling point, with the troughs and the peaks in the Curve C, the peaks indicating low aniline point. The peaks in both curves are indications of low paraffine content as compared with the low specific gravity and high aniline points of the troughs.

It is the object of our invention to separate these fractions of low paraffine hydrocarbon content by subjecting gasoline or petroleum or petroleum fractions containing gasoline-like constituents to highly efficient fractional distillation and to blend the low paraffine content fractions thus obtained to produce a motor fuel of high antidetonating properties. In some instances, it may be desirable to add to the blend thus obtained other petroleum fractions of suitable boiling range, as within the boiling range of gasoline.

Detonation is dependent not only upon the chemical composition of the hydrocarbons present in the fuel, but also upon the volatility of these hydrocarbons, those of lower boiling point having less tendency to detonate than the higher boiling hydrocarbons.

As a consequence, the lower boiling portion of the gasoline, for example that portion boiling below 80 degrees C., is of suitable antiknock properties and in general, need not be subjected to the efficient fractionation.

For example, in accordance with one method of practicing our invention the gasoline or oil containing gasoline-like components may be continuously efficiently fractionally distilled in a system, comprising the well-known pipe still and fractionating column, in which the oil is heated in the pipe still to a temperature sufficient to vaporize the desired components and is then introduced into a fractionating column in which the rising vapors are brought into intimate heat interchange contact with descending reflux liquid thereby effecting a separation of the vapors into liquid fractions, of varying antiknock properties, taken off as side-streams from the column. Those corresponding with one or more peaks of Curves B or C are the fractions selected for blending because of their high antidetonating characteristics. The low boiling portion of the vapors, of good antidetonating properties, is taken off overhead from the column as vapor and condensed. The condensate is, for example, of a character boiling below 80 degrees C.

Another method of effecting the fractionation is by a batch operation in which the petroleum fraction is charged to a shell still provided with a factionating column, and, as the distillation progresses and the character of the distillate changes, the stream is directed toward the proper storage tank according to whether it is at the time of high or low paraffine content.

Our process has been described with reference to Pennsylvania gasoline, but it is to be understood that it may be applied to oil from any source containing gasoline-like components, including cracked gasoline and crude petroleum, and any method of fractional distillation may be utilized which makes a sharp separation of the components within the gasoline boiling range into cuts of narrow range of boiling points and of relatively high and relatively low paraffine content respectively, so that, when the latter are blended together with or without the addition of other hydrocarbon fractions lying within the gasoline boiling range a motor fuel of relatively high antiknock properties is produced.

Fractional distillation of petroleum to produce gasoline and other fractions is well known in the art and that, per se, we do not claim as our invention. In such processes the gasoline is obtained, in general, as one fraction, the antidetonating properties of which are dependent primarily upon its source and the content of high boiling components. What we claim is the separation of such gasoline or suitable oil by fractional distillation into fractions of narrow range of boiling points and of progressively increasing boiling point, but of irregular antidetonating qualities, and blending the selected fractions of high antidetonating qualities to produce an improved motor fuel.

We prefer so to control the fractionation that each of the individual fractions obtained shall have a total boiling range of about 5 degrees C. and not more than 10 degrees C. when determined by the A. S. T. M. Distillation test No. D 86–27 modified in that the dry point is determined by noting the temperature at which the last drop of liquid disappears from the flask rather than the maximum temperature reached by the thermometer on continued heating of the flask as specified in the A. S. T. M. method.

For the fractionating system hereinbefore referred to there may be employed one generally, though not necessarily specifically, of the character disclosed in U. S. Patent No. 1,680,421. It shall be understood however, that there may be employed any suitable method of fractionation having the efficiency or yielding the sharpness of cuts or

fractions of the character hereinbefore described.

The charging stock or starting material is any suitable hydrocarbon oil. It may be crude petroleum or a product thereof. It may be a cut whose components have boiling points extending over a considerable range; more particularly and preferably it is a gasoline. The fractions of irregularly varying antidetonating qualities, from among which are selected those having relatively high antidetonating qualities, have boiling points lying within the gasoline boiling point range. The selected fractions are blended with each other and one of the fractions may comprise the lowest boiling components of the oil which is fractionated or a part thereof; or the selected fractions may be blended with any other suitable oil.

The fractions of high antidetonating quality selected for blending purposes, are those of relatively narrow range of boiling points substantially corresponding, respectively, with the peaks of the Curves B or C. With these selected fractions there alternate, in a sense, other fractions of low or lower antidetonating qualities corresponding substantially with the troughs or cusps of the Curves B or C, and these latter fractions are not utilized.

Our improved product is characterized by the fact that, first, it comprises a blend of fractions of relatively high antidetonating qualities, selected from a series of fractions, including the first-named fractions and others having antidetonating qualities which are low or lower than those of the selected fractions; and, second, it comprises a blend of such selected fractions with another fraction or fractions, preferably of substantial or high antidetonating quality, of a boiling range beyond or outside the boiling range of the selected fractions, and generally or preferably of a boiling point or range lower than that of the selected fractions.

What we claim is:

1. The process of obtaining gasoline of high antidetonating quality, which comprises separating hydrocarbon oil containing gasoline-like components by subjecting said oil to fractional distillation into a series of fractions of irregularly varying antidetonating qualities, and combining those fractions of relatively high antidetonating quality.

2. The process of improving the antidetonating value of hydrocarbon motor fuel, which comprises separating said motor fuel by subjecting it to fractional distillation into a series of fractions of irregularly varying antidetonating qualities, and combining those fractions having higher antidetonating quality than that of the original motor fuel.

3. The process of distilling hydrocarbon oils containing gasoline-like components, which comprises vaporizing at least a portion of the oil, separating by fractional distillation the vapors of the higher boiling portion of the gasoline-like components into a series of fractions of progressively increasing boiling points and irregularly varying antidetonating qualities, condensing the lower boiling portion of the gasoline-like components to form a single fraction, and blending those fractions of relatively high antidetonating qualities with the lower boiling portion of the gasoline-like components.

4. In the art of producing motor fuel, the process which comprises passing the vapors of gasoline-like oil through successive zones countercurrent to and in heat exchange contact with reflux oil, drawing off one or more sidestream fractions of progressively increasing boiling points and irregularly varying antidetonating qualities, condensing the lower boiling portion, and blending therewith said one or more sidestream fractions of relatively high antidetonating qualities.

5. The process of obtaining gasoline of high anti-detonating quality which comprises separating hydrocarbon oil containing gasoline-like components, by subjecting it to fractional distillation, into a series of fractions of progressively increasing boiling point some of which are more paraffinic and others less paraffinic than the original gasoline-like components, selecting those fractions so produced within the gasoline boiling range whose paraffin hydrocarbon content is relatively low and blending them to form a product whose content of paraffin hydrocarbons is less than that of the original gasoline-like components.

6. The process of distilling hydrocarbon oils containing gasoline-like components, which comprises vaporizing at least a portion of the oil, condensing the vapors of that portion of the gasoline-like components boiling below 80 degrees C. to form a single fraction, separating by fractional distillation the vapors of the gasoline-like components boiling above 80 degrees C. into a series of fractions of progressively decreasing volatility and irregularly varying paraffin hydrocarbon content, selecting those fractions of relatively low paraffin hydrocarbon content within the gasoline boiling range and blending them with the fraction boiling below 80 degrees C. to form an improved anti-detonating motor fuel.

7. The process of improving the antidetonating quality of a hydrocarbon motor fuel which comprises separating said motor fuel by fractional distillation into a series of fractions of progressively increasing 50% boiling points and of sufficiently close boiling range that when their specific gravities are plotted against their 50% boiling points a curve is obtained which shows a succession of peaks and troughs, the peak fractions being less paraffinic and more highly anti-

detonating than the trough fractions, and combining peak fractions to produce a motor fuel substantially more highly anti-detonating than the original motor fuel.

8. The process of improving the anti-detonating quality of a hydrocarbon motor fuel which comprises separating it by fractional distillation into a series of fractions of progressively increasing 50% boiling points and of sufficiently close boiling range that when their aniline points are plotted inversely against their 50% boiling points a curve is obtained which shows a succession of peaks and troughs, the peak fractions being less paraffinic and more highly anti-detonating than the trough fractions, and combining peak fractions to produce a motor fuel substantially more highly anti-detonating than the original motor fuel.

9. The process of producing a motor fuel of improved anti-detonating quality which comprises subjecting a hydrocarbon oil containing gasoline-like components to fractional distillation to separate said gasoline-like components into a series of fractions of progressively increasing 50% boiling points and of individual boiling range not greater than 10 degrees C. so that when their specific gravities are plotted against the 50% boiling points a curve is obtained which shows a succession of peaks and troughs, the peak fractions being less paraffinic and more anti-detonating than the trough fractions, and combining peak fractions to produce a motor fuel substantially more highly anti-detonating than the original gasoline-like components.

10. The process of producing a motor fuel of improved anti-detonating quality which comprises subjecting a hydrocarbon oil containing gasoline-like components to fractional distillation to separate said gasoline-like components into a series of fractions of progressively increasing 50% boiling points and of individual boiling range not greater than 5 degrees C. so that when their specific gravities are plotted against the 50% boiling points a curve is obtained which shows a succession of peaks and troughs, the peak fractions being less paraffinic and more anti-detonating than the trough fractions, and combining peak fractions to produce a motor fuel substantially more highly anti-detonating than the original gasoline-like components.

11. The process of obtaining a motor fuel of high anti-detonating quality from one of lower anti-detonating quality which comprises first submitting a portion of the fuel of lower anti-detonating quality to close fractionation to obtain a series of closely cut fractions and determining which of the fractions so obtained when combined produce a motor fuel of higher anti-detonating quality, then fractionally distilling the remainder of the motor fuel first mentioned to separate therefrom those fractions which the determination aforesaid indicates will produce the desired motor fuel, and blending them.

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