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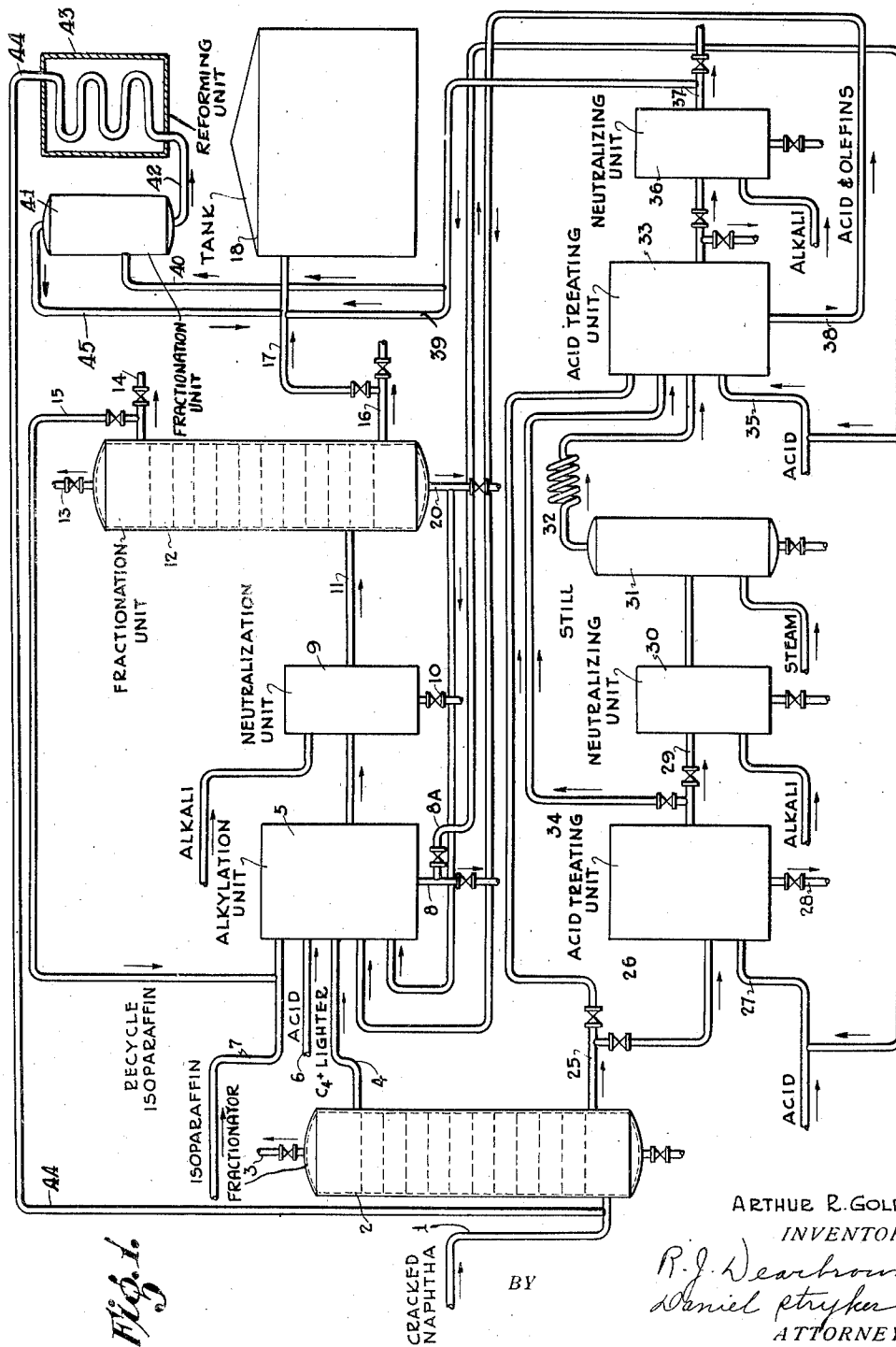
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2,383,056

MANUFACTURE OF MOTOR FUEL

Filed Jan. 25, 1941

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

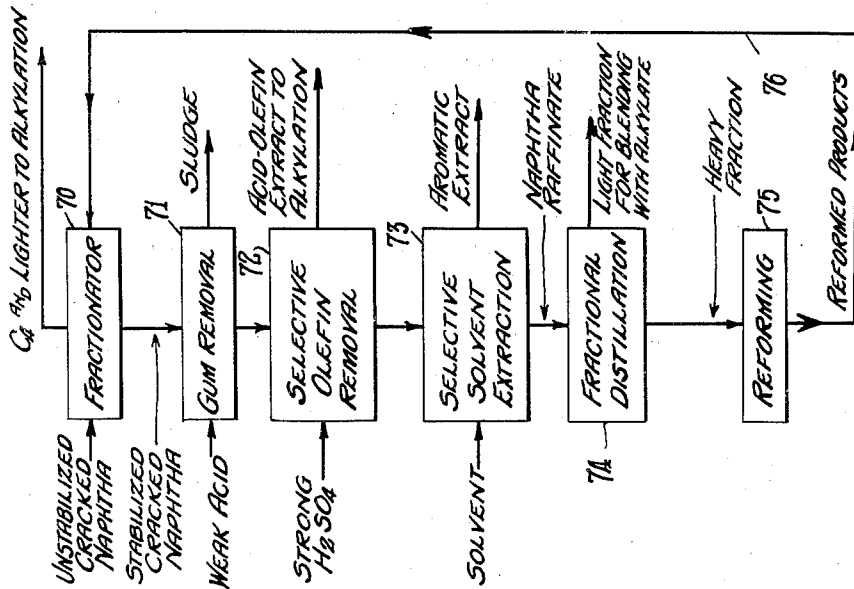


Fig. 3.

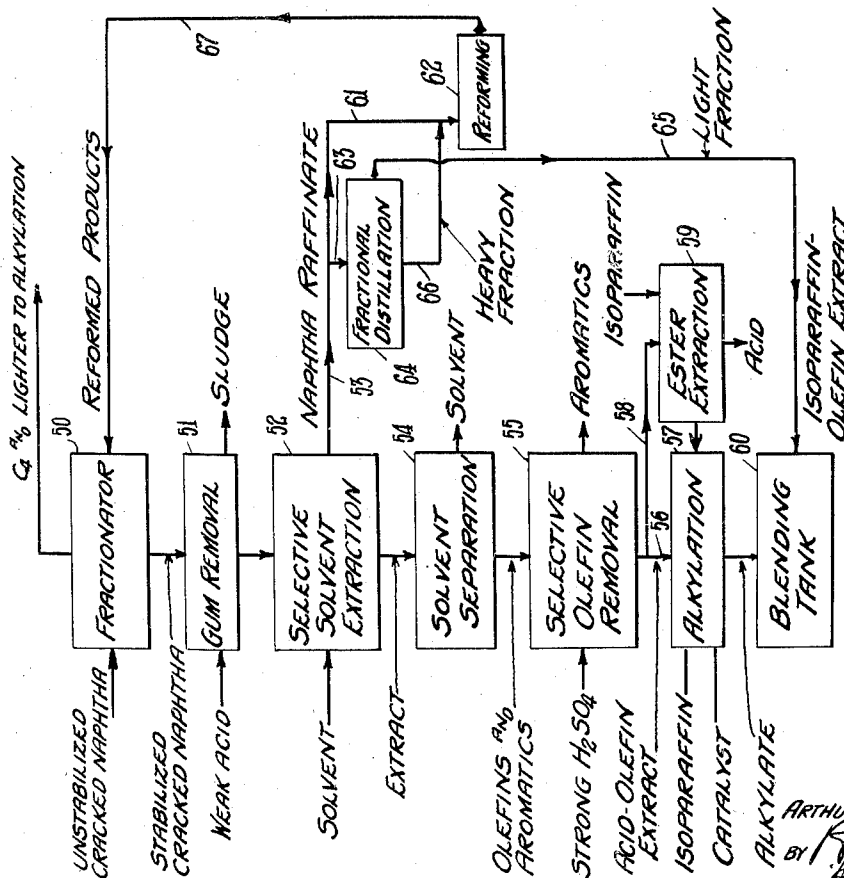


Fig. 2.

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MANUFACTURE OF MOTOR FUEL

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This invention relates to the manufacture of motor fuel and particularly to a process of treating naphtha involving alkylation of certain hydrocarbon constituents of naphtha.

The invention broadly contemplates treating naphtha to remove sulfur bodies, gum-forming constituents and other impurities. In addition it contemplates separating from the naphtha an olefinic fraction which is substantially free from aromatic and other constituents and therefore in a condition which is particularly suitable for alkylating isoparaffin hydrocarbons to produce additional gasoline hydrocarbons of high antiknock value.

More particularly, the invention contemplates treating naphtha with sulfuric acid or other refining agent so as to effect removal of unsaturated and olefinic constituents and produce a color and gum stable naphtha retaining aromatics and other constituents suitable for motor fuel. Olefinic constituents so removed from the naphtha are utilized, all or in part, for the alkylation of low boiling isoparaffin hydrocarbons and thereby produce an additional yield of high antiknock motor fuel.

An important object of the invention involves segregating the normally liquid olefinic constituents of naphtha or gasoline and then using them to alkylate isoparaffin hydrocarbons in the substantial absence of non-olefinic constituents of the naphtha or gasoline which interfere with the alkylation reaction and whose presence in the final product may be undesired. As a consequence an improved yield of alkylate of improved octane number is obtained as well as a decrease in catalyst deterioration.

A further object is to remove from the hydrocarbon feed to an alkylation reaction those constituents such as diolefins, sulfur compounds, etc., which if present in the alkylation reaction result in decreased catalyst life.

The invention is illustrated in the attached drawings which show preferred embodiments thereof, and wherein:

Fig. 1 is a diagrammatic illustration of apparatus for carrying out the method of the present invention;

Fig. 2 is a flow diagram in block form illustrating a modified method; and

Fig. 3 is a flow diagram in block form illustrating a further modification.

In accordance with one method of carrying out the invention as illustrated in Fig. 1, cracked naphtha is treated with concentrated acid at a temperature substantially below normal room

temperature, that is in the range about 10 to 60° F. and preferably at a temperature of about 10 to 30° F. Under these conditions the concentrated acid dissolves olefinic hydrocarbons without appreciably affecting other desirable constituents of the naphtha. After removal of the acid and dissolved hydrocarbons the remaining acid treated naphtha is neutralized with caustic soda solution or other alkaline neutralizing agent to produce a treated gasoline having an antiknock value usually not substantially lower than that of the raw naphtha.

The acid and dissolved hydrocarbon constituents are conducted to an alkylation process wherein the dissolved hydrocarbons are reacted with isobutane in the presence of concentrated sulfuric acid under alkylation conditions whereby the isobutane is converted to branched chain gasoline hydrocarbons having a high antiknock value. The gasoline produced in the alkylation operation may be blended all or in part with the acid-treated gasoline or separately disposed of in whatever manner desired.

According to another mode of operation also illustrated in Fig. 1, cracked naphtha is preliminarily treated in conventional manner to remove gum-forming and color-forming bodies, presumably consisting mainly of diolefins, which cause an increase in the catalyst consumption during alkylation. Subsequently it is treated with acid under suitable conditions to remove at least a substantial proportion of the remaining olefins namely, mono-olefins, while leaving valuable aromatic constituents in the treated naphtha.

The olefins removed in the second acid treating operation will comprise mono-olefins substantially free from diolefins and therefore will provide a purified olefinic charge for the alkylation operation. The acid used in extracting these olefins in the secondary acid treating operation advantageously comprises concentrated sulfuric acid and therefore the acid containing the dissolved olefins can be passed directly to the alkylation operation. Since the acid associated with the olefins is already highly concentrated it can be used to advantage to form at least a part of the catalyst employed in a sulfuric acid alkylation operation.

According to another modification illustrated in Fig. 2 the naphtha, either with or without the preliminary treatment to remove gum-forming constituents, may be treated with liquid sulfur dioxide or other selective solvent to extract from the naphtha a fraction consisting essentially of normally liquid olefins and aromatics. The frac-

tion so extracted from the naphtha, after removal of the solvent, is then treated with sulfuric acid to segregate therefrom a fraction consisting essentially of olefins substantially free from aromatic and other constituents including paraffinic constituents. The olefins thus obtained are passed to the alkylation reaction with or without the acid in which they were absorbed.

The process may be modified to effect removal of the color- and gum-forming constituents from the naphtha, or from the above-mentioned olefin-aromatic fraction extracted from the naphtha, by treatment with cuprous chloride, by solvent extraction, by treatment with acid, by contact with an adsorptive contact material such as acid treated clay, fuller's earth or other similar type material. Following this preliminary treatment the naphtha is treated with concentrated acid under non-alkylating conditions to extract the olefins.

Advantageously, the cracked naphtha, after removal of the gum-forming and color-forming constituents either by acid treatment or by contact with an adsorptive agent, is neutralized and subjected to steam distillation so as to separate undesired high boiling material, as shown in Fig. 1. Thereafter, olefin constituents are extracted from the naphtha to produce a treated naphtha retaining aromatic constituents and having a high antiknock value.

The conditions under which the acid treatment or treatments is effected will depend upon the nature or source of the cracked naphtha and also upon the nature of the particular products desired. For example, the nature of the acid treatment may depend upon whether the motor fuel product is for use in an aviation motor or in an automobile motor. Thus, in the case of an aviation motor fuel it is desirable that the product have a low unsaturated content as indicated by a low acid heat, and a low gum content. The extent to which it is desired to reduce the unsaturated content of the product governs the extent of the acid treatment or extraction. On the other hand, it will depend on the nature of the olefinic fraction which it is desired to segregate from the naphtha as a charge to the alkylation reaction.

It has been found that by subjecting cracked naphtha to treatment with concentrated sulfuric acid at relatively low temperature olefinic constituents can be extracted from the naphtha without removing substantial amounts of the aromatic, naphthenic and paraffinic constituents. Thus, the treated gasoline may have an octane number not substantially lower than that of the raw naphtha.

As indicating the nature of the acid treating step a cracked naphtha of about 284° F. end boiling point and having a CFRM octane number of 78.5 was treated with 98% sulfuric acid at a temperature of 20° F. in the proportion of 18 lbs. of acid per barrel of naphtha. The treated naphtha was neutralized and steam distilled to produce a treated product having a CFRM octane number of 77.1. The treated product amounted to about 90% by volume of the raw naphtha charged to the acid treating step, and had an acid heat value (determined by method D481-39 ASTM) of 10° F. as compared with an acid heat of about 100° F. for the raw naphtha. The treated product was further characterized by having a gum content of not in excess of 7 mg. per 100 cc. gasoline (copper dish test).

Consequently, the constituents dissolved and removed in the acid consist mainly of olefins and are, therefore, suitable for alkylating isobutane to produce gasoline hydrocarbons. The absence of aromatic constituents from the hydrocarbon charge to such an alkylation operation is desirable because such aromatics, if present in the sulfuric acid alkylation reaction, cause an increase in the catalyst consumption. In addition they result, for the most part, in the formation of alkylated hydrocarbons boiling outside the range for gasoline.

The invention illustrated in Fig. 3 also provides a method for processing cracked hydrocarbon fractions containing aromatic constituents whereby aromatic constituents such as toluene can be segregated for other purposes in more concentrated form. For example, a low boiling cracked hydrocarbon fraction, containing C₆, C₈ and C₇ hydrocarbons including toluene, can be treated with concentrated acid at low temperature so as to absorb the olefinic constituents while leaving the aromatic and paraffinic constituents undissolved. The olefinic hydrocarbons can be reacted with isobutane in the presence of concentrated sulfuric acid under alkylating conditions to produce valuable gasoline hydrocarbons. The undissolved aromatic and other constituents can be extracted with a suitable solvent to separate the aromatics from the paraffins and naphthenes.

The process is applicable to the treatment of either low boiling or high boiling cracked naphtha containing olefinic and aromatic constituents or to the treatment of various fractions of such naphtha. Thus, the invention is applicable to the treatment of gasoline or naphtha produced in the thermal conversion of hydrocarbons, with or without catalysts, and also to the treatment of naphtha reformed either with or without catalysts, or to hydroformed naphtha. It is also applicable to the treatment of naphthas which are composed mainly of olefinic and paraffinic constituents.

In order to describe the invention in more detail reference will now be made to Fig. 1 of the accompanying drawings showing one method of flow suitable for carrying out the invention.

Referring to the drawing cracked naphtha such as produced in a conventional cracking operation is conducted from a source not shown through a pipe 1 to a stabilizer unit 2. The stabilizer is operated under conditions such as to remove from the naphtha normally gaseous hydrocarbons comprising C₄ and lighter hydrocarbons. Gaseous constituents such as methane and ethane are removed through a pipe 3 while a side stream comprising mainly C₃ and C₄ hydrocarbons is drawn off through a pipe 4. This fraction will comprise propylene, propane, butylenes, normal butane and isobutane. It is conducted all or in part to an alkylation unit 5.

In the alkylation unit the olefin constituents are reacted with isobutane in the presence of concentrated sulfuric acid whereby branched chain hydrocarbons are formed. Concentrated acid, namely, acid containing about 96 to 100% H₂SO₄ is introduced through a pipe 6 while additional isobutane may be introduced to the alkylation unit through a pipe 7.

The alkylation reaction may be effected under pressure and at a temperature of about 30 to 50° F. A substantial excess of isobutane over olefins is maintained, for example, a ratio of isobutane to olefins in the feed ranging about 5:1 to 15:1 or

higher. The proportion of acid is ordinarily about 1 part by volume or more to 1 part of hydrocarbon in the reaction system. The time of reaction may vary from about 10 minutes to 1 hour.

Spent acid of about 85 to 90% concentration is discharged from the alkylation unit through a pipe 8 while the hydrocarbons are conducted to a neutralization unit 9 wherein they are treated with caustic or other alkaline agent for the purpose of neutralizing and removing retained acid.

The used acid drawn off from pipe 8 may be conducted through a branch pipe 8a for use in the acid treatment of the stabilized naphtha and to which further reference will be made.

The alkaline sludge is drawn off through a pipe 10 while the neutralized hydrocarbons are conducted through a pipe 11 to a fractionation unit 12.

In the operation of the fractionation unit light gaseous materials are discharged through a pipe 13 while a side stream comprising isobutane is drawn off through a pipe 14. All or a portion of the isobutane produced from the fractionation unit may be recycled through a pipe 15 to the alkylation unit 5 previously referred to.

Alkylated hydrocarbons boiling within the range suitable for motor fuel are drawn off through a pipe 16 and all or a part conducted through a branch pipe 17 to a tank 18.

Higher boiling constituents contained in the alkylated hydrocarbons are withdrawn from the fractionation unit through a pipe 20 and if desired a portion of these higher boiling constituents may be recycled to the alkylation unit. These higher boiling constituents can also be used as a source of safety fuel.

Referring again to the stabilizer unit 2 the stabilizer cracked naphtha is drawn off through a pipe 25 and according to one mode of operation, conducted to preliminary acid treating unit 26, the purpose of which is to remove color- and gum-forming constituents such as diolefins.

In this preliminary acid treatment, for example, about 93% H_2SO_4 is introduced to the treating unit through a pipe 27. This acid may be introduced in the proportion of about 2 to 3 lbs. of acid per barrel of stabilized naphtha. The acid and naphtha are subjected to intimate mixing at about 60 to 90° F. as, for example, by means of a turbo-mixer during which the acid is in contact with the naphtha for a relatively short period of time, such as about 30 to 60 seconds. Separation of the acid and dissolved constituents from the treated naphtha may be effected by settling or by centrifugal means.

The acid treatment effected at this stage of the process is of relatively mild nature. Consequently, it may be desirable to employ even weaker acid, for example, acid of about 60 to 75% concentration, and effect the treatment at about room temperature or at higher temperatures up to about 150° F., for example.

The acid and dissolved hydrocarbon constituents are withdrawn and conducted through pipe 28 and discarded or disposed of in any desired manner.

This acid treated naphtha is advantageously conducted through a pipe 29 to a neutralization unit 30 wherein it is neutralized by contact with caustic solution or other alkaline agent. Caustic treatment effects removal of sulfur compounds whose presence in the olefin charge to alkylation reaction result in catalyst deterioration. Following neutralization it may be steam distilled in a still 31 in order to remove undesired high boiling constituents.

The steam distilled naphtha is passed through a pipe 32 to an acid treating unit 33. However, as indicated in the drawings the previously mentioned neutralizing and steam distilling steps may be omitted in which case the preliminarily acid treated naphtha is passed through a branch pipe 34 directly to the acid treating unit 33.

Concentrated acid of about 96 to 100% H_2SO_4 is introduced to the acid treating unit 33 through a pipe 35 from a source not shown. As in the case of the acid treating unit 26 the acid and naphtha are subjected to intimate contact as, for example, by passage through a turbo-mixer. The proportion of acid used will depend upon the amount of olefinic material it is desired to extract from the naphtha. Thus, the acid used may be in the proportion ranging from about 10 to 50 lbs. of acid per barrel of naphtha.

The treatment may be carried out at a temperature in the range of 10 to 60° F. but preferably at a temperature about 10 to 30° F., employing a time of contact between acid and naphtha of about 30 to 60 seconds.

The acid treated naphtha is conducted to a neutralizing unit 36 wherein it is subjected to contact with an alkaline material to produce a neutral product which is removed through a pipe 37. This product may be conducted all or in part by line 39 to the previously mentioned tank 18 wherein it may be blended with the gasoline hydrocarbons formed in the alkylation operation.

Where the raw naphtha feed is of such nature that the acid treated naphtha from the treater 33 is of lower antiknock value than desired it may be subjected to a thermal or catalytic reforming action, or may be supplied by line 40 to fractionating unit 41 and fractionally distilled and the higher boiling fraction or fractions thereof supplied by line 42 to reforming unit 43 and subjected to reforming. The reformed naphtha may then be conducted by line 44 to the fractionator 2 for treating as already described, and the light naphtha fraction passed by line 45 for blending in tank 18.

The acid mixed with the olefins extracted from the naphtha in the acid treating unit 33 is withdrawn through a pipe 38 and conducted to the previously mentioned alkylation unit 5.

The olefins extracted from the naphtha in the acid treating unit 33 will comprise hydrocarbons having from 5 to 11 carbon atoms per molecule and preferably comprising olefins having from 5 to about 9 carbon atoms per molecule.

It is contemplated that the olefins associated with the acid, probably in the form of esters, withdrawn through the pipe 38 may be extracted from the acid prior to introduction to the alkylation operation. By so doing a weak acid, for example, of about 60-90% H_2SO_4 may be employed to extract the olefins from the naphtha. Such extraction may be effected, for example, by treating the mixture of acid and absorbed olefins with a substantial quantity of isobutane under conditions such that the olefins are separated from the acid. The resulting mixture of isobutane and olefins is then passed to the alkylation reaction.

It is also contemplated that the mixture of olefins and acid drawn off from the acid treating unit 33 may be used to alkylate isobutane or other low boiling isoparaffin hydrocarbons either in the presence or absence of olefin hydrocarbons obtained from extraneous sources.

The olefins dissolved in acid and drawn through the pipe 38 may be polymerized and

removed from the acid. The olefins thus separated as polymers from the acid can be used to alkylate an isoparaffin hydrocarbon.

Fig. 2 discloses the unstabilized cracked naphtha feed to a fractionator 50 from which C₄ and lighter is passed overhead as a charge stock for alkylation, and the stabilized cracked naphtha bottoms are removed to a gum removal unit 51 where the naphtha is treated with weak acid in the manner previously described. The treated naphtha is then passed to a solvent unit 52 where it is extracted with a selective solvent for olefins and aromatics in the manner described above. The naphtha raffinate is separated by line 53 from the solvent extract, which latter is passed to the solvent separation unit 54 where the solvent is removed from the olefinic and aromatic hydrocarbons. The latter are then treated in the acid treating unit 55 with strong sulfuric acid under the conditions previously described to effect selective olefin removal, from which an aromatic hydrocarbon layer is separated and recovered.

The acid-olefin extract may be passed directly by line 56 to the alkylation unit 57, or passed by line 58 to the ester extraction unit 59 where the absorbed olefin is extracted from the acid by means of an isoparaffin such as isobutane as previously described. The resulting isoparaffin-olefin extract is then passed to the alkylation unit 57. The resulting alkylate produced in the alkylation unit, or a selected fraction thereof, is passed to the blending tank 60.

The naphtha raffinate from line 53 may be passed directly by line 61 to the reforming unit 62, or may be passed by line 63 to the fractional distillation unit 64 where it is separated into a light fraction that is passed by line 65 to the blending tank 60, and a heavy fraction that is passed by line 66 to the reforming unit 62. Products of the reforming operation are returned by line 67 to fractionator 50.

In accordance with the method of Fig. 3, the unstabilized cracked naphtha is stabilized in fractionator 70, the resulting stabilized cracked naphtha treated for gum removal in treater 71, and the treated naphtha then passed to acid treating unit 72. In the latter it is subjected to the action of strong sulfuric acid for selective olefin removal in the manner previously described, and the resulting acid-olefin extract is supplied to alkylation. The hydrocarbon layer containing paraffins, naphthenes, and aromatics passes to the solvent extraction unit 73 where it is treated with a selective solvent as previously described to recover an aromatic extract. The resulting naphtha raffinate, from which olefins and aromatics have been removed, then passes to the fractional distillation unit 74 from which a light naphtha fraction is removed overhead for blending with the alkylate. The heavy naphtha fraction removed as bottoms from fractionator 74 is then reformed in reforming unit 75, and the reformed products returned by line 76 to fractionator 70.

The alkylation reaction may be effected by means of catalysts other than concentrated sulfuric acid. As examples of such catalysts mention may be made of $\text{BF}_3 \cdot n\text{H}_2\text{O}$ where n has a value ranging from 1 to 1.5. Still other examples are liquid hydrogen fluoride; the metallic halides such as AlCl_3 used in conjunction with a hydrogen halide such as HCl ; chlorosulfonic acid, etc.

As already indicated an important object in

the alkylation step is to effect reaction of a normally gaseous isoparaffin with an olefin hydrocarbon in the presence of an alkylation catalyst maintained under alkylating conditions so as to form normally liquid branched chain hydrocarbons of high antiknock value. The alkylation step is generally similar to and may be carried out in a manner substantially similar to that disclosed in the Goldsby-Watson U. S. Patent No. 2,211,747.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. In the manufacture of motor fuel of high antiknock value the method which comprises treating naphtha containing olefinic and aromatic constituents with concentrated sulfuric acid of 96-100% strength at a temperature of about 10-60° F. and with short contact time such that olefin constituents of the naphtha coextensive in boiling range with aromatic constituents thereof are preferentially absorbed by the acid without any substantial absorption of the aromatic constituents, separating the acid and absorbed olefins from the naphtha, passing absorbed olefins substantially free from aromatics to an alkylation zone and subjecting the mixture therein to contact with a substantial molar excess of low-boiling isoparaffin in the presence of an alkylation catalyst maintained under alkylating conditions whereby branched chain gasoline hydrocarbons of high antiknock value are obtained.

2. In the manufacture of motor fuel of high antiknock value the method which comprises treating naphtha containing paraffinic, aromatic and olefinic constituents including gum-forming constituents under conditions to selectively remove therefrom said gum-forming constituents, thereafter treating the naphtha with concentrated sulfuric acid of 96-100% strength at a temperature of about 10-60° F. and with short contact time such that olefinic constituents coextensive in boiling range with aromatic constituents thereof are preferentially absorbed in the acid without any substantial absorption of the aromatic constituents, removing the acid and absorbed olefinic constituents substantially free from aromatic constituents, passing absorbed olefinic constituents to an alkylation zone and reacting said constituents with isobutane in the presence of an alkylation catalyst maintained under alkylating conditions whereby branched chain gasoline hydrocarbons of high antiknock value are obtained.

3. The method of manufacturing gasoline of high anti-knock value from unstabilized naphtha containing normally gaseous and normally liquid hydrocarbons including olefins and aromatics, which comprises fractionating said unstabilized naphtha to separate a normally gaseous fraction containing C₄ olefins from a stabilized normally liquid naphtha fraction containing higher molecular weight olefins and aromatics, treating said normally liquid naphtha fraction to remove gum-forming constituents, then treating the resulting naphtha with sulfuric acid of 96-100% strength at a temperature of about 10-60° F. and with short contact time to selectively absorb higher molecular weight olefins coextensive in boiling range with aromatic constituents with-

out any substantial absorption of said aromatics, separating said acid with absorbed olefins from the stabilized and treated naphtha, and reacting both olefins of said normally gaseous fraction and absorbed olefin products from said stabilized naphtha fraction with low-boiling isoparaffins in the presence of an alkylation catalyst under alkylating conditions, whereby an alkylate of saturated branched chain hydrocarbons boiling within the gasoline range and of high anti-knock value is obtained.

4. The method according to claim 3, wherein at least a portion of the stabilized and treated naphtha fraction is subjected to a reforming operation, and products of reforming are returned to the said unstabilized naphtha fractionation step.

5. The method according to claim 3, wherein the stabilized and treated naphtha fraction is distilled to separate a lower boiling fraction from a higher boiling fraction thereof, the higher boiling fraction is subjected to a reforming operation, products of reforming are returned to the unstabilized naphtha fractionation step, and the lower boiling fraction is blended with the said alkylate.

6. In the manufacture of motor fuel from naphtha containing substantial proportions of olefinic and aromatic constituents, the method which comprises subjecting the naphtha to intimate and short contact with concentrated sulfuric acid of 96-100% strength at temperatures of about 10-60° F., whereby olefinic constituents coextensive in boiling range with aromatic constituents are selectively absorbed without any substantial absorption of the aromatic constituents, separating the said acid with absorbed olefins from the remaining naphtha alkylating an isoparaffin with absorbed olefins in the presence of an alkylation catalyst under alkylating conditions to produce alkylate gasoline of high anti-knock value, extracting the remaining naphtha with a solvent selective for aromatic constituents to thereby recover an aromatic extract from which aromatic constituents can be segregated in concentrated form, reforming at least a portion of said naphtha from which the said olefinic and aromatic constituents have been removed and returning reformed products to the olefin absorption step.

7. The method according to claim 6, wherein the naphtha is pretreated under mild conditions effective to remove gum-forming constituents prior to the said olefin absorption step.

8. The method of manufacturing gasoline of high anti-knock value from an unstabilized naphtha containing normally gaseous and normally liquid hydrocarbons including olefins and aromatics, which comprises fractionating said unstabilized naphtha to separate a normally gaseous fraction containing C₄ olefins from a stabilized normally liquid naphtha fraction containing higher molecular weight olefins and aromatics, treating said normally liquid naphtha fraction with acid under conditions to selectively absorb the higher molecular weight olefins coextensive in boiling range with aromatic constituents without any substantial absorption of said aromatics, separating the acid with absorbed olefins from the stabilized naphtha, then treating said stabilized naphtha with a solvent selective for aromatics, and separating a solvent extract of aromatic constituents from the remaining naphtha, reforming at least a portion of the remaining naphtha, passing products of said re-

forming step to the said unstabilized naphtha fractionation step, and reacting both olefins of said normally gaseous fraction and absorbed olefin products from said stabilized naphtha fraction with low-boiling isoparaffins in the presence of an alkylation catalyst under alkylating conditions, whereby saturated branched chain hydrocarbons boiling within the gasoline range and of high anti-knock value are obtained.

9. The method of manufacturing gasoline of high anti-knock value from an unstabilized naphtha containing normally gaseous and normally liquid hydrocarbons including olefins and aromatics, which comprises fractionating said unstabilized naphtha to separate a normally gaseous fraction containing C₄ olefins from a stabilized normally liquid naphtha fraction containing higher molecular weight olefins and aromatics, treating said stabilized normally liquid naphtha fraction to remove and separately recover olefinic compounds and aromatic constituents therefrom which are coextensive in boiling range, reforming at least a portion of the stabilized and treated naphtha from which the said olefins and aromatics have been removed, passing products of reforming to the said unstabilized naphtha fractionation step, and reacting both olefins of said normally gaseous fraction and olefinic compounds from said stabilized normally liquid naphtha fraction with low-boiling isoparaffins in the presence of an alkylation catalyst under alkylating conditions, whereby saturated branched chain hydrocarbons boiling within the gasoline range and of high anti-knock value are obtained.

10. In the manufacture of motor fuel from naphtha containing normally liquid olefinic, aromatic and paraffinic hydrocarbon constituents of coextensive boiling range, the method which comprises treating said naphtha to remove and separately recover normally liquid olefinic and aromatic constituents thereof including the step of extracting said olefinic constituents in the presence of said aromatic constituents with concentrated sulfuric acid of 96-100% strength at a temperature of about 10-60° F. and with short contact time such that normally liquid olefinic constituents are preferentially absorbed in the acid without any substantial absorption of aromatic constituents, separating the acid containing absorbed normally liquid olefins, and alkylating a low-boiling isoparaffin with said absorbed olefins substantially free from aromatics in the presence of an alkylation catalyst under alkylating conditions, whereby branched chain gasoline hydrocarbons of high anti-knock value are obtained.

11. The method of manufacturing a high anti-knock gasoline from naphtha containing olefins, aromatics and paraffins of coextensive boiling range while at the same time reducing the unsaturation of the naphtha and recovering an aromatic concentrate therefrom, which comprises extracting the cracked naphtha with a solvent selective for aromatic and olefinic constituents, separating a solvent extract containing olefins and aromatics from a naphtha raffinate containing the paraffins and of reduced unsaturation, removing the solvent from the extract, then treating the extract with 96-100% H₂SO₄ at a temperature of about 10-60° F. and with short contact time to selectively absorb olefins in the acid without any substantial absorption of aromatics, separating an aromatic concentrate from the acid extract, and then

alkylating an isoparaffin with absorbed olefins substantially free from aromatics in the presence of an alkylation catalyst under alkylating conditions to produce high anti-knock alkylate gasoline.

12. The method according to claim 11, wherein the said extract containing olefinic and aromatic constituents is treated under mild conditions to remove gum-forming constituents prior to the said acid-olefin absorption step.

13. The method according to claim 11, wherein the alkylate gasoline is blended with at least a portion of the said naphtha raffinate.

14. The method according to claim 11, wherein the naphtha raffinate is separated into lower boiling and higher boiling fractions, the low boiling fraction is blended with the alkylate, and the higher boiling fraction is reformed and liquid products of the reforming are returned to the solvent treating step.

15. The method which comprises fractionating cracked naphtha to separate a liquid naphtha

fraction containing olefins, treating the said naphtha fraction to remove gum-forming constituents, selectively extracting olefin constituents from said treated naphtha to provide a charge for catalytic alkylation, reforming at least a portion of the treated naphtha from which olefinic constituents have been extracted, returning products of the reforming operation to the cracked naphtha fractionating step, and alkylating an isoparaffin with the extracted olefins in the presence of an alkylation catalyst under alkylating conditions to produce a saturated alkylate gasoline of high anti-knock value.

16. The method according to claim 15, wherein the treated naphtha from which the olefinic constituents have been extracted is distilled to separate it into lower boiling and higher boiling fractions, passing the higher boiling fraction to the said reforming operation, and blending the lower boiling fraction with the said alkylate.

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