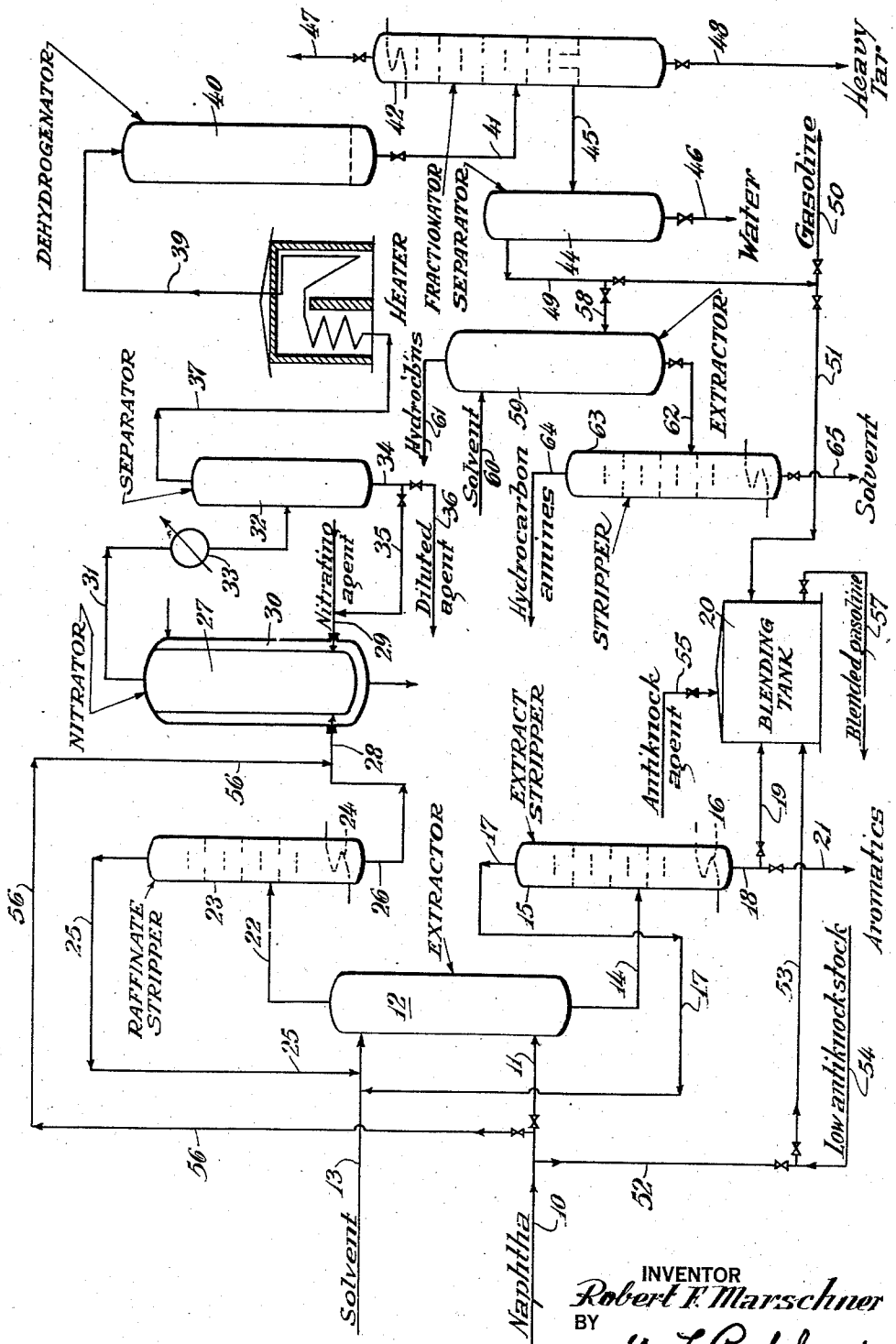
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HYDROCARBON CONVERSION

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HYDROCARBON CONVERSION

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This invention relates to an improved process for the conversion of hydrocarbon materials into motor fuels characterized by high octane numbers. More particularly, it relates to an improved process for the production of high octane number gasoline containing hydrocarbon amines produced in situ. The invention also relates to an improved process for producing aromatic amines, such as aniline, from the saturated cyclic hydrocarbons present in petroleum naphthas.

It is an object of this invention to provide an improved process for the conversion of hydrocarbons into high octane number gasolines. Another object is to provide a process whereby a low octane number hydrocarbon feed stock containing naphthenes is converted into a high antiknock gasoline. It is a still further object of my invention to provide a method and means for nitrating hydrocarbon feed stock and converting nitro hydrocarbons into hydrocarbon amines simultaneously with dehydrogenation of the hydrocarbon material. Another object of this invention is to provide a process for the conversion of saturated cyclic hydrocarbons into aromatic amines. Other objects and advantages will become apparent as the description of this invention proceeds.

I have discovered that nitrated naphtha need not contain aromatic hydrocarbons in order to produce aromatic amines in a subsequent reducing step. In brief, the present application is concerned with a process in which saturated cyclic hydrocarbons present in petroleum naphthas, and particularly cyclohexane and its homologues are converted to aromatic amines. The cyclic hydrocarbons are nitrated, and the nitrated product is then subjected to dehydrogenation, preferably catalytic, so that the hydrogen produced in the dehydrogenation step is utilized in situ to reduce the nitro-hydrocarbons to hydrocarbon amines.

When naphtha is treated with nitric acid in the vapor phase, water and nitro-hydrocarbons (such as nitrocyclohexane) result. After separating the nitrocyclohexane and its homologues from the water and small amounts of higher and lower-boiling by-products, probably dinitrated cyclohexanes and oxidation products, it is passed over a catalyst of the dehydrogenation type. The reaction product from this step, after the removal of unreacted hydrocarbons and the separation of the water produced, consists mainly of aniline and its homologues. Detectable amounts of other products such as benzene, phenol, diphenylamine and unidentified substances are often also formed. While such products are valuable chemical compounds, it is desired to obtain as large a yield of aniline and hence as little of these various other products as possible. The aniline is useful in raising the octane number of naphthas and because of its relatively high boiling point (363° F.) is particularly valuable in increasing the octane number of the heavier fractions of the naphtha, such as those boiling between 320 and 392° F., which usually show a low octane number, sometimes below zero. In effect, the present process converts cyclohexane which is present in the lighter high-octane number fractions to aniline which markedly raises the octane number of the heavier low-octane number fractions. Use of higher cyclohexane hydrocarbons such as those containing 9 to 11 carbon atoms tend to give aromatic amines which boil above the gasoline range.

Because of their large antiknock effect, permissible quantities of aromatic amines are desirable in ordinary gasoline, but it is also contemplated to remove the gasoline by distillation and to add the residual amine mixture to a naphtha having an initial boiling point of 350° F. or to a synthetic hydrocarbon mixture to produce a very high octane number safety fuel.

In employing my process to increase the octane number of a typical motor fuel, the simple process of nitrating and dehydrogenating a naphtha without intermediate distillation or final close fractionation is permissible. Because the feed need not contain aromatic hydrocarbons, a wide variety of poor octane number stocks may be charged.

The accompanying drawing is a flow diagram which illustrates schematically one method for carrying out my process.

Referring now to the drawing, a naphtha feed stock enters through line 10. A suitable hydrocarbon feed stock may be obtained by the distillation of crude oils to obtain a cut boiling between 100° F. and 300° F. These are ordinarily referred to as "straight-run" or "virgin" naphthas and will contain varying amounts of paraffins, aromatics and naphthenes. Since the aromatic constituents possess a high octane number and a high blending value when mixed with hydrocarbon mixture of low antiknock characteristics, it is desirable to carry out the process on an aromatic-free stock. Moreover, I prefer to use a naphthene-rich naphtha such as the naphthas from Coastal, South American or

European crudes and from certain Mid-Continent crudes.

In order to remove the greater part of the aromatics which may be present the naphtha from line 10 is directed through valved line 11 to a solvent extraction tower 12 wherein it is contacted with a solvent having an affinity for the aromatic hydrocarbons. Suitable solvents include sulfur dioxide, furfural, aluminum chloride-hydrocarbon complex, etc. For purposes of illustration the process will be described relative to a sulfur dioxide extraction process. The solvent enters through line 13 and is thoroughly mixed with the naphtha. The extract containing the major portion of the sulfur dioxide plus the aromatics and olefins is withdrawn through line 14 and directed to extract stripper 15. Heating means 16 in stripper 15 serve to separate the solvent from the dissolved hydrocarbons, the sulfur dioxide passing overhead through line 17 which rejoins line 13 for recycling of the solvent. The hydrocarbons are withdrawn through line 18 and may be directed through valved line 19 to blending tank 20 or may be withdrawn from the system through valved line 21.

The aromatic-free naphtha plus some solvent passes overhead through line 22 to raffinate stripper 23. Heating means 24 therein aids in stripping the sulfur dioxide from the naphtha, the solvent passing overhead through line 24 and returning to the solvent extraction system through line 13. The aromatic-free naphtha is withdrawn through line 26 and directed to a nitration reactor 27 through line 28. A nitrating agent is added to nitrator 27 through line 29.

In nitrator 27 the hydrocarbon feed stock is incompletely converted into nitro-hydrocarbons. Traces of aromatic hydrocarbons, if present, will usually nitrate completely. Since there are preferably large amounts of naphthenes present these will nitrate in preference to the paraffinic hydrocarbons. The nitration can be carried out in any one of a number of different ways. For example, a mixture of concentrated sulfuric acid and concentrated nitric acid may be employed, the temperature being maintained sufficiently low, as by means of cooling jacket 30, to avoid the formation of dinitro compounds or oxidation products. Nitration may also be carried out by means of aluminum nitrate or ferric nitrate. It is preferable, however, to carry out the reaction in the vapor phase with nitric acid alone, since the higher temperature employed appears to give a more selective nitration of naphthenes.

The reactor may consist of a simple coil or of a packed vessel, but in any event is mounted in a bath or other suitable device which not only may be maintained at the desired temperature, but also serves to absorb heat from the exothermic nitration reaction. The packing may consist of any suitable inert material, such as that of which the container is constructed, but preferably in finely divided, granular, porous, acicular or spatulate form. This serves the multiple purpose of creating turbulent flow, providing an increased adsorptive surface, and assisting in maintaining temperature control. The particular manner of nitrating the hydrocarbon material is not essential to my invention, any known means for accomplishing this result may be used. For example, nitration can be carried out according to the method of Hopkins in U. S. Patent 1,558,027 in which aluminum nitrate and nitric acid act as the nitrating agents, the reaction being carried out at approximately 265° to about 300° F.

The nitrated hydrocarbons plus excess hydrocarbons pass overhead through line 31 to separator 32. A condenser 33 may be interposed in line 31 to reduce the temperature of the reactants prior to separation. In separator 32 water separates from the solution of nitro-hydrocarbons and excess hydrocarbons, and may be withdrawn through line 34. At high rates of flow through the reactor, some of the nitric acid may remain unchanged, and it may be desirable to recycle the mixture together with the water formed to nitrators 27 through valved line 35 which joins line 29. If the nitrating agent has been diluted by the formation of too great an amount of water, it may be withdrawn through valved line 36 and reconcentrated or discarded as desired. Partially nitrated naphtha may also be recycled through the nitrator (by means not shown), but because this usually leads to the formation of undesirable oxidation products this method of operation is often not desirable.

The solution of nitro-hydrocarbons in naphtha pass overhead from separator 37 and is heated in furnace 38. The heated hydrocarbons leave furnace 38 through line 39 and are directed to dehydrogenator 40. The dehydrogenation is carried out preferably by catalytic means. The catalyst may comprise metallic chromites, particularly magnesium chromite, chromium oxide gels, mixtures of aluminum oxide and chromium oxide, chromic oxide supported upon preformed alumina, supported molybdenum oxide, ceria, and vanadia. Tungstic oxide and urania are also satisfactory catalysts when supported in relatively small amounts upon alumina and other supports.

The nitrated hydrocarbons are contacted with the catalyst at a temperature of about 750 to 900° F. and preferably at about 850° F. at low pressure, i. e., atmospheric to about 50 pounds per square inch with a space velocity of about 0.5 to 3 volumes (liquid basis) preferably about 1 volume, of nitrated naphtha per volume of catalyst space per hour. The catalyst may be employed in fixed beds, in movable beds or as a powder suspended in the gaseous stream, the conversion in all cases being in the vapor phase.

In dehydrogenator 40, cyclohexanes are converted to aromatics and some olefins are produced by dehydrogenation of paraffins and cyclopentanes, the hydrogen evolved acting as a reducing agent for the conversion of the nitro-hydrocarbons to amines. Simultaneously, dehydrogenation of the nitrated hydrocarbons takes place yielding a mixture of aniline and alkyl anilines together with other compounds which probably include aliphatic amines. The converted hydrocarbons and nitro-hydrocarbons are withdrawn through line 41 and directed to fractionator 42 through valved line 43. Water can either be removed in a separator before fractionator 42, or from a separator 44 in line 45.

In fractionator 42 the hydrocarbons and hydrocarbon amines of the desired boiling range are withdrawn through line 45. The hydrogen and normally gaseous hydrocarbons are taken overhead through line 47 and the hydrocarbons heavier than those desired for gasoline or blending purposes are withdrawn through line 48.

Water is separated from the product in separator 44 and withdrawn through line 46, the hydrocarbons and hydrocarbon amines being withdrawn through line 49. The octane number of the gasoline withdrawn through line 49 will depend to a large degree on the extent of the nitration of the hydrocarbon feed stock.

Aniline or its derivatives which will constitute one of the chief constituents of the dehydrogenation product is well known to have an antiknock effect similar to that exhibited by such well known antidetonants as tetraethyl lead but is often more desirable than tetraethyl lead in that there is less harmful effect from the addition of large quantities. If the nitration has been carried out to the extent that the resulting product has an octane number in the general range found desirable for gasolines the product may be withdrawn through valved line 50 and used as such for gasoline. If the nitration has been carried to such an extent that the product has an octane number much above that found successful for commercial gasolines, it may be withdrawn through valved line 51 and directed to blending tank 20 wherein it may be blended with a low antiknock stock, such as, for example, another portion of the original stock used. This may be added to blending tank 20 through valved line 52 which joins line 53. A low antiknock stock from extraneous sources may be added to line 53 through line 54. It is also possible to add through line 55 tetraethyl lead or other antiknock agent in order to increase further the octane number of the low octane stock, the amount of tetraethyl lead in the stock conforming to customary optimum concentrations. As an advantage of the present process it may be noted that the effect of aniline upon sensitive fuels such as cracked gasoline containing olefins or extracts containing aromatics does not depreciate to as great a degree as does that of tetraethyl lead. The blended gasoline can be withdrawn through line 57.

I contemplate the removal of aniline and its homologues from the product when the feed contains a large portion of cyclohexane hydrocarbons and homologues thereof. This is readily accomplished by a variety of methods. For example, they may be extracted with an aqueous solution of an acid such as hydrochloric acid, or with an inert solvent such as ammonia, or with organic solvents such as phenol. The extract may be then fractionated to give pure aniline, toluidine, xylidene, etc., which may be employed as dye intermediates, etc. For example, the mixture of hydrocarbons and hydrocarbon amines may be directed from line 49 through valved line 58 to extractor 59. A suitable solvent is added through line 60 and the unconverted hydrocarbons withdrawn overhead through line 61. If necessary, the product from line 61 may be purified by water washing, etc. by means not shown, to remove traces of solvent. The solvent containing the hydrocarbon amines is withdrawn through line 62 and directed to fractionator 63 wherein the solvent and the hydrocarbon amines are separated, the solvent free amines being withdrawn through line 64 for use in blending or as a dye intermediate, etc. The solvent is withdrawn through line 65, and discarded or returned to extractor 59.

I also contemplate nitration of relatively pure cyclohexane, or the nitration of mixtures containing cyclohexane, and isolating relatively pure nitrocyclohexane, subsequently dehydrogenating the product to aniline. Similarly, homologues of cyclohexane, after such a process, will give homologues of aniline.

Although I have illustrated the solvent extraction of aromatics from the feed stock it is quite possible that the amount of aromatics in the hydrocarbon mixture is sufficiently low so that the solvent extraction step becomes economically undesirable. In this event, the naphtha will be added directly to line 28 from line 10 through valved line 56. Aromatics present in the feed stock will also be nitrated in nitrator 27 and reduced to aniline and alkyl anilines by the hydrogen formed in dehydrogenator 40 to form desirable antiknock hydrocarbons. However, I do not in general desire to subject the aromatic constituents of the hydrocarbon feed stock to my process since they themselves are valuable for their high antiknock qualities. Moreover, the aromatic hydrocarbons nitrate in preference to the cycloparaffins and the paraffinic stocks so that in order to convert these latter hydrocarbons it is necessary to carry out the nitration to a much greater extent than would otherwise be necessary. Generally speaking, the aromatics have a very much higher octane number rating and a much higher blending octane number than the corresponding cyclo-paraffins; therefore, it is my desire to increase the octane number of the cycloparaffins and omit, if possible, the conversion of the aromatics. The aromatics as has been pointed out, may be blended with the converted hydrocarbons or may be utilized for purposes other than motor fuels such as, for instance, high solvency naphthas, the formation of dyestuffs, etc. By my process a hydrocarbon feed stock of low octane number may be converted to a high octane number motor fuel or may be converted to a blending stock for increasing the octane number of an overall mixture of unconverted low octane number stock and the dehydrogenation product.

My process is particularly advantageous in that by utilizing in situ the hydrogen formed during the dehydrogenation process an active hydrogen for reducing nitrohydrocarbons to amines is immediately available and, at the same time, the formation of additional unsaturated hydrocarbons is promoted by the removal of hydrogen from the process. Under ordinary circumstances the dehydrogenation of saturated hydrocarbons is limited by the amount of hydrogen present since under the conditions of operation it is possible also to hydrogenate the unsaturated hydrocarbons formed, in a reversible reaction, and an equilibrium is set up. By removing the hydrogen through the formation of hydrocarbon amines from nitro-hydrocarbons the saturated-unsaturated hydrocarbon equilibrium is thrown in the direction of greater amounts of unsaturated hydrocarbons. The unsaturated content and thus the octane number due to hydrocarbons alone is consequently appreciably increased, while in addition, the formation of an antidetonating agent is carried out in situ.

I claim:

1. A process for the production of a high antiknock fuel from a low antiknock fuel containing a substantial amount of naphthenic hydrocarbons which comprises nitrating at least a portion of the naphthenic hydrocarbons in said low antiknock fuel and subjecting the product from said nitration to catalytic dehydrogenation to reduce the naphthenic hydrocarbons to aromatic amines in an amount sufficient to increase substantially the antiknock value of said low antiknock fuel.

2. A process for the production of a high antiknock motor fuel from a low antiknock motor fuel containing a substantial amount of naphthenic hydrocarbons which comprises nitrating at least a portion of said naphthenic hydrocarbons in said low antiknock motor fuel to form nitro-naphthenes, catalytically dehydrogenating the unnitrated hydrocarbons in said low anti-

knock motor fuel and simultaneously subjecting said nitro-naphthenes to said catalytic dehydrogenation to reduce the nitro-naphthenes to aromatic amines in an amount sufficient to increase substantially the antiknock value of said low antiknock motor fuel.

3. A process for the production of a high antiknock motor fuel comprising, nitrating a naphtha containing a substantial amount of naphthenic hydrocarbons, said naphtha being substantially free of aromatic hydrocarbons, and catalytically dehydrogenating said nitrated naphtha to reduce the nitro-hydrocarbons to organic amines in an amount sufficient to increase substantially the antiknock value of said naphtha.

4. A process for the production of a high antiknock motor fuel comprising, subjecting a substantially aromatic-free naphtha containing cyclohexane to nitration, and dehydrogenating said nitrated naphtha while simultaneously converting said nitrated naphtha to organic amines in an amount sufficient to increase substantially the antiknock value of said aromatic-free naphtha.

5. In a process for the production of a high antiknock motor fuel, the steps comprising removing substantially all aromatic hydrocarbons from a petroleum naphtha containing a substantial amount of saturated cyclic hydrocarbons, nitrating said cyclic hydrocarbons contained in aromatic-free naphtha to form nitro-hydrocarbons, and subjecting said aromatic-free naphtha containing said nitro-hydrocarbons to catalytic dehydrogenation wherein aromatic amines are formed in an amount sufficient to increase substantially the antiknock value of said petroleum naphtha.

6. In a process for the production of a high antiknock motor fuel, the steps comprising removing substantially all aromatic hydrocarbons from a petroleum naphtha containing a substantial amount of saturated cyclic hydrocarbons, nitrating said saturated cyclic hydrocarbons in said aromatic-free naphtha to form nitro-hydrocarbons, subjecting said aromatic-free naphtha containing said nitro-hydrocarbons to catalytic dehydrogenation whereby aromatic amines are formed in an amount sufficient to increase substantially the antiknock value of said petroleum naphtha and blending said naphtha containing aromatic amines with a low octane number naphtha.

7. In a process for the production of a high antiknock motor fuel, the steps comprising removing substantially all aromatic hydrocarbons from a petroleum naphtha containing a substantial amount of saturated cyclic hydrocarbons, nitrating said saturated cyclic hydrocarbons and said aromatic-free naphtha to form nitro-hydrocarbons, subjecting said aromatic-free naphtha containing said nitro-hydrocarbons to a catalytic dehydrogenation wherein aromatic amines are formed in substantial amounts, separating said aromatic amines from said naphtha, and blending said aromatic amines with a low antiknock gasoline to increase the octane number thereof.

8. In a process for the production of high antiknock motor fuels, the steps comprising removing substantially all aromatic hydrocarbons from a light petroleum naphtha containing a substantial amount of saturated cyclic hydrocarbons, nitrating said saturated cyclic hydrocarbons and aromatic-free naphtha to form nitro-hydrocarbons, subjecting said aromatic-free naphtha containing said nitro-hydrocarbons to catalytic dehydrogenation wherein aromatic amines are formed, separating said aromatic amines from said naphtha, and blending said aromatic amines with a heavy low antiknock gasoline to form a safety aviation fuel of high octane number.

9. In a process for the production of a high antiknock motor fuel, the steps comprising removing substantially all aromatic hydrocarbons from a petroleum naphtha containing a substantial amount of saturated cyclic hydrocarbons, nitrating said cyclic hydrocarbons contained in said aromatic-free naphtha to form nitro-hydrocarbons, subjecting said aromatic-free naphtha containing said nitro-hydrocarbons to catalytic dehydrogenation wherein aromatic amines are formed in an amount sufficient to increase substantially the antiknock value of said petroleum naphtha, and blending said removed aromatic hydrocarbons with said petroleum naphtha of increased antiknock value to form an improved motor fuel.

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