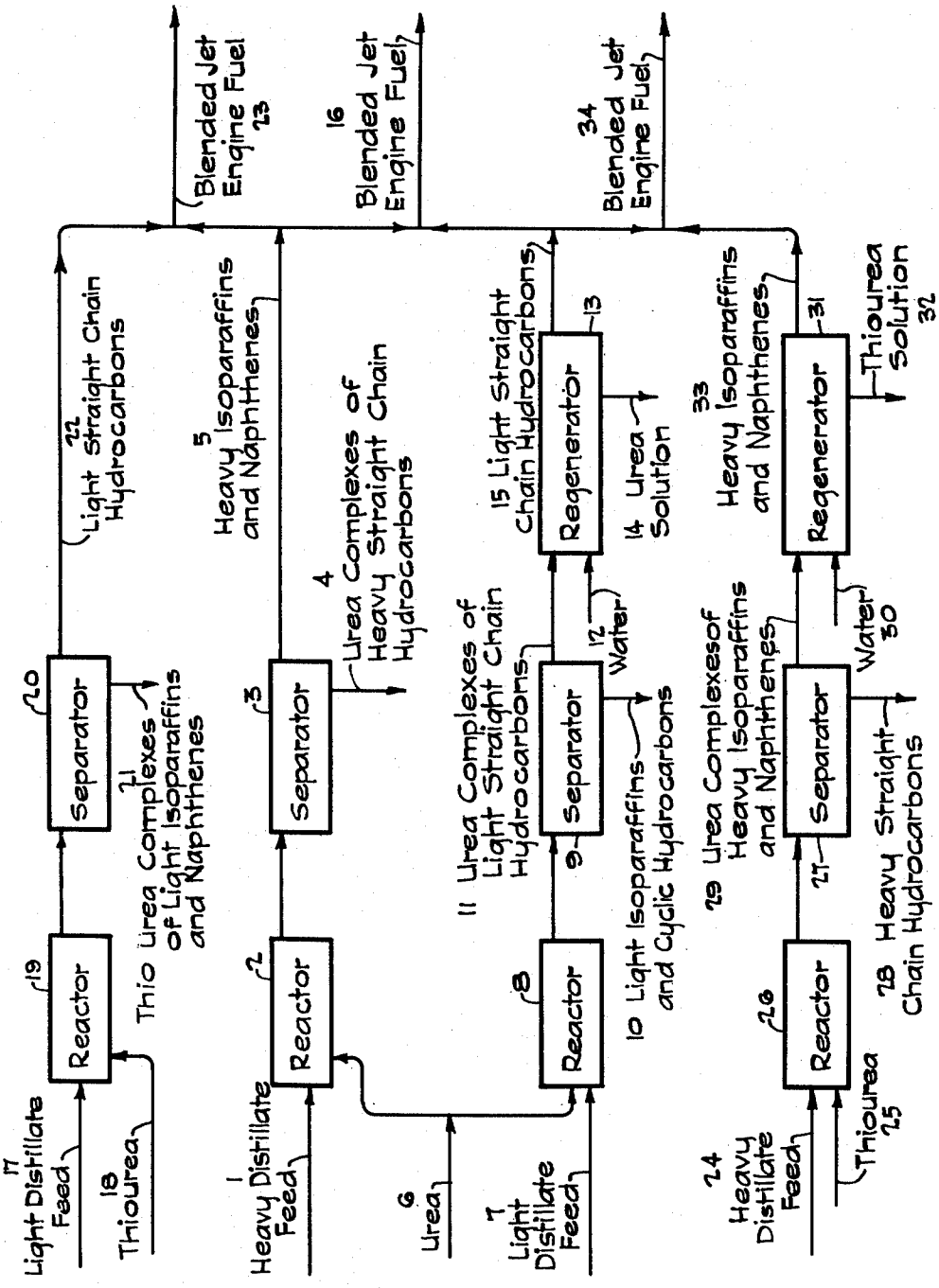
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FUEL AND PROCESS FOR PREPARING SAME

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FUEL AND PROCESS FOR PREPARING SAME

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1

This invention is concerned with fuel compositions designed especially for use at extremely low temperatures. More particularly, this invention is directed to fuel oils or compositions suitable for use in jet engines and in diesel engines, especially under arctic conditions.

The fuels presently available in substantial amounts are suitable for use only under operating conditions normally encountered in the more temperate climates. Fuels which are suitable for use in jet-propelled aircraft or in diesel-powered equipment have heretofore been limited by the inherent characteristics which they necessarily possessed, due to the mixture of components present therein. While artificially blended fuels have been prepared from time to time, which fuels have properties which permit their use under low operating temperatures, these have been mere laboratory curiosities since it has heretofore been impossible to produce them in any effective quantities. In the event of a national emergency and due to the rapid development of jet engines, an enormous demand may be expected to develop for jet and diesel-engine fuels for use under frigid conditions.

The most serious shortcoming of the usual jet and diesel fuels, when low operating conditions must be considered, is their low temperature susceptibility. The high pour point of the fuel stocks available precludes their use at temperatures substantially below about −30° F; however, it has been recently recognized that the pour point of a given material is not strictly indicative of its performance at low operating temperatures. It has been found that if stocks of a given pour point are held at about their low pour temperature (even above their pour points), certain components therein eventually commence to crystallize. This becomes apparent by the appearance of a cloud or haze in the fuel. Under more stringent temperature conditions, the fuel eventually solidifies or freezes.

Even at the temperatures at which the cloud first appears, i. e., the cloud point, the technical consequences commence to become extremely serious. Jet and diesel engines, the fuel lines of which are exposed for any substantial period to temperatures below the cloud-point temperature of the fuel contained in said lines, will be found to be impossible to operate due to plugging

2

of the lines because of components which have crystallized therein from the fuel. A more sensitive but necessary part of jet engines is the filter, through which all the fuel must pass from the feed line into the combustion chamber. Any crystallization of fuel components will rapidly cause this filter to become clogged, thus cutting off the fuel supply to the engine.

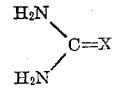
While the pour point of some fuel stocks is related in a general way to the cloud point and freezing point thereof, this relationship is neither universal nor uniform. Some stocks which have relatively low pour points have been found unsuitable for use in cold climates because of their unaccountably poor cloud points.

An effort to overcome these difficulties has been made by employing more volatile fuels having lower pour points. In such circumstances, however, it has been found that the fuels are relatively volatile and, consequently, are a fire hazard, particularly when used in various aircraft engines.

The conventional methods for the preparation of fuels from petroleum sources do not permit the preparation of fuels having suitable properties for use under frigid conditions. It is well known that petroleum distillates contain a number of types of configurations, including substantially straight-chained paraffin hydrocarbons, isoparaffins, naphthenes and aromatics. If the fuels are prepared from cracked stocks, the mixtures of hydrocarbons also contain acyclic unsaturated materials such as olefins. Fractional distillation, the normal means of treating petroleum stocks, has substantially no effect upon the composition of the distillate except in regard to boiling point. Therefore, any of the distillates may, and usually do, contain a mixture of all of the components listed above.

As pointed out hereinbefore, these heterogeneous fuel mixtures are unsuitable for use in cold climates because of one or more components present in the fuel. Probably the worst offenders in this regard are the substantially unbranched hydrocarbons, hereinafter referred to as the "normal hydrocarbons." Another class of constituents of the usual fuels which tends to have adverse operating characteristics includes the aromatics, since these have relatively poor cetane numbers.

Recently a method has been developed for the fractionation of mixtures of organic compounds according to structural type. As more particularly described hereinafter, this method comprises treatment of the mixture with a complex-forming agent having the general configuration:



wherein X is an element selected from the right-hand side of groups 6 of the periodic table, and preferably having an atomic weight of less than about 128. Compounds falling within this class include especially urea, thiourea, selenourea and telluourea. Also, the acid salts of these compounds, such as the hydrochlorides or acetates, are suitable as the complex-forming agents. The complexes appear to fall within the general classification known as "clathrate compounds."

It has been found that fractionation by means of complex formation with urea results in th e formation of crystalline complexes of urea with normal, i. e., straight-chained, organic compounds. Furthermore, it has been noted that urea will not usually form complexes with branched or cyclic compounds. Hence, it is possible, by the use of this agent, to separate substantially unbranched materials from their mixtures with branched and/or cyclic substances. Thiourea, on the other hand, has been found to form crystalline complexes with highly branched derivatives and with naphthenes, but appears to be substantially inert toward normal (straight-chained) compounds and aromatics. Selenourea has a more general complex-forming action and appears to form crystalline complexes with a wide variety of structural configurations.

Up to the present time, this method has been used simply for the separation of a particular fraction from its mixtures. No particular use has been advanced for the raffinate in any instance. Throughout the present specification and claims, the term "raffinate" will refer to that portion of a mixture of organic compounds which is substantially inert toward a complex-forming agent under the conditions employed. The term "extract" is meant to include that portion of the mixture of organic compounds forming a complex with the agent and thereby extracted from the mixture.

It is an object of the present invention to provide a novel fuel especially suitable for use under frigid (very low temperature) operating conditions. It is another object of this invention to provide a fuel particularly designed for use in jet engines and diesel engines. It is a further object to provide a method for the preparation of fuels having desirably low cloud points and freezing points. It is still another object to provide a method for the preparation of a blended fuel having improved low-temperature startability as well as superior low-temperature operating characteristics. Other objects will become apparent during the following discussion.

Now, in accordance with this invention, it has been found that a highly improved fuel, especially suitable for use under frigid operating conditions, comprises a minor amount of substantially normal hydrocarbons boiling within the range of from about 275° F. to about 425° F., blended with a major proportion of substantially non-normal (i. e., non-straight-chained) hydrocarbons boiling within the range of from about 415° F. to about 660° F. It has also been found that the mixture of non-normal hydrocarbons boiling within the range 415°–660° F. may be used without substantial modification as an arctic diesel or jet engine fuel, even in the absence of the above-mentioned lower-boiling normal hydrocarbons.

A still more highly preferred fuel for use under arctic conditions comprises the combination of a relatively minor amount of normal hydrocarbons boiling within the range 275°–425° F. and of a major amount of isoparaffins and/or naphthenes boiling within the range 415°–660° F., said composition containing no appreciable amounts of aromatics.

Again in accordance with this invention, it has been found that fuels such as those described above may be prepared by use of the extractive crystallization methods referred to hereinbefore. One of such methods comprises the treatment of a petroleum distillate having a boiling range within the limits 415°–660° F. with a complex-forming agent such as urea, whereby the normal hydrocarbons are extracted from the distillate. The raffinates so produced have been found to have exceptionally low cloud and freezing points and to be suitable without substantial modification for use as a fuel under frigid conditions.

An improvement upon said fuel comprises the separate treatment of a petroleum distillate having a boiling range within the limits 275°–425° F. with a complex-forming agent such as urea for the purpose of separating the substantially normal hydrocarbons therefrom. A minor amount of the hydrocarbons extracted is combined with a major proportion of the first hydrocarbon raffinate for the preparation of an arctic diesel or jet fuel having the added property of improved startability and a higher cetane number.

A still greater improvement in the basic fuel may be effected by treatment of the raffinate having a boiling range within the limits 415°–660° F. by the Edeleanu process, or its equivalent, for the purpose of removing therefrom at least a large proportion of the aromatics. The optimum fuel, therefore, comprises a mixture of 5–15% normal paraffins boiling within the range 275°–425° F. and at least 85% of a mixture of isoparaffins and naphthenes boiling within the range 415°–660° F. Heretofore, it has been impossible to produce such a fuel except on a very small scale, completely inadequate for practical use.

The stocks to be treated in accordance with the present invention are preferably straight-run distillates since they contain practically no olefins. However, cracked stocks may be used, especially if they are hydrogenated for the purpose of converting the olefins to paraffins. The stocks may be prepared or modified by any of the normal conversion procedures such as alkylation, hydro-forming or similar procedures. In the case of the blended fuel described above, it is preferable to choose two stocks; the first of which has a high normal paraffin content while the higher-boiling stock has a relatively high proportion of isoparaffins or naphthenes.

The process of the present invention comprises treatment of the selected stock with the complex forming agent, separation of the complexes so formed from the unaffected portions of the stock and utilization of the fractions so produced. Typical procedures illustrating the various al-

ternatives which may be employed are outlined in the accompanying diagram. In the diagram the term "heavy distillate feed" refers to a petroleum distillate falling within the range 415°–660° F. The term "light distillate feed" refers to a petroleum distillate falling within the range 275°–425° F. As shown in the diagram, the heavy distillate feed 1 enters a reactor 2 together with urea 6. Under the conditions to be described hereinafter, crystalline complexes are formed between urea and the normal hydrocarbon portion of the distillate. The slurry containing the crystalline complexes and the remaining liquid portions of the reaction mixture are sent to a separator 3, wherein the crystalline complexes are separated from the liquid components by such means as filtration or centrifuging. The complexes 4 are further processed to remove the normal hydrocarbons for further utilization. The heavy isoparaffins aand naphthenes 5, which comprise the liquid components remaining from the original feed, are blended with the lighter normal hydrocarbon products as follows:

The light distillate feed 7 is treated with urea 6 in a similar reactor 8 to produce a slurry containing urea complexes of the normal hydrocarbons suspended in the liquid components which are not affected. The slurry is conducted to separator 9 where the liquid isoparaffins and cyclic hydrocarbons 10 are removed and utilized for other purposes. The complexes of the normal hydrocarbons 11 are transferred to a regenerator 13, preferably together with a suitable quantity of water 12. The complexes, when heated in the presence of water, decompose and thus permit regeneration of the light normal hydrocarbons 15 therefrom. The urea simultaneously regenerated dissolves in the water which is present and separates from the hydrocarbons in the form of an aqueous solution. For the purpose of producing the blended jet fuel described hereinbefore, a minor amount of the light normal hydrocarbons 15 is combined with the heavy non-normal hydrocarbons 5 to give the blend 16.

Two alternative procedures also are illustrated in the diagram. The heavy non-normal hydrocarbons 5 may be combined with light normal hydrocarbons produced in the following manner: A light distillate feed 17 is treated with thiourea 18 in a reactor 19. The isoparaffin and naphthene portions of the feed form complexes with thiourea, while the substantially normal hydrocarbons are not affected. The slurry so produced is conducted to a separator 20 wherein the unwanted thiourea complexes 21 are separated from the desired liquid normal hydrocarbons 22. The latter are then combined in their proper proportion with the heavy non-normal hydrocarbons 5 to give the blended fuel 23.

The choice of the complex-forming agent to be employed will depend, in a major extent, upon the feed to be treated. At times it is advantageous to isolate the heavy non-normal fraction by a thiourea treatment as follows: The heavy distillate feed 24 is treated with thiourea 25 in a reactor 26. The mixture so produced is conducted to a separator 27, wherein the unaffected normal hydrocarbons 28 are separated from the thiourea complexes of isoparaffins and naphthenes 29. The complexes are conducted to a regenerator 31, where they are mixed with water 30 and heated to the decomposition temperature. The thiourea regenerated from the complexes by this treatment dissolves in the water and is removed in the form of a solution 32. The regenerated heavy isoparaffins and naphthenes 33 may be combined in a major proportion with the light normal hydrocarbons 15 to give the blended jet-engine fuel 34.

As pointed out hereinbefore, the superior arctic diesel or jet fuel forming the essence of this invention comprises at least about 85% of a mixture of non-normal hydrocarbons having a boiling range within the limits 415°–660° F. This fuel comprises isoparaffins and/or naphthenes and may contain a minor proportion of aromatics within the same boiling range. Preferably, however, the stock contains a minimum amount of aromatic hydrocarbons. Still more preferably, the boiling range of the hydrocarbons should be within the range 425°–650° F. It has been found that such a mixture has the unexpected advantage of remaining completely fluid at temperatures lower than —76° F. as indicated by both the pour and cloud points. Similar stocks containing the unbranched paraffins normally present are found to have cloud points as high as from —5° to +10° F., respectively. While the hydrocarbons are preferably isolated from petroleum distillates, they may be obtained from other large-volume sources such as polymerized hydrocarbon gases or from synthetic coal hydrocarbons.

In the preparation of fuels having improved startability at low temperatures, the normal hydrocarbons to be added to the above fuel should comprise 5–15% by volume having a boiling range within the limits 275°–425° F. More preferably, however, the normal hydrocarbons should boil within the range 300°–400° F. An optimum blend is obtained when the composition contains a minimum of 10% of the described normal hydrocarbons together with at least 85% of the isoparaffins or naphthenes discussed above. Fuels for use at extremely low temperatures should be modified by the addition of correspondingly greater amounts of the lower-boiling normal hydrocarbons.

It has been discovered that the blends described above have a characteristic of prime importance in jet-engine operation: The lean blow-out characteristics have been found to be highly satisfactory as compared with other fuels containing a higher proportion of normal paraffins, even though the boiling range of the other blends is similar. Optimum lean blow-out characteristics will vary with the airspeed and with the operating altitude, but it has been noted that the present fuel shows little susceptibility to change under these two variables.

The fuels described may be modified by the addition of suitable improving agents such as amyl nitrate or ditertiary butyl peroxide for the improvement of cetane number. Viscosity index improving agents also may be added, such as polymers of the methacrylic esters, or polymerized isobutylene. Anti-oxidants may be employed if desired, such as para-phenylene diamine. However, the proportion of such additives should be held to a minimum so that combustion residues will not be unduly large.

In the preparation of the present fuels by extractive crystallization, advantage may be taken of numerous operating conditions. For example, the complex-forming agent may be used in the form of a solid or of a solution. The preferred solvent is one which is largely aqueous or aqueous alcoholic in character. The alcohols which may be employed include especially the lower alcohols, such as methyl and ethyl alcohol. The agent or

solution thereof should be present in the reactor in substantial excess of the amount necessary for maximum complex formation.

It has been found that the extent of such formation is dependent, in part, upon the concentration of the complex-forming agent in its solvent. In order to maintain a high degree of complex formation, the solution of the agent should be kept near the saturation point at all times. However, circumstances may arise where the maximum complex formation would be undesirable. For example, a stock having an initial boiling point below the minimum desired may be treated in such a way as to permit only the higher molecular weight hydrocarbons to form crystalline complexes. This is effected by adjusting the concentration of the complex-forming agent in its solvent so as to permit selective formation. It has been noted that each hydrocarbon requires a critical minimum concentration of the agent for any given temperature before complex formation is possible. Hence, by adjusting the concentration of the agent to a point below this critical minimum for the lighter hydrocarbons present, it is possible to cause the heavier hydrocarbons to form crystalline complexes while the lighter materials are unaffected.

The mixtures of hydrocarbons to be treated may be contacted with the complex-forming agent without substantial modification or, if it is desired, in the form of a diluted solution. The diluent for the hydrocarbon mixture should be one which is substantially inert toward the complex-forming agent under the conditions employed. A suitable non-polar solvent for this purpose is pentane, which may be used at the usual temperatures at which complex formation is carried out. Certain polar solvents have been found particularly suitable due to their special solubility characteristics. Methyl isobutyl ketone is a particularly outstanding example of this type of medium. It has been found that this solvent permits optimum crystal structure in the complex and allows the formation to proceed at a maximum rate. These properties appear to be due to the fact that the solvent is completely miscible with the petroleum fraction and, in addition thereto, dissolves to a certain extent in the aqueous solution of the complex-forming agent which is used. Methyl isobutyl ketone may be employed when urea is the complex-forming agent. At low temperatures the solvent will form a complex with thiourea, apparently due to its isoalkyl substituents. It is preferred practice to use methyl ethyl ketone as the solvent medium when thiourea is present as the complex-forming agent. This material appears to be substantially inert toward thiourea, probably because of its unbranched alkyl groups.

A special group of solvents which may be profitably employed in the present process comprises those which will dissolve both the complex-forming agent and simultaneously extract the aromatic fraction from the petroleum distillate which is being treated. A suitable solvent of this type is liquid sulfur dioxide. In effect, the use of this type of medium enables what may be regarded as a combined Edeleanu treatment and an extractive crystallization treatment. This is particularly desirable when it is preferred to eliminate aromatics from the fuel being prepared.

The agent and the petroleum distillate are normally contacted by rapid mixing at about room temperature or below. Higher temperatures may be employed as the molecular weight of the hydrocarbons is increased. A continuous process of complex formation has been found especially effective as opposed to a batch process.

The crystalline complexes are usually formed after a period of apparent inactivity. The period between initial contact of the agent and the hydrocarbons before the first crystals become apparent is usually called the "induction period." This period may be only a matter of seconds but, at times, may be as long as several minutes or even as much as two to four hours. The combination of high agent concentration and low reaction temperature encourages short induction periods Once the complex has commenced to form, the reaction appears to proceed rapidly to completion. If a large amount of the complex is formed relative to the amount of the liquid components present, the reaction mixture may be difficult to handle; hence, it is advisable to maintain at least a sufficient amount of liquid components in the reaction mixture to enable facility in transporting and otherwise handling the material.

The design of the reactor should be such as to permit the hydrocarbon feed and the complex-forming agent to be introduced at the bottom thereof and to continuously flow upwards in such a manner that the reaction is complete at the exit near the top. The take-off is led to a separation area wherein the crystalline complexes are separated from the liquid components of the reaction mixture. Suitable methods of separation comprise basket centrifuges or rotary filters. The complexes may be purified to a certain extent by washing with a selective solvent such as pentane. This step has been found to be of some importance since the surfaces of the crystals are easily wet by the liquid hydrocarbons present. In order to obtain clean fractionation and to avoid contamination of the complexes by the remaining liquid fractions, the washing step appears to be particularly desirable.

The crystalline complexes have been separated from the liquid fraction of the distillate, the step remains of regenerating hydrocarbons therefrom. The regeneration preferably comprises the application of heat, preferably in the presence of a solvent, either for the hydrocarbons or for the complex-forming agent. For example, if a crystalline complex of a normal hydrocarbon and urea is heated in the presence of water to a temperature above about 80° C., the complex decomposes to yield the hydrocarbon and the complex-forming agent. The latter dissolves in the water which is present and forms a solution which is immiscible with the hydrocarbon. Alternatively, a dilute solution of the complex-forming agent may be heated with the complexes. Under these circumstances, the complex decomposes to yield the regenerated hydrocarbon and a solution of the agent whose concentration has been incurred by the addition of the regenerated complex-forming agent. The augmented solution may be used subsequently in the formation of additional complexes.

The arctic diesel or jet fuels which may be prepared by the method of the present invention will have the following critical characteristics:

Cloud point, ° F., maximum	−75
Freezing point, ° F., maximum	−76
Viscosity centistokes at −65° F., maximum	50
Viscosity centistokes at 100° F., minimum	0.7
ASTM initial boiling point, ° F., minimum	275
ASTM final boiling point, ° F., maximum	660

The process of the present invention may be illustrated by the following example:

A 50 cetane diesel fuel was prepared by Edeleanu treatment of a fraction of a Los Angeles basin crude, the fraction boiling between 415° F. and 660° F. The raffinate from said treatment, which constituted the diesel fuel, contained 5% aromatics 13.5% straight-chain hydrocarbons, the remainder being a mixture of branched-chain hydrocarbons and naphthenes.

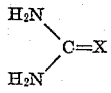
The raffinate described above was diluted with an equal volume of methyl isobutyl ketone and mixed at 70° F. with a saturated aqueous solution of urea. The crystalline complexes which formed between the straight-chain hydrocarbons and urea were removed by filtration, leaving a raffinate containing less than 1% straight-chain hydrocarbons and having the following properties:

Cetane number	45
Viscosity, centistokes at 100° F	3.1
Viscosity, centistokes at −65° F	299
Initial boiling point, ° F	415
Final boiling point, ° F	650
Pour point, ° F—lower than	−76
Cloud point, ° F—lower than	−76

I claim as my invention:

1. The method of operating an aircraft turbine engine which comprises burning therein a fuel having 5–15% substantially normal hydrocarbons with a boiling range within the limits 275°–425° F., and at least 85% of substantially non-normal hydrocarbons with a boiling range within the limits 415°–660° F.

2. The process for the preparation of an engine fuel having improved startability, high end-point and low pour point comprising separately treating two petroleum distillates, the first of which has a boiling range within the limits 275°–425° F., and the second of which has a boiling range within the limits 415°–660° F., with at least one complex-forming agent having the general configuration



wherein X is an element selected from the right-hand side of group VI of the periodic table, whereby complexes are formed between the agent and a fraction of each distillate, said complex formation in each case causing separation of normal hydrocarbons of each distillate from the non-normal fractions thereof, and subsequently blending 5–15% of the substantially normal hydrocarbons of the first distillate with 85–95% of the non-normal hydrocarbons of the second distillate.

3. A novel engine fuel having improved startability, high end-point and low pour point consisting essentially of 5–15% of substantially normal hydrocarbons having a boiling range within the limits 275°–425° F., and 85–95% of substantially non-normal hydrocarbons having a boiling range within the limits 415°–660° F.

4. A fuel composition according to claim 3, wherein a preponderant proportion of the non-normal hydrocarbons are isoparaffins and naphthenes.

5. The process which comprises separately contacting urea with two petroleum distillates, the first of which has a boiling range within the limits 275°–425° F., and the second of which has a boiling range within the limits 415°–660° F., whereby crystalline urea complexes of the substantially normal hydrocarbons present in each distillate are formed, the non-normal fractions thereof being unaffected, separating said complexes from the non-normal fractions, regenerating the normal hydrocarbons of the first distillate from their urea complexes, and blending said regenerated normal hydrocarbons with the non-normal hydrocarbons of said second fraction, so that the resulting blend contains 5–15% of normal hydrocarbons.

6. A novel engine fuel having a high end-point and a low pour point comprising a straight-run stove oil having a boiling range within the limits 415° F.–660° F. being substantially free from straight-chain hydrocarbons, said fuel having a pour point substantially below about −30° F.

7. A novel jet-engine fuel having improved startability, high end-point and low pour point consisting essentially of 5–15% of substantially straight-chain hydrocarbons obtained from straight-run gasoline having a boiling range within the limits 275° F.–425° F., together with 85–95% of a straight-run petroleum distillate having a boiling range within the limits 415° F.–660° F., from which the substantially straight-chain hydrocarbons have been removed.

8. The process for the preparation of novel engine fuels comprising contacting a straight-run petroleum distillate having a boiling range within the limits 415°–660° F. with liquid sulfur dioxide to produce an extract phase and a raffinate phase, contacting said raffinate phase with urea whereby the substantially normal hydrocarbons present therein form crystalline urea complexes, separating said complexes from the remaining liquid fraction of said raffinate and blending the remaining liquid fraction with normal hydrocarbons obtained by urea extraction of a petroleum distillate having a boiling range within the limits 275°–425° F. so that the resulting blend contains 5–15% of normal hydrocarbons.

9. The process which comprises contacting a first petroleum distillate having a boiling range within the limits 275°–425° F. and having a high normal paraffin content with thiourea, whereby the non-normal hydrocarbons present therein form crystalline thiourea complexes, separating said thiourea complexes from the substantially normal hydrocarbons of the first distillate, contacting a second petroleum distillate having a boiling range within the limits 415°–660° F. and having a relatively high proportion of isoparaffins and naphthenes with urea, whereby the substantially normal hydrocarbons present therein form crystalline urea complexes, separating said urea complexes from the isoparaffins and naphthenes of the second distillate, and blending the normal hydrocarbons of the first distillate with the isoparaffins and naphthenes of the second distillate so that the resulting blend contains 5–15% of normal hydrocarbons.

10. A novel engine fuel having improved startability, high end-point and low pour point consisting essentially of 5–15% of substantially normal hydrocarbons having a boiling range within the limits 300°–400° F., and 85–95% of substantially non-normal hydrocarbons having a boiling range within the limits 425°–650° F.

LLOYD C. FETTERLY.

(References on following page)

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,025,409	Black	Dec. 24, 1935
2,049,062	Howard	July 28, 1936
2,090,007	MacKenzie	Aug. 17, 1937
2,096,218	Voorhees	Oct. 19, 1937
2,312,360	Risk	Mar. 2, 1943
2,361,054	Pevere	Oct. 24, 1944
2,361,080	Bolt et al.	Oct. 24, 1944
2,366,490	Cloud	Jan. 2, 1945
2,403,267	Davis	July 2, 1946
2,433,943	Zwicky et al.	Jan. 6, 1948

OTHER REFERENCES

Sachanen, Chemical Constitutents of Petroleum, pp. 201, 230, 231, 232. Published in 1945 by Reinhold Publishing Corp., N. Y., N. Y.

Technical Oil Mission, Reel 143, 6 page translation of German patent application No. B190, 197, deposited in the Library of Congress May 22, 1946.

Petroleum Engineer, Aug. 1948, pp. 177, 180, 182, 185, 186. Article by H. A. Murray, presented before Texas Mid-Continent Oil and Gas Association 28th Annual Meeting, San Antonio, Texas, Oct. 17, 1947.