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POLYFURCOUS FUEL

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4 Claims. (Cl. 44—9)

This invention relates to motor fuels for internal combustion engines and particularly to automotive gasoline fuels adapted to ignite adequately at relatively low engine temperatures. It involves the treatment of hydrocarbons of the gasoline type and related fuels to confer inexpensively thereon improved ignition qualities and reduced knocking tendencies. It also involves the regulated and controlled addition to such fuels of polyfurcous acetals, suitable polyfurcous esters, and, in general, polyfurcous products from the condensation of suitable alcohols and oxidation derivatives of alcohols, namely, ketones, aldehydes, and acids.

This application is a continuation-in-part of my application Serial No. 4,301, filed January 31, 1935, issued as Patent No. 2,143,870 on January 17, 1939, and relates more particularly to the improvement of motor fuels by the addition of suitable polyfurcous esters and related compounds containing two or more oxygen atoms per molecule and containing at least one oxygen atom in a carbonyl group.

In an internal combustion engine, ignition of gasoline, or other motor fuel, takes place under a pressure considerably greater than atmospheric pressure, say 75 to 100 pounds per square inch. Under such pressures, the air or other oxygen-containing supporter of combustion apparently exerts a different degree of selectivity than at atmospheric pressure.

In the starting of cold engines, or when the engine is run at low temperatures, for example an airplane motor at high altitudes, vaporization of the fuel under engine pressures may not take place sufficiently rapidly to allow smooth and sustained combustion of the fuel. These ignition difficulties may be eliminated, or to a large degree palliated and counteracted, by the utilization of selective priming compounds, including those of petroleum origin or "self-made," which are intended to become extremely flammable or ignitible at engine pressures thereby resulting in the easy ignition of the compressed fuel vapors. Such selective priming compounds although conferring upon gasoline, or other motor fuels, an increased ignitibility at engine pressures do not necessarily render the fuel more ignitible at atmospheric pressure and, therefore, the fire-hazard connected with the use and handling of a motor fuel of such increased ignitibility should not be greater than that ordinarily encountered under similar conditions with a normal motor fuel, e. g., gasoline.

One method whereby I obtain ignition temperature depressants is by treating the fuel with a nitrating agent. Nitration may be carried out at room temperature, or at slightly higher temperatures. Nitration can be effected by treating the motor fuel with higher oxides of nitrogen, in which case the oxides in gaseous form are passed into the fuel which may be mechanically agitated. Oxides of nitrogen may be prepared, for example, by the action of sulphuric acid on sodium or potassium nitrite, by the action of nitric acid on copper, by the passage of air (i. e., a gas containing both oxygen and nitrogen) through an electric arc, by the catalytic oxidation of ammonia, or by any other convenient method. Preferably a small proportion of air, or of other oxygen-containing gas, is mixed with the oxides of nitrogen before passing into the fuel. In some instances dilute nitric acid is employed for nitration. For example, in some cases a fuel may be nitrated by warming and thoroughly agitating 100 volumes thereof with 5 volumes of nitric acid of specific gravity 1.05. After nitration, any acidic or corrosive compounds present in the motor fuel may be removed by washing the treated fuel with water or a dilute solution of caustic soda or other water-soluble alkali, or by any other appropriate means.

It is desirable in the nitrating operation that vigorous oxidation or other undesirable reactions resulting in the formation of sludge be avoided as far as possible. For this reason the proportion of nitrating agent and the temperature of nitration will vary with different fuels.

Substances included in the term nitro compounds are not only those in which a nitro, or NO_2, group is infixed or implanted in the moleclule, and which are often produced by the action of nitric acid and sulphuric acid on paraffinic or cyclic hydrocarbons, but also such nitrogen-containing compounds as nitrosites and nitrosates. The former type (nitrosites) are compounds formed by the interaction of nitrogen trioxide and olefins, while the latter (nitrosates) are the result of the reaction between olefins and nitrogen tetroxide. The olefins are either acyclic or cyclic. In some instances nitric acid reacts directly with certain types of unsaturated hydrocarbons forming addition products of the nitro type. All such compounds, containing these various nitrogen-oxygen groupings, when present in the fuel, may serve alone or with addition of other selective primers to depress ignition temperature sufficiently.

In making motor fuel of improved ignitibility

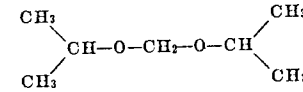
is preferable in many cases to treat only a portion of the fuel and then add this treated portion to the main body of the fuel. For instance, ordinary gasoline is a mixture of various hydrocarbons whose boiling ranges extend from, say, 60° to 400° F., or thereabouts. Such a fuel may be separated, for example, by distillation into two fractions boiling, say between 60° and 175° F. and 175° and 400° F. The latter, or higher boiling, fraction may be nitrated by any of the foregoing procedures, and then blended with the lower fraction to furnish a motor fuel of the proper boiling range.

Any light mineral oil distillate which can be used as a gasoline type of motor fuel may be nitrated and the distillate so treated employed in the preparation of motor fuel. By the term mineral oil is meant petroleum oil, rock-oil, shale-oil, and the like.

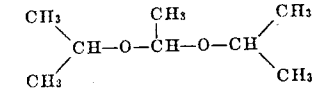
While the nitrated higher boiling fuels having high flash points thus obtained are particularly suitable for addition as such to motor fuels used in high compression engines, for example, engines having a compression ratio above 8 to 1, the lower boiling nitro compounds may be advantageously modified in accordance with this invention to obtain oxygen-containing polyfurcous compounds of the high anti-knock type particularly adapted for improving fuels used in spark ignition engines having compression ratios of about 5 to 1 to about 8 to 1, e. g., Otto cycle types engines and semi-Diesel type engines.

The procedure whereby I may obtain a fuel of improved ignitibility and anti-knock qualities, particularly in lower compression and spark ignition engines includes the addition of oxygenated hydrocarbons, particularly those oxygenated hydrocarbons which contain polyfurcous structures. Such compounds embrace acetals of secondary and tertiary alcohols, esters of these alcohols with alkyl substituted organic acids, and polyfurcous ketones. An example of an acetal is diisopropyl formal made from formaldehyde (or trioxymethylene) and isopropyl alcohol. Examples of the esters are tertiary butyl ester of trimethyl-acetic acid, isopropyl isobutyrate, isopropyl isovalerate, and the like. Substituted acetals, such as acetone-diethyl-acetal, which is derived from acetone and ethyl alcohol, may be employed also. Addition of such compounds, possibly because of the presence therein of one or more oxygen atoms per molecule, not only assists in increasing the ignitibility or flammability of the fuel under engine operating conditions, but also because of their polyfurcous structures, which is associated with the property of anti-knocking, maintain or improve the anti-detonating qualities of the motor fuel. Thus, by incorporating one or more oxygenated hydrocarbons of the above-mentioned types with the fuel there results, on the one hand, an increase in ignitibility of the fuel, and, on the other hand, a decrease in its tendency to knock during combustion in the engine. Substances which exhibit simultaneously these dual properties are designated anti-knock-igniters.

As an oxygenated anti-knock-igniter I prefer to use a compound which contains at least three carbon atoms in its molecular trunk or stem and which possesses bifurcous terminals. By stem or trunk is meant those atoms which may be represented as joined together in a straight line. Branching is considered as consisting of at least two radicals, e. g., two methyl groups, attached to one carbon atom. On the other hand, a radical and an element (say, a methyl group and a hydrogen atom) attached to a carbon atom is not considered as branching. For example, diisopropyl formal

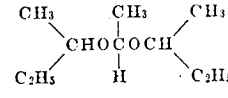


contains a trunk of five units, three carbon-hydrogen and two oxygen (indicated by the dotted lines), and two bifurcous branches. Diisopropyl acetal



also contains a five unit trunk, and two bifurcous branches. Such oxygenated compounds containing two or more bifurcous terminals, or one or more trifurcous terminals (e. g., a tertiary butyl group), are termed polyfurcous compounds. A motor fuel containing anti-knock-igniters of the polyfurcous type are called polyfurcous fuels.

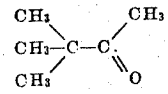
Preferably I select as anti-knock igniters those oxygenated compounds which may or may not be asymmetric with respect to side chains or branches, in order to secure a maximum degree of ignition-temperature depression, quick pick-up, and knock reduction. In so far as possible I desire to make such anti-knock-igniters from hydrocarbons present in crude petroleum or its distillates, or which are procured as by-products from various refinery operations, such as distillation, cracking, hydrogenation, etc. To illustrate, the cracking gases obtained during cracking of high-boiling petroleum distillates contain a substantial proportion of olefin hydrocarbons, e. g., ethylene, propylene, and butylenes. A part of these gases can be submitted to pyrolytic treatment under suitable conditions, such as passage through the electric arc, to furnish a good proportion of acetylene. Catalytic hydration of acetylene furnishes acetaldehyde. Another part of the olefin-containing gas is treated with sulphuric acid to give alkyl sulphuric acid esters, which on hydrolysis and distillation yield secondary and tertiary alcohols, e. g., isopropyl and tertiary butyl alcohols. Similarly, secondary and tertiary amyl and hexyl alcohols can be made from the low-boiling condensate separated from cracking gases by compression and/or absorption processes. Acetaldehyde can be condensed, for example, with secondary butyl alcohol, in the presence of a catalyst, such as hydrogen chloride or phosphine, to give the anti-knock-igniter, acetaldehyde-di-sec-butyl acetal,



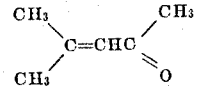
In addition to using olefin-containing gases as the source of acetylene I may employ also gases consisting substantially of saturated or paraffinic hydrocarbons. Such gases are obtained, for example, by the distillation of crude petroleum or by the stabilization of gasoline or casing-head naphtha. These gaseous paraffin hydrocarbons when passed through an electric arc yield a substantial proportion of acetylene, which can be hydrated to acetaldehyde. The aldehyde can be condensed with alcohols made as described above. In some instances hydration of acetylene may be omitted, and direct etherization to polyfurcous anti-knock-igniters be effected by passing acetylene into the alcohol, at somewhat ele-

vated temperatures, in the presence of catalysts.

Secondary alcohols prepared from cracking gas, as described above, may serve as the source of anti-knock-igniters. For example, acetone is obtained by the catalytic oxidation of isopropyl alcohol and this ketone can be converted by suitable methods to the dihydroxy alcohol, pinacol. The latter in acid media undergoes molecular rearrangement (with the loss of water) to give the polyfurcous ter-butyl-methyl ketone,



or when subjected to the action of alkalies, e. g., calcium oxide, acetone yields a branched-chain unsaturated ketone, mesityl oxide,



Furthermore, subjecting isopropyl alcohol to high temperatures (500°–700° C.) furnishes a composition (cracked isopropyl alcohol) containing acetone and unchanged alcohol, the major proportion of the composition being acetone. Cracked isopropyl alcohol, with or without the addition of definite proportions of anti-knock-igniters, can be blended with gasoline to secure a motor fuel of increased ignitibility. Alternatively, cracked isopropyl alcohol may be subjected to the action of alkalies whereby the acetone therein is converted, wholly or in part, to the anti-knock-igniter mesityl oxide and various proportions of the alkali-treated cracked isopropyl alcohol blended with gasoline. The use of condensation products of acetone with aldehydes, for example formaldehydes, is not precluded provided the addition of such products to gasoline does not result in the motor fuel exhibiting objectionable features.

The polyfurcous esters which I have found to have a high octane blending value for reducing knocking are those containing two bifurcous branches, as in the case of the acetals. These esters may be obtained by the condensation of branched alcohols with branched acids as herein described. In some instances, the dihydric alcohol may be condensed with the branched acids to obtain branching at both terminals of the alcohol, and this is particularly useful in starting with a low boiling nitroparaffin which on condensation in an alkaline medium with an aldehyde forms the nitro dihydric alcohol for the esterification. Suitable low boiling nitro compounds such as nitro ethane are obtained by nitrating gaseous paraffins in the vapor phase. The polyfurcous nitro esters are further enhanced in anti-knock value by reduction of the nitro group to an amino group.

In general, it has been observed that the preferred oxygenated compounds of high anti-knock value may be characterized as compounds containing at least seven carbon atoms and two oxygen atoms per molecule. In the esters, at least one of these oxygen atoms is in a carbonyl group, while the other links adjacent carbon atoms together. The compounds should preferably contain no more than about twelve carbon atoms per molecule. The polyfurcous esters, in particular, are of greater value when the characteristic trunk possesses branched alkyl groups at both terminals. It is important, however, that the carbonyl oxygens should not be linked to conjugated nor to adjacent carbon atoms, because compounds with distribution of oxygen in such a manner and in any tautomeric form of the compounds do not possess desirable anti-knock characteristics in spark ignition engine fuels. For example, isopropyl acetoacetate and similar acetoacetates have been found to have a low octane blending value.

Anti-knock-igniters are particularly advantageous in the production of racing fuels. With fuels of this type it is especially necessary that they be readily ignitible at low engine temperatures, possess high anti-knock value, burn cleanly in order to eliminate as much as possible carbon formation and deposition in the engine and on the valves, and exhibit a quick pick-up. For these reasons the proportion of anti-knock-igniter in racing fuels is much greater than in fuels intended for use in the usual types of internal combustion engines, preferably the proportion of anti-knock-igniter being as high as 50 or 60 per cent, or even higher.

Combinations of the foregoing procedures can be employed in making fuels of improved ignitibility. For example, ordinary gasoline, as previously mentioned, can be separated by distillation into two fractions, one boiling between 60° and 175° F., and the other between 175° and 400° F., and the higher-boiling fraction subjected to a nitrating operation. To the lower-boiling fraction is added a minor proportion of an anti-knock-igniter. The two fractions are then blended to furnish a motor fuel of the proper boiling range. Or, a portion of the gasoline may be nitrated, and an anti-knock-igniter added to the other portion. These two portions can be blended in any desired proportions. In some instances the nitration step may result in a decrease in anti-knock value of the motor fuel. Any decrease in anti-knock value can be compensated to a greater or lesser degree by the direct addition of a suitable proportion of anti-knock-igniter. In some instances an increase in anti-knock value of the composite fuel is obtained by employing a sufficiently large proportion of the anti-knock-igniter.

I regard the step of lowering the normal temperature of ignition by incorporating substantially at the time of use small proportions of a substance, or of substances, capable of causing such lowering to be of advantage when, for example, as in the case of an aviation engine, the air supplied to the engine for combustion of the fuel is subjected to rapid changes in density due to movement of the aircraft upwards into more and more rarified air or downward from a high altitude into a denser atmosphere. In such cases, there is permitted a further adjustment of the fuel to fit changing conditions, namely, the addition of variable amounts of the ignition temperature depressant to the fuel, thus to activate combustion under the immediate conditions presented by altitude changes.

One way of accomplishing this regulation is the introduction of activating agents, such as various oxygenated and/or nitro compounds, in requisite proportion, the activating agent preferably being first dissolved in some of the motor fuel to make a concentrate and the latter added slowly in gradual and regulated flow to the fuel feed to the engine, there mixing with the main fuel feed supply in the desired proportion to secure ignition temperature reduction and other qualities that may be required with fluctuations in altitude. If

desired, the flow of the activating concentrate to the mixing chamber or zone may be adjusted automatically with the altitude by appropriate means. In this manner, the proportion of anti-knock-igniter or other catalyst of temperature-lowering ignition admitted to the combustion chamber is altered in accordance with pressure fluctuation due to rapid variation in atmospheric pressure. It should be noted that this proportion, roughly speaking, may be regarded as an inverse ratio, that is, the lower the atmospheric density the greater the proportion of catalyst of temperature-lowering ignition admitted. The initiation of activated combustion in desired degree thus may occur without the attention of the operator.

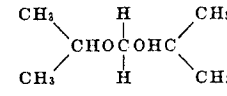
In addition to the foregoing ignition-temperature depressants I may find it desirable to incorporate a small proportion of substances, such as soaps or thickeners, lubricants, and dyes, provided such substances are not incompatible with the ignition-temperature depressants employed in the motor fuel. Adding small proportions of soaps or thickeners, of which cobalt naphthenate or cobalt salts of acids made by oxidation of paraffin wax, ozokerite, Montan wax, and the like, are examples, increase the viscosity of the fuel to a very slight degree. This increase in viscosity, although almost imperceptible to the eye, is sufficient to decrease the flow of fuel through the carburetting device slightly, thereby resulting in somewhat less fuel consumption without decreasing the efficiency of the engine. Addition of a small proportion of highly refined lubricating or solvent oils, which have no value as volatile motor fuels, serves to prevent or remove gum deposits on such portions of the engine as the intake manifold or the valves. Oil-soluble dyes, of any desired color, can be employed to distinguish the fuel of improved ignitibility from other fuels. Addition of extraneous ignition-temperature depressants, such as aldehydes, may result in the fuel becoming acidic in character during storage due to oxygen of the atmosphere slowly reacting with such substances. To overcome this I may add to the fuel an oxidation inhibitor such as α-naphthol, and/or other substances, e. g., ammonia or oil-soluble bases, which form addition compounds with the aldehydes and thus reduce their acid-forming tendency.

From the foregoing it will be seen that the invention contemplates a motor fuel comprising a volatile, preferably petroleum, oil containing self-made ignition-temperature depressants, an example of such being a nitrated volatile petroleum oil. Certain other aspects of the invention contemplate the regulated addition of predetermined proportions of extraneously-formed depressants, especially oxygenated polyfurcous hydrocarbons of the anti-knock-igniting type. Still another aspect is that which involves the gradual and continuous addition of such depressants to the fuel as fed to the engine. The composition herein thus constitutes a motor fuel preferably neutral and preferably substantially non-corrosive which contains an ignition-temperature depressant preferably of a pressure-activated type, that is, a substance or mixture of substances which at the ignition pressures of the engine become adequately responsive to ignition as compared with gasoline or normal ignitibility; the improved motor fuel preferably possessing a degree of ignitibility at atmospheric pressure which approximates that of ordinary or normal gasoline but which under engine compression presents a degree of ignitibility greater in proportion than would correspond to the ease of ignition of the same gasoline untreated or of normal gasoline under like conditions of compression.

The following examples will serve to illustrate my invention:

Example 1.—Distill 400° F. end-point gasoline, taking over the fraction boiling up to 175° F. After cooling to atmospheric temperature, add 5 volumes of nitric acid of specific gravity 1.05 to 100 volumes of the higher-boiling fraction. Thoroughly agitate the mixture keeping the temperature at 70° F. After agitation let the mixture stand whereby separation into two layers takes place. The lower, or acid, layer is withdrawn and the upper, or oil, layer is washed with water and then with a dilute solution of sodium carbonate. Addition of the low-boiling fraction to the treated high-boiling fraction gives a nitrated gasoline.

Example 2.—To 80 parts of isopropyl alcohol add 15 parts of trioxymethylene and into this mixture pass some dry gaseous hydrogen chloride. Let the mixture stand at atmospheric temperature for 20 hours. Filter any undissolved material, neutralize the filtrate with sodium bicarbonate and distill, preserving the fraction boiling between about 90° and 120° C., which contains a large proportion of diisopropyl formal,



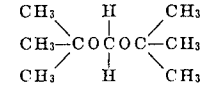
Add 20 parts of this fraction to 100 parts of 325° F. end-point gasoline to produce an aviation fuel containing a polyfurcous anti-knock-igniter.

Example 3.—Prepare the reaction product of isopropyl alcohol and formaldehyde as described in Example 2. The fraction boiling between 90° and 120° C. is washed with water, dried, and added to 400° F. end-point gasoline in the proportion of 25 volumes of anti-knock-igniter to 100 volumes of gasoline.

Example 4.—Add 10 volumes of cracked isopropyl alcohol, prepared by conducting the vapors of isopropyl alcohol through a copper tube heated to 600° C., and 30 volumes of diisopropyl formal, prepared as described in Example 2, to 150 volumes of 400° F. end-point straight-run gasoline thereby to obtain a motor fuel containing both a polyfurcous anti-knock-igniter and an ignition temperature depressant.

Example 5.—Add 20 volumes of the acetal, as prepared in Example 2, and 2 volumes of acetaldehyde to 100 volumes of 400° F. end-point gasoline thereby to obtain a motor fuel containing both a polyfurcous anti-knock-igniter and an ignition temperature depressant.

Example 6.—Add 15 parts of trioxymethylene to 100 parts of tertiary butyl alcohol, and then pass in dry hydrogen chloride gas. Proceed as in Example 2, with the exception that the portion distilling above 83° C., and containing a substantial proportion of di-tertiary butyl formal,

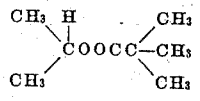


is preserved. Add 5 volumes of this fraction to 100 volumes of 325° F. end-point gasoline, thus giving a polyfurcous motor fuel.

Example 7.—To the nitrated high-boiling fraction of Example 1, add diisopropyl formal in the ratio of 200 volumes of the nitrated fraction to 5

volumes of the acetal. The low-boiling fraction is united with this mixture to give a nitrated gasoline containing a polyfurcous anti-knock-igniter.

Example 8.—Prepare diisobutylene from olefins of cracked gasoline (vapor phase) by suitable polymerization. Pass this dimer, admixed with air, over heated vanadium catalyst to obtain an acid mixture containing a large proportion of trimethylacetic acid. Esterify this crude acid mixture with isopropyl alcohol to yield a mixture of esters with isopropyl trimethylacetic ester,



a predominating component. Mix the well-dried crude trimethylacetic ester with 400° F. end-point gasoline in the proportion of 92 gallons of gasoline to 8 gallons of this branchy type of ester.

Example 9.—To provide for top lubrication in the engine, add 1 quart of a highly refined oil of the gas oil type to 25 gallons of the fuel as prepared according to Example 8.

Example 10.—Prepare cobalt salts of oxidized paraffin wax acids by the interaction of a soluble cobalt salt and the sodium salts of the acids. The washed and dried cobalt salts are dissolved in gasoline to give a 1 per cent solution. Add one volume of this solution to 100 volumes of gasoline of Example 8 to furnish a thickened motor fuel.

Example 11.—Prepare a winter gasoline as described in Example 6. Prepare a summer anti-knock gasoline by the catalytic hydrogenation of high-boiling petroleum fractions (i. e., fractions of the gas oil range or higher). The summer gasoline is colored by the addition of about 0.001 per cent of an oil-soluble red dye. Summer gasoline and winter gasoline are mixed in the proportion of equal volumes.

Example 12.—Distill cracked gasoline taking over the fraction boiling up to 320° F. The higher boiling fraction is nitrated as in Example 1. Add 20 volumes of this nitrated fraction to 100 volumes of safety fuel, the latter being obtained by the catalytic hydrogenation of high-boiling petroleum distillates.

Example 13.—Separate cracked gasoline into two fractions by distillation and nitrate the higher-boiling fraction as described in Example 1. To 100 volumes of the lower-boiling fraction add 10 volumes of a mixture of about equal volumes of ethylene and propylene oxides and 30 volumes of an anti-knock-igniter prepared from secondary butyl alcohol and acetaldehyde. Blend the two fractions thereby obtaining a 400° F. end-point gasoline containing both nitrated ignition temperature depressants and anti-knock-igniters.

Example 14.—Separate cracked gasoline into two fractions by distillation and treat each fraction separately as described in Example 13. To the high-boiling nitrated fraction add about 0.5% by volume of a highly refined petroleum oil of the gas oil type. To the low-boiling fraction, containing the added olefin oxides and anti-knock-igniter, is added about 0.005 per cent of a red oil-soluble dye. The two fractions are then blended. To the blended gasoline add about 0.1 per cent by weight of a gum-inhibitor, e. g., α-naphthol, and about 0.01 per cent by weight of the cobalt salts of wax acids as thickeners.

Example 15.—Crack the gas oil fractions, obtained by the distillation of crude petroleum, at a temperature of 900° F. and a pressure of 200 pounds per square inch. Pass a portion of the olefin-containing gases from this cracking operation through an electric arc to make acetylene. Hydrate separately the acetylene to acetaldehyde and the remaining portion of olefin-containing gas to a mixture of secondary and tertiary alcohols. Condense the acetaldehyde with the alcohols to obtain a mixture of polyfurcous anti-knock-igniters.

Example 16.—Make an olefin-containing gas as described in Example 15. Pass such a gas through sulphuric acid, absorbing the olefins and leaving a residual gas containing saturated or paraffinic hydrocarbons. Dilute the sulphuric acid solution with water, and distill to obtain alcohols. Conduct the residual gas through an electric arc whereby acetylene is formed, and hydrate acetylene to acetaldehyde. Condense the alcohols and acetaldehyde to form a mixture of polyfurcous anti-knock-igniters.

Example 17.—The uncondensed gases (consisting of paraffin and olefin hydrocarbons having from 1 to 4 carbon atoms per molecule) from the stabilizing unit for cracked gasolines are treated as described in Example 16. The alcohols and acetaldehyde are condensed, in the presence of hydrogen chloride as a catalyst, to give a mixture of polyfurcous anti-knock-igniters.

Example 18.—Still gases from the distillation of a petroleum crude oil are subjected to an absorption operation whereby the less volatile constituents are removed by absorption in a high boiling petroleum fraction. Pass the residual gases, consisting substantially of propane and butanes, through an electric arc. Hydrate the acetylene formed to acetaldehyde, and condense the acetaldehyde with the alcohols, as prepared in Example 15, to yield polyfurcous anti-knock-igniters.

Example 19.—Add 40 volumes of isopropyl trimethylacetic ester, as prepared in Example 8, to 60 volumes of 375° F. end-point gasoline to obtain a racing fuel containing polyfurcous anti-knock-igniters.

Example 20.—Prepare a racing fuel of the polyfurcous anti-knock-ignition type by the addition of 60 volumes of product prepared as in Example 15 to 40 volumes of 375° F. end-point gasoline.

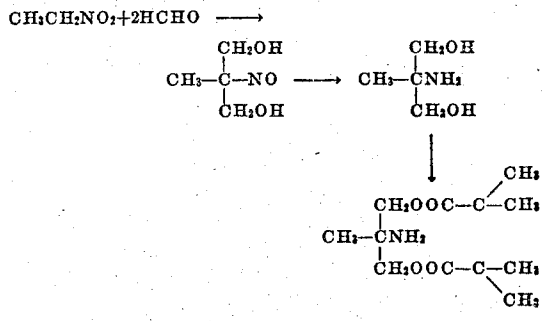
Example 21.—Prepare a racing fuel by the addition of 80 volumes of the polyfurcous anti-knock-igniter made by the condensation of isopropyl alcohol and isovaleric acid to 20 volumes of 325° F. end-point gasoline.

Example 22.—Prepare a racing fuel by the addition of 80 volumes of the polyfurcous anti-knock-igniter made by condensation of secondary butyl alcohol and acetaldehyde to 20 volumes of 325° F. end-point gasoline.

Example 23.—Prepare ethylene glycol from ethylene of cracking gas of petroleum oil cracking. Also by the electric arc treatment of natural gas, propane, butane, or refinery gas produce acetylene and convert this to acetaldehyde. Heat the ethylene glycol with the acetaldehyde with or without catalysts, at 150°–160° C. under pressure to form cyclic acetals. Rectify by distillation. Incorporate this with gasoline in proportions represented by ratios 1:2, 1:3, 1:4, 1:7, and the like.

Example 24.—Prepare dihydric nitroalcohol by reacting a primary or secondary nitroparaffin with an aldehyde in the presence of a base. The resulting nitroalcohol is esterified with a secondary or tertiary carboxylic acid, e. g., isobutyric acid, to form a polyfurcous nitroester, useful as an anti-knock-igniter.

Example 25.—Prior to the esterification in Example 24, the nitro group in the nitroalcohol is reduced by nascent hydrogen in the presence of a metal to an amino group to enhance the anti-knock qualities of the polyfurcous ester. The formation of the dihydric alcohol and the diester may be represented in the following manner:



Example 26.—Proceed as in Example 23 except use formaldehyde.

Example 27.—Use trioxymethylene in place of formaldehyde in Example 26, in which case heating can be carried out at atmospheric pressure. Diethylene glycol may be used instead of ethylene glycol.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

1. An anti-knock motor fuel for high-compression spark-ignition engines comprising a major proportion of gasoline hydrocarbons blended with a substantial anti-knock improving amount of an aliphatic mono-ester having two branched alkyl terminals and containing 7 to 12 carbon atoms in the molecule with oxygen present only in the ester linkage.

2. An anti-knock motor fuel for high-compression spark-ignition engines comprising a major proportion of gasoline hydrocarbons blended with a substantial anti-knock quality improving amount of an aliphatic mono-ester of a branched alkyl monocarboxylic aliphatic acid and a branched alkyl monohydric aliphatic alcohol, said ester containing from 7 to 12 carbon atoms in the molecule.

3. An anti-knock motor fuel for high-compression spark-ignition engines comprising a major proportion of gasoline hydrocarbons blended with a substantial anti-knock quality improving amount of the ester of isovaleric acid and isopropyl alcohol.

4. An anti-knock motor fuel for high-compression spark-ignition engines comprising a major proportion of gasoline hydrocarbons and a substantial anti-knock quality improving amount of the ester of trimethyl-acetic acid and tertiary butyl alcohol.

CARLETON ELLIS.