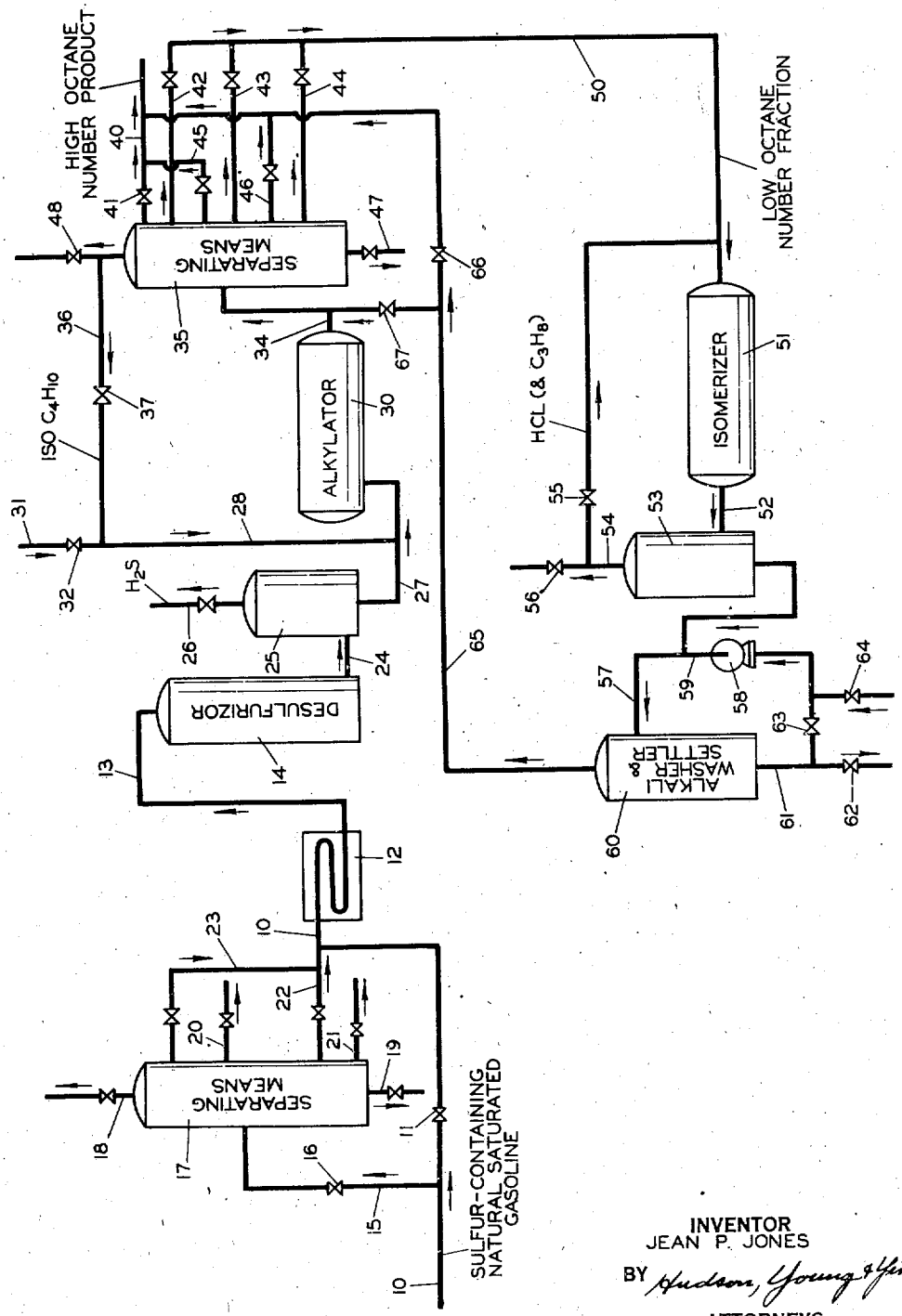
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PRODUCTION OF MOTOR FUEL

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PRODUCTION OF MOTOR FUEL

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This invention relates to the production of normally liquid hydrocarbons of high octane number from a sulfur-containing hydrocarbon material of a lower octane number. It relates particularly to the production of a relatively sulfur-free saturated hydrocarbon fraction boiling in the motor fuel range from a sufur-containing normally liquid hydrocarbon fraction.

Many specifications for premium motor fuels, particularly those for use in air-cooled aviation engines, require that the motor fuel be substantially saturated in character and that it have not only a high octane number but also that this octane number be secured with the addition of only small amounts of anti-detonants, such as the commonly used tetraethyl lead. Motor fuels of this nature are generally prepared by blends of synthetically produced isoparaffin hydrocarbon fractions, together with fractions of naturally occurring hydrocarbons having more or less narrow boiling ranges. Most of the synthetic hydrocarbon fractions are inherently sulfur-free, either because sulfur is readily removed from the charge stock to the synthesis steps or because the synthesis processes tend to remove sulfur-containing compounds from the hydrocarbon materials treated. However, such synthesis processes are generally carried out in the presence of a catalyst which is adversely affected by sulfur-containing compounds which may be present in the charge stock. Furthermore, considerable difficulty often results from sulfur-containing compounds which are present in the fractions of hydrocarbons obtained from natural sources such as natural gasoline and straight-run gasoline. Among the means which are used to remove such sulfur-containing compounds from these fractions are included processes wherein such compounds are decomposed and the sulfur removed as hydrogen sulfide. Although in most instances such processes are simple and inexpensive as well as being highly efficient, they are at times somewhat disadvantageous in that the products are unsaturated to an extent greater than may be desired.

In accordance with the present invention such sulfur containing hydrocarbon fractions are made suitable as blending stocks for motor fuels, which must attain the highest antiknock values and must be unsaturate-free, by subjecting those stocks to catalytic desulfurization at elevated temperatures whereby the sulfur compounds are converted to hydrogen sulfide and olefins, and the hydrogen sulfide is removed and the fraction is passed to an alkylation step wherein the olefins formed in the desulfurization operation are reacted with isoparaffins to form paraffin hydrocarbons. As a modification of this invention the materials resulting from this alkylation step, or at least fractions thereof which have an octane number lower than that of the material as a whole, are subjectd to isomerization to form isoparaffins having higher octane numbers. In one particular modification of this invention the hydrocarbon effluent from the alkylation step is passed to a separating means, fractions of low octane number are separated therefrom and subjected to isomerization, the hydrocarbon effluents of this isomerization are returned to the same separating means, and from this separating means is recovered a hydrocarbon material of high octane number, containing isoparaffins resulting both from the alkylation and from the isomerization steps, which is essentially saturated in character and which is also essentially sulfur-free.

An object of this invention is to produce hydrocarbons of high octane number boiling in the motor fuel range.

A further object of this invention is to convert a sulfur-containing hydrocarbon fraction into a saturated sulfur-free hydrocarbon fraction boiling in the motor fuel range.

Further objects and advantages of my invention will become apparent to one skilled in the art from the accompanying disclosure and discussion.

Reference will now be made to the drawing which forms a part of this specification which shows diagrammatically an arrangement of apparatus which may be used in practicing my invention, the said discussion serving also to exemplify the invention.

A sulfur-containing hydrocarbon material, preferably one which is normally liquid and boiling in the motor fuel range and has been obtained from a natural gasoline or a straight-run gasoline as hereinafter discussed, is charged through line 10 and passed through valve 11 to a suitable heater 12, and then through line 13 to a desulfurizer 14.

If desired, such a charge stock may be separated by an initial fractionation into one or more fractions which contain the major part of the sulfur compounds present in the initial charge so that the material treated in desulfurizer 14 will not have such a large volume. Such a fractionation may be effected by passing the charge from line 10 through line 15 controlled by valve 16 to separating means 17. Undesirable low boiling

material may be discharged through valved line 18 and undesirable high boiling materials may be discharged through valved line 19. One or more fractions which are low in sulfur content may be separated and discharged, as through valved lines 20 and 21. One or more fractions which are high in sulfur content may be separated as through valved lines 22 and 23 and passed to line 10 on the far side of valve 11 for treatment in desulfurizer 14. In heater 12 the sulfur-containing hydrocarbon material is heated to a suitable desulfurizing temperature, which will be generally between about 500 and 750 or 800° F., and is passed through line 13 into contact with a suitable desulfurization catalyst in desulfurizer 14. Such a catalyst may be bauxite, bauxite treated with sodium hydroxide or barium hydroxide, brucite, caliche or other suitable contact materials. The pressure is preferably between about 0–100 pounds gage and the contact time is preferably between about 0.1 and 2.0 seconds. Under these conditions most of the sulfur-containing compounds, especially the mercaptans, are converted to hydrogen sulfide and olefins and a minimum of hydrocarbon decomposition takes place. In some instances, particularly with the longer contact times, and/or at the higher temperatures, an appreciable although not extensive amount of dehydrogenation of hydrocarbons to olefins and hydrogen may take place, and such reactions are not deleterious to the successful application of my invention. However, it is generally desired that dehydrogenation should not take place to an extent greater than that of about 8 or 10 per cent.

From desulfurizer 14 the effluents pass through line 24 to sulfur removal means 25. This may be a simple fractional distillation column whereby hydrogen sulfide, and any free hydrogen, are removed by fractional distillation, and may be discharged through valved line 26. Such fractional distillation may, if desired, be supplemented or replaced by washing with a suitable alkali such as sodium hydroxide or sodium carbonate. A substantially sulfur-free material, which contains unsaturated hydrocarbons, is passed from unit 25 through line 27 to alkylator 30. In some instances the material may of itself contain sufficient low boiling isoparaffin to react satisfactorily with the unsaturated hydrocarbons present under the alkylation conditions existing in alkylator 30. However, it will generally be desired to add a low-boiling isoparaffin, particularly isobutane from other sources, through line 28. This low-boiling isoparaffin may be introduced from a suitable outside source through line 31 and valve 32, or may comprise or consist of isobutane produced in a subsequent step of the process as will be later described and passed from separating means 35 through line 36 and valve 37. The alkylation carried out in the alkylator or alkylation zone 30 is preferably conducted in the presence of a suitable alkylation catalyst since the product is generally more saturated than that resulting from a noncatalytic alkylation carried out at elevated temperatures and pressures. Suitable catalysts include hydrofluoric acid, sulfuric acid, aluminum chloride, phosphoric acid, sodium chloro-aluminate and the like. Temperatures, pressures, and reaction times will depend to a certain extent upon the catalyst used and can be readily ascertained for any particular instance by one skilled in the art. It is desirable that the olefin concentration in the alkylation zone be kept at a low value and if it is not sufficiently low in the charge to alkylator 30 the desired effect may be secured by adding the olefin containing charge to a circulating reaction mixture, or by adding it at a plurality of points to a reacting stream, as will be appreciated by one skilled in the art. It is desired that the products of such alkylation reactions will boil in the motor fuel range, and the isoparaffin introduced and which is reacted should be chosen with regard to olefinic material present in the hydrocarbon fraction passing through line 27 with this in mind. Effluents of the alkylation reaction pass through line 34 to separating means 35 and a fraction of high octane number, which is saturated and sulfur free, can be recovered through line 40 controlled by valve 41.

As a desired modification of my invention it is preferred to separate the hydrocarbon material which is charged to separating means 35 into one or more fractions of low octane number and into one or more fractions of high octane number and to subject the fraction, or fractions, of low octane number to an isomerization reaction whereby saturated fractions of high octane number are obtained. When this modification is included, fractions of low octane number are recovered as by means of one or more valved lines 42, 43 and 44, and fractions of high octane number are recovered by one or more of the valved lines 40, 45 and 46. Undesired high-boiling material may be discharged from valved line 47. Low-boiling isoparaffinic material may be removed through line 36 and recycled entirely or in part through valve 37 or discharged through valve 48.

A paraffinic hydrocarbon material of low octane number comprising one or more of the fractions of low octane number separated from separating means 35, and substantially free from sulfur-containing compounds which are injurious to many isomerization catalysts, is passed through line 50 to isomerizer 51, wherein it is subjected to an isomerization catalyst under reaction conditions of time, temperature and pressure such as to effect a substantial conversion of normal or only slightly branched paraffin hydrocarbons into more highly branched paraffin hydrocarbons. Catalysts suitable for the isomerization reaction include hydrogen fluoride, or one or more of the metal halides commonly identified as Friedel-Crafts catalysts, especially aluminum chloride, aluminum bromide, ferric chloride and the like. With such metal halides it is preferable to operate in the presence of small amounts of corresponding hydrogen halide. The hydrocarbon material being treated may be present in either liquid or vapor phase with any of these catalysts, satisfactory operation having been secured with both conditions. The metal halide may be used alone or on a suitable support such as activated charcoal, dried silica or alumina gel, dehydrated bauxite or the like, or it may be dissolved in the hydrocarbon material when such is being treated in the liquid phase. Suitable conditions for the use of aluminum chloride include a temperature in the range of about 175 to 250° F., 1 to 5% of hydrogen chloride, with a reaction time between about 5 minutes and an hour. With hydrofluoric acid as the isomerization catalyst, the reaction is preferably carried out to 200 to 350° F. and a similar reaction time. With the catalysts mentioned, it is generally preferable to limit the reaction time so that between about 30 and 50% of the paraffins charged enter into the isomerization reaction. From isomerizer 51 the

effluents are passed to the separator 53 through line 52. When the catalyst is aluminum chloride deposited on a porous support the aluminum chloride will remain in the equipment included in the isomerizer 51, and the material passed through line 52 will include hydrogen chloride, and low boiling paraffin hydrocarbons, particularly propane, produced by side reactions during the isomerization. In this instance a fraction comprising propane and hydrogen chloride is removed from separating means 53 through line 54 and can be recycled at least in part through valve 55 back to the isomerizer 51. Generally it is desirable to discharge a part of this material from the system as through valve 56. A hydrocarbon material is removed from separating means 53 through line 57, and is mixed with an alkaline solution which is passed by pump 58 through line 59, to neutralize any residual HCl and other acidic materials which may be present. The mixture is passed to separator 60 and the alkaline solution settles and may be withdrawn through line 61. A part or all of this solution may be withdrawn through valve 62, but preferably a part is recycled through valve 63 to pump 58. Fresh alkaline solution may be introduced through valve 64. A hydrocarbon fraction containing isoparaffins of high octane number is recovered through line 65 and may be recovered as a product of the process through valve 66. However, it is often desirable to subject this material to further fractionation to separate fractions of high octane number as products and also to separate fractions of low octane number which can be recycled to isomerizer 51. I find it desirable to effect such a separation by passing the hydrocarbon effluents of the isomerization from line 65 through valve 67 to line 34 and to separating means 35, so that effluents of the alkylation and effluents of the isomerization are fractionated together. This has the added advantage of giving a unified cyclic process for the production of a single product of high octane number which can be recovered through line 40. When isobutane is produced in isomerizer 51 it will constitute or be contained in the material passed from separating means 35 through valve 37 and line 28 to alkylator 30 and in some instances will supply all of the low boiling isoparaffin which is used in alkylator 30. In such a case it will be unnecessary to add other isoparaffins and other isoparaffinic material to the process through valve 32 except perhaps when a continuous run is first being put into operation. It will be appreciated, of course, that when more than one fraction of low octane number is available for isomerization from separating means 35, each fraction may be subjected to isomerization separately in apparatus not shown, but similar to that shown and discussed, so that each fraction is reacted under conditions which are optimum for that particular fraction. However, in many instances the additional expense is not warranted and the single isomerization step shown will be found entirely satisfactory.

Many modifications and variations of this invention may obviously be used and can be adapted by one skilled in the art without departing from the spirit of the disclosure. It will be understood that the flow diagram is schematic, that only essential pieces of equipment and conditions have been described, and the function and modifications are discussed in sufficient detail to serve as sufficient guides.

I claim:

1. A process for producing a saturated motor fuel having an improved octane number and an improved response to the addition of antidetonants, which comprises subjecting a sulfur-containing normally liquid paraffinic hydrocarbon material boiling in the motor fuel range to desulfurization at an elevated temperature in the presence of a desulfurization catalyst to convert sulfur-containing compounds to hydrogen sulfide and olefins, removing hydrogen sulfide from effluents of said treatment, passing a resultant desulfurized, hydrogen sulfide-free normally liquid hydrocarbon material to an alkylation zone, passing also to said alkylation zone a low-boiling isoparaffin in an amount sufficient to effect a reaction with the unsaturated hydrocarbons in said desulfurized hydrocarbon material, effecting an alkylation reaction between said unsaturated hydrocarbons and said low-boiling isoparaffins to form higher boiling paraffins, passing hydrocarbons effluent from said alkylation to a separating means, separating from said hydrocarbons a normally liquid paraffinic hydrocarbon fraction of low-octane number and a normally liquid paraffinic hydrocarbon fraction boiling in the motor fuel range of higher octane number, subjecting said fraction of low octane number to isomerization to convert paraffin hydrocarbons contained therein into paraffin hydrocarbons of more highly branched structure including isobutane, recovering from effluents of said isomerization a paraffinic fraction boiling in the motor fuel range and combining said fraction with the aforesaid fraction of higher octane number to form a composite product of the process, recovering also from effluents of said isomerization isobutane and passing said isobutane to said alkylation zone as at least a part of said low-boiling isoparaffin.

2. A process for producing a saturated motor fuel having an improved octane number and an improved response to the addition of antidetonants, which comprises subjecting a sulfur-containing normally liquid paraffinic hydrocarbon material boiling in the motor fuel range to desulfurization at an elevated temperature in the presence of a desulfurization catalyst to convert sulfur-containing compounds to hydrogen sulfide and olefins, removing hydrogen sulfide from effluents of said treatment, passing a resultant desulfurized hydrogen sulfide-free normally liquid hydrocarbon material to an alkylation zone, passing also to said alkylation zone a low-boiling isoparaffin in an amount sufficient to effect a reaction with the unsaturated hydrocarbons in said desulfurized hydrocarbon material, effecting an alkylation reaction between said unsaturated hydrocarbons and said low boiling isoparaffins to form higher boiling paraffins, passing hydrocarbons effluent from said alkylation to a separating means, separating from said hydrocarbons a normally liquid paraffinic hydrocarbon fraction of low-octane number, subjecting said fraction of low octane number to isomerization to convert paraffin hydrocarbons contained therein into paraffin hydrocarbons of more highly branched structure, passing hydrocarbons effluent from said isomerization to the aforesaid separating means, and recovering from said separating means a paraffinic hydrocarbon fraction boiling in the motor fuel range of high octane number and containing paraffin hydrocarbons resulting from said alkylation and also paraffin hydrocarbons resulting from said isomerization.

3. A process for producing a saturated motor fuel having an improved octane number and an

improved response to the addition of antidetonants, which comprises subjecting a sulfur-containing normally liquid paraffinic hydrocarbon material boiling in the motor fuel range to desulfurization at an elevated temperature in the presence of a desulfurization catalyst to convert sulfur-containing compounds to hydrogen sulfide and olefins, removing hydrogen sulfide from effluents of said treatment, passing a resultant desulfurized hydrogen sulfide-free normally liquid hydrocarbon material to an alkylation zone, passing also to said alkylation zone a low-boiling isoparaffin in an amount sufficient to effect a reaction with the unsaturated hydrocarbons in said desulfurized hydrocarbon material, effecting an alkylation reaction between said unsaturated hydrocarbons and said low boiling isoparaffin to form higher boiling paraffins, passing hydrocarbons effluent from said alkylation to a separating means, separating from said hydrocarbons a normally liquid paraffinic hydrocarbon fraction of low-octane number, subjecting said fraction of low octane number to isomerization to convert paraffin hydrocarbons contained therein into paraffin hydrocarbons of more highly branched structure including isobutane, passing hydrocarbons effluent from said isomerization to the aforesaid separating means, separating from said means an isobutane fraction containing isobutane produced in said isomerization and passing said isobutane fraction to said alkylation zone as at least a part of said low-boiling isoparaffin, and recovering from said separating means a paraffinic hydrocarbon fraction boiling in the motor fuel range of high octane number and containing paraffin hydrocarbons resulting from said alkylation and also paraffin hydrocarbons resulting from said isomerization.

4. A process for producing a saturated motor fuel having an improved octane number and an improved response to the addition of antidetonants, which comprises subjecting a sulfur-containing normally liquid paraffinic hydrocarbon material boiling in the motor fuel range to desulfurization at an elevated temperature in the presence of a desulfurization catalyst to convert sulfur-containing compounds to hydrogen sulfide and olefins, removing hydrogen sulfide from effluents of said treatment, passing a resultant desulfurized hydrogen sulfide-free normally liquid hydrocarbon material to an alkylation zone, passing also to said alkylation zone an isobutane fraction from a subsequent fractional distillation as hereinafter recited in an amount sufficient to effect a reaction with the olefin content of said liquid hydrocarbon material, maintaining the contents of said alkylation zone under alkylation reaction conditions in the presence of an alkylation catalyst to produce a paraffinic hydrocarbon product, passing hydrocarbons effluent from said alkylation to a fractional distillation, removing from said fractional distillation a plurality of normally liquid paraffinc hydrocarbon fractions of low octane number and in the motor fuel range, subjecting said fractions of low octane number to isomerization to convert paraffin hydrocarbons contained therein into low-boiling isoparaffinic hydrocarbons including isobutane, passing hydrocarbons effluent from said isomerization to the aforesaid fractional distillation, recovering an isobutane fraction from said fractional distillation and passing same to said alkylation as aforesaid, and recovering also from said fractional distillation a plurality of substantially sulfur-free normally liquid paraffinic hydrocarbon fractions of high octane number boiling in the motor fuel range and containing paraffin hydrocarbons resulting from said alkylation and also paraffin hydrocarbons resulting from said isomerization as well as paraffin hydrocarbons originally contained in the first said sulfur-containing hydrocarbon material, and combining said fractions to form a paraffinic motor fuel product of high octane number.

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CERTIFICATE OF CORRECTION.

Patent No. 2,376,060. May 15, 1945.

JEAN P. JONES.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 7, for "subjectd" read --subjected--; line 43, for "hereinafter" read --hereinbefore--; page 4, second column, line 20, claim 4, for "paraffinc" read --paraffinic--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 21st day of August, A. D. 1945.

Leslie Frazer

(Seal) First Assistant Commissioner of Patents.

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4. A process for producing a saturated motor fuel having an improved octane number and an improved response to the addition of antidetonants, which comprises subjecting a sulfur-containing normally liquid paraffinic hydrocarbon material boiling in the motor fuel range to desulfurization at an elevated temperature in the presence of a desulfurization catalyst to convert sulfur-containing compounds to hydrogen sulfide and olefins, removing hydrogen sulfide from effluents of said treatment, passing a resultant desulfurized hydrogen sulfide-free normally liquid hydrocarbon material to an alkylation zone, passing also to said alkylation zone an isobutane fraction from a subsequent fractional distillation as hereinafter recited in an amount sufficient to effect a reaction with the olefin content of said liquid hydrocarbon material, maintaining the contents of said alkylation zone under alkylation reaction conditions in the presence of an alkylation catalyst to produce a paraffinic hydrocarbon product, passing hydrocarbons effluent from said alkylation to a fractional distillation, removing from said fractional distillation a plurality of normally liquid paraffinc hydrocarbon fractions of low octane number and in the motor fuel range, subjecting said fractions of low octane number to isomerization to convert paraffin hydrocarbons contained therein into low-boiling isoparaffinic hydrocarbons including isobutane, passing hydrocarbons effluent from said isomerization to the aforesaid fractional distillation, recovering an isobutane fraction from said fractional distillation and passing same to said alkylation as aforesaid, and recovering also from said fractional distillation a plurality of substantially sulfur-free normally liquid paraffinic hydrocarbon fractions of high octane number boiling in the motor fuel range and containing paraffin hydrocarbons resulting from said alkylation and also paraffin hydrocarbons resulting from said isomerization as well as paraffin hydrocarbons originally contained in the first said sulfur-containing hydrocarbon material, and combining said fractions to form a paraffinic motor fuel product of high octane number.

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