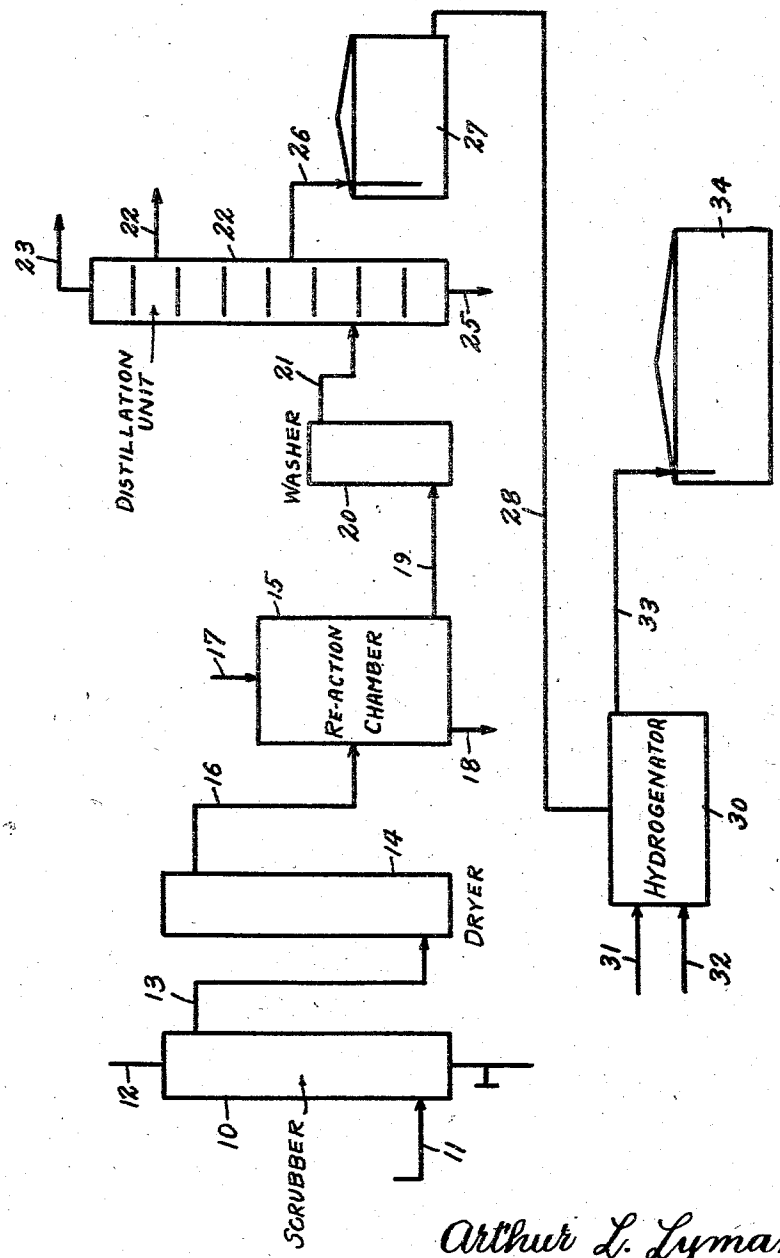
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SYNTHETIC HYDROCARBON OILS AND METHOD OF MAKING THE SAME

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This invention relates to a process whereby novel liquid hydrocarbon products may be produced and to the novel liquid oils resulting from such process. The liquid hydrocarbon products to which this invention is directed are saturated compounds composed essentially of branched chain paraffins. The products of this invention are also characterized by the fact that they are liquid at lower temperatures than any paraffins isolated or described heretofore and of corresponding molecular weights. In addition, the products of this invention are characterized by a peculiar hydrogen to carbon atomic ratio.

Heretofore stable, highly purified, saturated, petroleum oils have been derived from crude petroleum or coal tar oils by suitable fractionation followed by intensive chemical treatment generally with strong sulfuric acid. These acid-refining processes attempt to remove unsaturated and aromatic constituents present in the original oil being treated. For example, turbine oils, spray oils and medicinal or technical white oils are ordinarily obtained from petroleum oil distillates by treatment with large quantities of concentrated or fuming sulfuric acid, usually in several successive steps, with removal of sludge between each such acid-treating step. The purpose of this acid treatment is to remove from the petroleum lubricating oil distillates, unstable or oxidizable hydrocarbons in order that there may remain only those constituents which are inert and stable under all of the conditions of exposure to light, heat and/or air to which the products are subjected in use. In order to accomplish such substantially complete removal of unstable or oxidizable hydrocarbons, it is often necessary to use as much as 20 or more pounds of fuming sulfuric acid per gallon of finished oil produced. In such heavy acid treatment, yields are very low. Not only is the treating cost extremely high in this type of process but in addition the disposal of the large amounts of strong sulfuric acid sludge produced thereby creates a serious refinery problem.

This invention is directed to a process of producing stable, substantially saturated hydrocarbon products virtually free from unsaturated compounds and answering all of the requirements now believed desirable for turbine oils, transformer oils, spray oils, technical or medicinal white oils, etc., without the necessity of treating lubricating oil distillates as has hitherto been the case. Instead, liquid hydrocarbon products having unusually desirable characteristics and properties are produced in accordance with this process from acyclic or aliphatic olefines or homologues of ethylene, without the necessity of employing drastic treatments. The term "olefines" as used herein refers to aliphatic olefines substantially free from cyclic olefines, i. e., cyclo-olefines, cyclo-diolefines, cyclo-triolefines, and aliphatic diolefines and triolefines, etc.

Briefly stated, the process of this invention comprises polymerizing an olefine, and preferably a lower olefine or mixture of olefines, and then hydrogenating the polymerized olefine. Before hydrogenation, the polymerized olefines may be fractionated and the hydrogenation thus limited to the treatment of a specific fraction of the polymerized olefines. It has been found that in this manner, hydrocarbon products capable of remaining liquid at low temperatures, say at temperatures of 0° F. and below and consisting essentially of branched chain paraffins may be produced. Naphthenes may be present to some extent in the products of this invention but their formation may be minimized by carrying out the process under controlled conditions, referred to hereinafter. The term "naphthenes" as used herein is understood to refer to monocyclic saturated hydrocarbons having the formula C_nH_{2n}. Furthermore, it has been discovered that these products contain hydrogen and carbon in an atomic ratio greater than two to one, this ratio distinguishing the products of this invention from the products obtained by distillation and acid treatment of lubricating oil distillates. By applying the process to olefines of a particular molecular weight and by properly fractionating and hydrogenating, a resulting product may be obtained which has very unusual properties, adapting it to new uses heretofore not reached by hydrocarbon oils of the prior art. One of the unusual characteristics which may be selectively developed is the production of an extremely viscous, substantially colorless oil which is a true liquid free from cloud or wax crystals at temperatures as low as 0° F., said product having a viscosity at temperatures of 100° F. or even 200° F. which is several thousand times as high as the viscosities of previously made oils.

An object of this invention, therefore, is to disclose and provide a method of producing saturated hydrocarbons from aliphatic olefines.

An object of the invention is to disclose and provide a method of producing saturated hydrocarbon products consisting essentially of branched chain paraffins and naphthenes from gaseous or liquid hydrocarbons containing aliphatic olefines, by polymerizing the olefines and then hydrogenating the products of polymerization.

Another object of this invention is to disclose and provide a method of utilizing volatile unsaturated hydrocarbons such as olefines, in the preparation of saturated hydrocarbon products suitable for use as spray oils, turbine and transformer oils, and for medicinal and other purposes.

An object of this invention is to disclose and

provide a method by means of which it is possible to economically separate and produce fractions consisting essentially of a single series of hydrocarbons from hydrocarbon gases or liquids containing low boiling olefines.

Another object of this invention is to disclose and provide a process of producing substantially odorless, tasteless and colorless saturated hydrocarbon products from unsaturated low boiling olefines, by polymerizing such olefines and then hydrogenating the polymerized olefines.

A further object of this invention is to disclose and provide a process by means of which highly refined high boiling point saturated hydrocarbons may be economically produced from low boiling point olefines.

A still further object of this invention is to disclose and provide a method of producing substantially odorless, tasteless and colorless substantially saturated oils from hydrocarbons containing olefines by polymerizing the olefines in the presence of a suitable catalyst, fractionating the polymerized olefines, and then hydrogenating the polymerized fractions in the presence of catalyst.

Another object of this invention is to disclose and provide a method of making synthetic hydrocarbon oils which are saturated, composed essentially of branched chain paraffins and naphthenes, and which are liquid at a temperature of 0° F. and below, said saturated hydrocarbons containing hydrogen and carbon in an atomic ratio greater than two to one.

Another object of this invention is to disclose and provide saturated liquid hydrocarbons having a pour point of 0° F. and below and an empirical formula varying from C_nH_{2n} to C_nH_{2n+2}, said liquid hydrocarbon consisting of branched chain paraffins in major proportion.

A still further object is to disclose a novel hydrocarbon oil which is distinguishable from previously known oils in that it has a higher viscosity for a given specific gravity than oils known heretofore, remains a liquid free from cloud at temperatures as low as 0° F., and has an empirical formula ranging from C_nH_{2n} to C_nH_{2n+2}.

The characteristics, properties and uses of the novel hydrocarbon oil will be more fully understood from the following description of preferred methods of manufacture embraced by this invention. For purposes of facilitating understanding of the invention, the appended drawing illustrates diagrammatically the sequence of steps in the treatment of olefines in the manner described herein.

The products of this invention may be produced by applying the process of this invention to any aliphatic olefine or mixture of gases or liquids containing the same, and substantially free from cyclo-olefines, aliphatic diolefines or aromatics. Higher boiling olefines such as heptenes and octenes may be used, particularly when products of high viscosity index are desired, but for most purposes the lower boiling olefines such as ethylene propylene, the various butylenes and amylenes are preferred. All of these olefines may be classed as aliphatic unsaturated monoolefines. Diolefines and triolefines may be present in small proportion but are not desirable. Gaseous or liquid hydrocarbons consisting of or containing unsaturated cyclic hydrocarbons are not suitable for use in this process. Gases produced in the pyrogenetic cracking of petroleum oil for the production of motor fuels, etc., may be used as the source of charging stock. The reactive or polymerizable constituents of such gases comprise aliphatic monoolefines in major proportion but the gases may contain small amounts of aliphatic diolefines. Cyclic olefines are generally absent from such gases or if present are contained therein only exceedingly small and negligible amounts. Prior to the polymerization of the olefine-containing material (whether gaseous or liquid) it may be desirable to subject the olefine-containing material to a purifying step.

The first step in the process is the polymerization of the olefines. Polymerization is preferably carried out at a fairly low temperature, that is, at any temperature below about 350° F. The polymerization may take place at atmospheric temperature and pressure, or at superatmospheric temperature and atmospheric pressure. Preferably, the polymerization takes place in the presence of a suitable catalytic agent such as, for example, aluminum chloride, boron fluoride, ferric chloride, zinc chloride, etc., these catalysts being preferably anhydrous. Of these mentioned, aluminum chloride and boron fluoride have been found to be best. When a gas containing olefine is being treated, the catalytic agent may be suspended in a suitable carrier such as petroleum ether, or any highly refined petroleum distillate or a portion of a previously polymerized product. A carrier may also be used when treating a liquid charging stock. In actual operation, the carrier is present in relatively small amounts in comparison to the total product.

After polymerization, the catalyst together with its polymerized addition products is separated from the polymerized olefines or polymerized olefines and carrier. The carrier is then separated from the polymerized olefines. The polymerized olefines thus produced may be fractionated into fractions suitable for various purposes. Some of these polymerized olefines are valuable per se as constituents of anti-knock motor fuels. If the novel saturated oils of this invention are to be produced, however, the polymerized olefines, in toto or fractions thereof, are subjected to a saturating hydrogenation (to be distinguished from a cracking hydrogenation). The hydrogenating step is preferably carried out at superatmospheric temperature and superatmospheric pressure in the presence of a suitable hydrogenating catlyst such as, for example, nickel, platinum, palladium, cobalt, etc. Temperatures may vary from about 100° F. to 450° F. or 500° F. and pressures of from about 1 atmosphere to about 50 atmospheres may be employed during this step.

For example, a complete process of polymerizing olefines when applied to gases produced in the pyrogenetic cracking of petroleum oil, may include the following steps:

The olefine-containing gas is treated with an aqueous caustic soda solution for the removal of hydrogen sulfide and mercaptans. The resulting gas in a particular illustrative example had the following composition:

	Per cent by volume
Hydrogen and methane	13.6
Ethane	23.7
Ethylene	2.5
Propane	26.1
Propylene	16.2
Butane	9.7
Butenes	8.2

It will be seen that the gas contained 26.9% of olefines. This gas was then contacted with

anhydrous aluminum chloride suspended in petroleum ether held at room temperature and atmospheric pressure. An aluminum chloride tar and an oily liquid were obtained as immiscible layers. Upon continuous bubbling of the gases through the aluminum chloride-ether suspension, these layers increased gradually in volume and about 5 gallons of polymers (exclusive of the ether originally present as the carrier) per pound of anhydrous aluminum chloride, were produced before the activity of the catalyst had appreciably diminished. The gaseous olefines were substantially entirely polymerized in the process and the polymers were contained within the oily liquid together with the inert light solvent. The tar contained aluminum chloride and polymerization or addition products in loose chemical combination.

The oily liquid was separated from the tar and washed free of suspended aluminum chloride. The resulting mixture consisted of polymers and the ether. This mixture was then distilled to remove the original light solvent and the saturated gaseous hydrocarbons absorbed in the contacting process. The resulting product was a hydrocarbon oil with an initial boiling point of 200° F. at atmospheric pressure and an end point above 700° F. at 10 mm. of mercury. This product consisted entirely of olefines; no paraffins or naphthenes were produced. The characteristics of this polymerized product were as follows:

Specific gravity	0.826
A. P. I. gravity	40.0
Viscosity Saybolt at 100° F	91
Viscosity Saybolt at 130° F	59
Viscosity Saybolt at 210° F	38
Molecular weight	260
Bromine No	0.62
Olefines, per cent	100
Carbon, do	85.6
Hydrogen, do	14.4
Sulfur, do	.02
Empirical formula	C_nH_{2n}

Similar polymerization may be carried out at temperatures up to about 350° F. At temperatures above about 350° F. when aluminum chloride is the polymerizing agent used, decomposition of the polymers with the production of low boiling point paraffins begins to be apparent. For this reason, temperatures above about 350° F. should be avoided if a product consisting essentially of olefines is desired. As a matter of fact, very long time of contact of the polymers with the polymerizing catalyst at temperatures of 250° F. and above is conducive to the formation of naphthenes as well as olefines.

In general, it may be stated that the time of contact of the original olefines with the polymerizing catalyst determines the percentage of heavy to light olefine polymers and consequently the boiling point range of the polymerized product produced. For example, long time of contact with the polymerizing catalyst is conducive to the production of heavy or high boiling polymers while short time of contact with early separation of the produced polymers from the polymerizing catalyst decreases the yield of heavy polymers and increases the yield of light and intermediate boiling polymers.

In other words, by regulating the time of contact between the olefines and the polymerizing catalyst, the characteristics of the polymerized product may be controlled. If, for example, it is desired to produce a product suitable for use as a motor fuel for internal combustion engines (similar in characteristics to gasoline and kerosene), the time of contact should be short and the polymerized components should be removed from the contact area and from the polymerizing catalyst shortly after the formation of the polymers. If, however, it is desired to produce a polymerized product suitable for subsequent use in the manufacture of viscous oils such as turbine oils or white medicinal oils, the time of contact should be lengthened so as to produce higher boiling point polymerized olefines.

A polymerized product such as, for example, the product whose characteristics are specifically defined hereinabove, may then be fractionated to form polymerized stocks suitable for various special purposes. The polymerized product specifically defined hereinabove, upon fractionation, produced about 20% by volume of a gasoline type distillate having an initial boiling point of about 200° F. and an end point of 437° F. This distillate, composed of olefines having from 6 to 12 carbon atoms, is an excellent non-detonating fuel suitable for use in high compression internal combustion engines. This gasoline-type fraction of polymerized olefines had better anti-knock properties than straight run California gasolines containing 50% by volume of xylol, benzol or toluol. This property is due to the fact that olefines, naphthenes, aromatics or branched chain paraffins, which are the most desirable non-detonating hydrocarbons, are in part removed by acid treatment of gasoline distillates whereas the straight chain paraffins which possess the least desirable anti-knock properties, remain in the finished product. The olefine polymers obtained in the first step of this process, however, require but slight acid treatment in order to meet standard fuel requirements and possess very high anti-knock properties. In addition, the polymerized olefines having a boiling point range of between 200 and 437° F. obtained by fractionating the total polymerized product, contained less than 0.1 sulfur and showed no deposition of gum in the standard copper bowl test.

The total polymerized olefine product was further fractionated so as to produce about 25% by volume of a fraction boiling between about 400° F. at atmospheric pressure and 475° F. at 10 mm. of mercury. This fraction had the following characteristics:

Specific gravity	0.815
A. P. I. gravity	42.0
Flash	150
Viscosity Saybolt at 100°	46
Pour	−5
Refractive index	1.455
Molecular weight	240
Carbon, per cent	85.7
Hydrogen, do	14.3
Olefines, do	100
Empirical formula	C_nH_{2n}

Polymerized olefines boiling between about 300° F. at atmospheric pressure and 500° F. at 10 mm. of mercury, are suitable for use in the process of this invention in the manufacture of saturated, stable and novel oils suitable for many uses, such as transformer oils, insecticidal spray oils, etc. Higher boiling fractions of polymerized olefines such as, for example, fractions boiling between about 450° F. at 10 mm. of mercury and 650° F. at 10 mm. of mercury are par-

ticularly suitable for use as a stock in the manufacture of hydrogenated synthetic oils of higher viscosity adapted for use as turbine oils, technical and medicinal white oils, etc.

Illustrative of the hydrogenating step of this process, the following results were obtained by hydrogenating an intermediate polymerized olefine fraction produced as described hereinabove, the hydrogenation being carried out in this specific example at about 500° F. and 350 pounds hydrogen pressure, using nickel as a catalyst, the nickel being carried on a porous inert material such as diatomaceous silica. The following table shows the characteristics of such an intermediate fraction before and after hydrogenation:

	Boiling range: From 400° atm. pr. to 500° at 10 mm. pr.	
	Before	After
Specific gravity	0.8115	0.8028.
A. P. I. gravity	42.9	44.8.
Refractive index	1.4564	1.4500.
Viscosity Saybolt at 100°	55	52.
Percent carbon	85.7	85.2.
Percent hydrogen	14.3	14.8.
Bromine No.	0.59	0.016.
Percent unsaturated	100	2.0.
Empirical formula	C_nH_{2n}	$C_nH_{2n+1.3}$.
Pour point		Below −25° F.
Molecular weight		260.

Attention is called to the fact that before hydrogenation, the fraction was completely unsaturated and composed of olefine-type hydrocarbons. The hydrogenation almost completely saturated the hydrocarbons, the product being 97.4% saturated and composed essentially of branched chain paraffins in preponderant part and an immaterial quantity of naphthenes. It is to be noted that the viscosity at 100° F. has been changed but very slightly. It is also to be noted that the carbon-hydrogen ratio indicates an empirical formula of $C_nH_{2n+1.3}$.

The hydrogenation of heavier polymers, that is, polymers having a boiling point range of between about 475° F. and 600° F. at 10 mm. of mercury, produces substantially water-white odorless and tasteless oils which are liquid at low temperatures, say at temperatures of 10° F. or lower. The effect of hydrogenation of a fraction of this character is illustrated in the following tabulation:

	Boiling range: From 500° at 10 mm. pr. to 600° at 10 mm. pr.	
	Before	After
Specific gravity	0.8337	0.8192.
A. P. I. gravity	38.2	41.2.
Refractive index	1.4675	1.4570.
Viscosity Saybolt at 100°	407	185.
Molecular weight	391	349.
Percent carbon	85.7	85.3.
Percent hydrogen	14.3	14.7.
Bromine No.	0.41	0.015.
Percent unsaturate	100	3.3.
Empirical formula	C_nH_{2n}	C_nH_{2n+1}.
Type of hydrocarbon	Olefine	Substantially branched chain paraffin.

The polymerized olefines having a boiling point range of between 500 and 600° F. at 10 mm. of mercury, described immediately hereinabove, were also hydrogenated at about 500° F. and 350 pounds hydrogen pressure in the presence of a nickel catalyst. It is to be noted that unsaturation was decreased from 100% to 3.3%. The time required for hydrogenation under these conditions was about 4 hours. The product was substantially incapable of further hydrogenation under these conditions.

The hydrogenated oils may or may not be further treated. Under certain conditions and for the production of special products, the hydrogenated oils may be subjected to a light acid treatment and contacted with an adsorbent such as fuller's earth. For example, medicinal white oils may be produced by the hereinabove described process of polymerization and hydrogenation, the hydrogenated product being then treated lightly with fuming sulfuric acid (about 3 pounds of 15% acid), the acid treatment being followed by filtration with fuller's earth. Synthetic medicinal white oils produced in this manner may be compared with white oils prepared from California, Pennsylvania and Mid-Continent crude petroleums as follows:

	Synthetic white oil	White oils from crudes		
		Calif.	Penn.	Mid-Cont.
Specific gravity	0.831	0.887	0.852	0.867
A. P. I. gravity	38.8	28.0	34.5	31.7
Flash	240	365	440	395
Viscosity Saybolt at 100°	270	270	218	200
Viscosity Saybolt at 130°	126	125	116	106
Viscosity Saybolt at 210°	47	47	50	47
Pour, ° F.	−25	−20	35	30
Cloud point, ° F.	Below −70	−10	45	40
Refractive index	1.4670	1.4820	1.4705	1.4700
Percent carbon	85.4	86.4	85.8	86.0
Percent hydrogen	14.6	13.6	14.2	14.0
Empirical formula	C_nH_{2n+1}	C_nH_{2n-4}	C_nH_{2n-1}	C_nH_{2n-2}
Bromine No.	0	0	0	0
Molecular weight	400	460	470	445
Percent unsaturates	0	0	0	0
Sol. 98.5% H_2SO_4	0	0	0	0

It is to be noted in the above tabulation that the synthetic white oil produced by the method of this invention contains hydrogen and carbon in an atomic ratio greater than two to one. Furthermore, it is to be noted that the pour point of the synthetic products is −25° F. It is also to be noted that the oils of this invention when compared with petroleum oils made by previously known processes and having the same viscosity will be found to have a lower specific gravity. Furthermore, the mean molecular weight of the synthetic product of this invention is lower than the mean molecular weight of previously made oils having a comparable viscosity. A highly acid refined petroleum oil made in the usual manner and having a viscosity of 56 S. U. at 100° F. will have a molecular weight of about 280 and a specific gravity of 0.8660 but an oil made in accordance with this invention having a viscosity of only 52 S. U. will have a specific gravity of only 0.8063 and a molecular weight of 265.

Oils of the molecular weights corresponding to these synthetic oils, having empirical formulas between C_nH_{2n} and C_nH_{2n+2} and possessing pour points or melting points similar to those of the synthetic oils, have never been isolated from petroleum oils or even described in the chemical literature, to our knowledge. Thus, saturated paraffins described heretofore, having molecular weights of the materials herein described, are solid waxes. For example, dodecane ($C_{12}H_{26}$), which is a typical straight chain paraffin hydrocarbon, has a molecular weight of 170 but has a melting point of about 7° F. Straight chain paraffin hydrocarbons of higher molecular weight have very much higher melting points and therefore none of these are liquids at temperatures of 0° F. as is the case with the novel hydrocarbon

product of this invention. Nor is it possible to duplicate the products of this invention by forming mixtures of naphthenes (C_nH_{2n}) with normal paraffins (C_nH_{2n+2}) and thereby form a mixture which is a liquid at 0° F. and which has a molecular weight of between about 200 and 700 and at the same time a hydrogen to carbon atomic ratio greater than 2 to 1. The novel products of this invention generally have molecular weights ranging from between 200 and 700 or between about 300 and 500 but oils having mean molecular weights of 800, 1000, 1400, or even higher can be produced. These novel oils are characterized by the fact that they are substantially free from cloud or crystals of wax at temperatures as low as 0° F., have a very much higher viscosity for the same specific gravity than other oils known heretofore, and are virtually completely saturated, consisting essentially of branched chain paraffins and have hydrogen and carbon in an atomic ratio greater than 2 to 1.

Freedom from cloud when subjected to temperatures of 0° F. or therebelow is used in identifying products of this invention, particularly those having high mean molecular weights, instead of a pour point of 0° F. since oils of high viscosity will not respond to the A. S. T. M. test for pour point. For example, a water-white oil made in accordance with this invention had the following characteristics:

Gravity A. P. I. at 60° F	27.0
Specific gravity at 60° F	0.893
Viscosity at 100° F. S. S. U	155,000
Viscosity at 210° F. S. S. U	2580
Viscosity index (Dean & Davis)	112
Cloud point ° F	below −70
Pour point	40
Molecular weight	1380

The pour point of 40° F. is not a valid determination since the oil is too viscous to respond accurately to the test. The lack of cloud at −70° F. showed that no formation of solid phase took place at even this extremely low temperature, the oil remaining a liquid.

The product may occasionally contain some naphthenes in addition to the branched chain paraffins but as noted above, when temperatures of polymerization are kept below about 350° F. and when undue length of time of contact between polymers and polymerizing catalyst is avoided, naphthene formation is suppressed. In substantially all cases, more than 50% of an oil made in accordance with this invention will consist of branched chain paraffins and in most instances it will contain 70% to 90% of branched chain paraffins, and for this reason the products are said to be composed of branched chain paraffins in major proportion.

The polymerized and hydrogenated product described herein is therefore a novel, new hydrocarbon compound capable of being employed in a large number of different ways. The use of this new product in spray oils, lubricating oils, turbine oils, medicinal oils, etc., has been noted. It can be employed to good advantage in lubricating motor valves or wherever it is desired to obtain a lubricating film at high temperatures. Due to the high hydrogen to carbon ratio, the products of this invention do not carbonize upon combustion. For instance, when employed in automobile motor valve lubrication, either by introduction to the fuel or as such in overhead valve oiling mechanisms, combustion is complete with no carbon or coke formation in the motor cylinders, as is the case with petroleum lubricating oils when employed similarly. Also in the lubrication of machinery at such high temperatures that ordinary petroleum lubricants decompose with the deposition of asphalty and tarry or coke residues, the products of this invention decompose with the formation of volatile products only, without the deposition of tar, asphalty matter or coke. The rate of disappearance of the truly lubricating film itself is no faster than with ordinary petroleum lubricating oils but upon disappearance the surfaces desired to be lubricated remain clean, thereby preventing the formation of score marks due to coky residues and the actual lubricating service performed by the products of this invention is vastly superior and more long-lasting.

As shown in the drawing, the gaseous or liquid mixtures containing olefines may be first scrubbed with any suitable material, such as sodium hydroxide, in the scrubbing tower 10 to remove hydrogen sulfide and mercaptans, the olefine-bearing gas or liquid being admitted by the line 11 and passed upwardly through a downwardly ascending current of the washing material admitted by line 12. The washed olefine-bearing material is then discharged by line 13 and passed through a drier 14. The dry sulfur-free olefines are then polymerized in the reaction chamber 15, being supplied thereto by means of line 16. The line 17 indicates an inlet for the catalyst, such as aluminum chloride, whereas the line 18 represents a discharge line for the sludge or other reaction products. The polymerized olefines may then be discharged by line 19 into a washer 20 so that the catalyst may be separated from the polymerized products. The polymerized products are in turn sent by line 21 into a distillation unit 22 to remove a part of the raw material which has not been polymerized, that is, saturated hydrocarbon, and to separate it into the desired fractions.

Line 23 indicates a discharge of saturated hydrocarbon gas, light oil being discharged at 24 and heavy bottoms at 25. The desired polymerized fraction is charged at 26 into a suitable storage 27 from whence it is conveyed by line 28 into the hydrogenating unit 30 supplied with hydrogen as by line 31, and a suitable catalyst, as by line 32. The hydrogenated oil is then sent by line 33 into storage 34.

The process described hereinabove therefore consists essentially of three steps:

(1) The polymerization of gaseous or liquid aliphatic olefines free from cyclic olefines or unsaturated cyclic hydrocarbons for the production of higher boiling point olefines.

(2) The separation by fractionation of the produced higher boiling point olefines into fractions of any desired viscosity or boiling point range.

(3) The hydrogenation of some or all of the separated fractions for the production of saturated hydrocarbons of novel characteristics.

Although the molecular configuration of the olefine polymers differs with the molecular weight of the olefines polymerized, the viscosity-temperature relationship is the only characteristic apparently affected by the molecular weight of the olefines chosen for use in the process. Generally stated, the lower olefines produce polymers consisting of a number of short, branched, side chains while the higher olefines produce polymers of the same or similar molecular weights but with somewhat fewer but longer side chains. The

polymers produced from the higher olefines possess higher viscosity indices than those produced by the polymerization of the lower olefines.

Any method of hydrogenation capable of accomplishing the desired results can be used. As stated hereinabove, the hydrogenation of the olefine polymers in liquid phase, using nickel as a catalyst, is preferably carried out at a superatmospheric temperature and superatmospheric pressure.

The products produced by hydrogenation do not appear to vary with the method employed in obtaining the olefine polymers. For example, the products obtained by hydrogenating olefine polymers obtained by contacting with the polymerizing catalyst at temperatures above atmospheric, are saturated compounds substantially identical in all respects with those obtained upon the hydrogenation of olefine polymers produced by contact with the polymerizing catalyst at atmospheric temperatures.

Those skilled in the art will readily appreciate the advantages obtained by the combination of steps disclosed hereinabove and the novel character of the products produced.

All changes and modifications as come within the scope of the appended claims are embraced thereby.

This application is a continuation-in-part of Serial No. 605,110, filed April 13, 1932.

We claim:

1. A process of producing from the gases resulting from the pyrogenetic cracking of the petroleum oil for the production of motor fuels substantially saturated liquid hydrocarbon products having a pour point of 0° F. or therebelow and containing hydrogen and carbon in an atomic ratio greater than 2 to 1, comprising: polymerizing the mixture of hydrocarbon gas containing polymerizable constituents, said polymerizable constituents virtually consisting of aliphatic mono-olefines of molecular weight no higher than octene and being substantially free from cyclo-olefines and aromatic hydrocarbons, with a catalytic agent of the group of aluminum chloride, boron fluoride, ferric chloride and zinc chloride; fractionating the resulting polymers to form a fraction having a boiling point range of between 300° F. at atmospheric pressure and 650° F. at 10 millimeters of mercury, and then subjecting the fractionated polymers to a saturating hydrogenation without the formation of hydrocarbons of lower molecular weight.

2. A process of producing from the gases resulting from the pyrogenetic cracking of the petroleum oil substantially saturated liquid hydrocarbon products having a pour point of 0° F. or therebelow and containing hydrogen and carbon in an atomic ratio greater than two to one, comprising: polymerizing the mixture of hydrocarbon gases containing polymerizable constituents, said polymerizable constituents virtually consisting of aliphatic mono-olefines of molecular weight no higher than octene and being substantially free from cyclo-olefines and aromatic hydrocarbons, with a catalyst from the group consisting of anhydrous aluminum chloride and boron fluoride, and at a temperature of below 350° F.; fractionating the resulting polymers; and then subjecting the fractionated polymers to a saturating hydrogenation without the formation of hydrocarbons of lower molecular weight, at a superatmospheric temperature and pressure.

3. A process of producing from the gases resulting from the pyrogenetic cracking of petroleum oil substantially saturated liquid hydrocarbon products having a pour point of 0° F. or therebelow, and having an empirical formula varying from C_nH_{2n} to C_nH_{2n+2} comprising polymerizing the mixture of hydrocarbon gases containing polymerizable constituents, said polymerizable constituents virtually consisting of aliphatic mono-olefines of molecular weight no higher than octane, and said mixture being substantially free from cyclo-olefines and aromatic hydrocarbons with a catalytic agent of the group of aluminum chloride, boron fluoride, ferric chloride, and zinc chloride, fractionating the resultant polymers and then subjecting the resultant polymers to a saturating hydrogenation without the formation of hydrocarbons of lower molecular weight in which the saturating hydrogenation is carried out at superatmospheric temperature and pressure.

4. A process of producing substantially saturated liquid hydrocarbon products having a pour point of 0° F. or therebelow and containing hydrogen and carbon in an atomic ratio greater than 2 to 1, comprising: polymerizing a mixture of hydrocarbons containing polymerizable constituents, said polymerizable constituents virtually consisting of aliphatic mono-olefines of molecular weight no higher than octene and being substantially free from cyclo-olefines and aromatic hydrocarbons, with a catalyst from the group consisting of anhydrous aluminum chloride and boron fluoride; separating the catalyst from the polymers, and then subjecting the resulting polymers to a saturating hydrogenation at a temperature of between 100° F. and 450° F. at a pressure of from 1 to 50 atmospheres without the formation of hydrocarbons of lower molecular weight.

5. A process of producing substantially saturated liquid hydrocarbon products having a pour point of 0° F. or therebelow and containing hydrogen and carbon in an atomic ratio greater than 2 to 1, comprising: polymerizing a mixture of hydrocarbons containing polymerizable constituents, said polymerizable constituents virtually consisting of aliphatic mono-olefines of molecular weight no higher than octene and being substantially free from cyclo-olefines and aromatic hydrocarbons, with a catalyst from the group consisting of anhydrous aluminum chloride and boron fluoride, wherein a temperature of below 350° F. is employed during polymerization, separating the catalyst from the resulting polymers, and then subjecting the resulting polymers to a saturating hydrogenation at a temperature of between 100° F. and 450° F. and at a pressure of from 1 to 50 atmospheres without the formation of hydrocarbons of lower molecular weight.

6. A process of treating aliphatic olefine-containing gases resulting from the pyrogenetic cracking of petroleum oil for the production of motor fuels and substantially free of hydrogen sulfide and mercaptans for the production of saturated liquid hydrocarbon products, comprising: contacting the said gaseous mixture containing lower aliphatic olefines and substantially free from cyclic olefines and aromatics, with a catalytic agent of the group of aluminum chloride, boron fluoride, ferric chloride and zinc chloride suspended in a liquid carrier at a temperature below about 350° F. to polymerize said olefines, separating said olefine polymers from the catalytic agent and carrier, fractionating the resultant polymers and then subjecting said fractionated olefine polymers to a saturating hydrogenation at a superatmospheric temperature and

pressure without forming hydrocarbons of lower molecular weight so as to produce a liquid hydrocarbon product composed essentially of branched chain paraffins and having an empirical formula varying from C_nH_{2n} to C_nH_{2n+2}.

7. A process of treating olefines for the production of saturated liquid hydrocarbon products comprising: polymerizing olefines lower than heptene and substantially free from cyclic olefines and aromatics, fractionating the olefine polymers to produce a fraction having a boiling point range between 300° F. and 650° F. at 10 mm. mercury pressure, and then subjecting the fractionated olefine polymers to a saturating hydrogenation without forming hydrocarbons of lower molecular weight, so as to form a liquid hydrocarbon product consisting essentially of paraffins and naphthenes and substantially free from unsaturated compounds.

8. A process of treating olefines for the production of saturated liquid hydrocarbon products comprising: polymerizing aliphatic olefines lower than heptene and substantially free from cyclic olefines and aromatics in the presence of a suitable catalyst, separating the olefine polymers from the catalyst, fractionating the olefine polymers to form a fraction having a boiling point range at 10 mm. mercury pressure of between about 450° F. and 650° F., and then subjecting said olefine polymer fraction to a saturating hydrogenation at superatmospheric temperature and pressure without forming hydrocarbons of lower molecular weight, so as to form a liquid hydrocarbon product consisting essentially of branched chain paraffins and naphthenes and composed of hydrocarbons containing hydrogen and carbon in an atomic ratio greater than 2 to 1.

9. A process of treating olefines for the production of saturated liquid hydrocarbon products comprising: polymerizing aliphatic olefines lower than heptene and substantially free from cyclic olefines and aromatics, in the presence of a suitable catalyst at a temperature below about 350° F., separating the olefine polymers from the catalyst, fractionating the olefine polymers to form a fraction having a boiling point range at 10 mm. mercury pressure of between about 450° F. and 650° F., and then hydrogenating said olefine polymer fraction at superatmospheric temperature and pressure without forming hydrocarbons of lower molecular weight, to form a liquid hydrocarbon product consisting essentially of branched chain paraffins and naphthenes and composed of hydrocarbons having a mean molecular weight of between about 300 and 500 and containing hydrogen and carbon in an atomic ratio greater than 2 to 1.

10. A process of treating olefines for the production of saturated liquid hydrocarbon products comprising: contacting a gaseous mixture containing aliphatic olefines lower than heptene with a catalytic agent suspended in a liquid carrier to polymerize said olefines, separating said olefine polymers from the catalytic agent and carrier, fractionating said olefine polymers to produce a fraction having a boiling point range at 10 mm. of mercury of between 450° F. and 650° F., and then hydrogenating said fraction of olefine polymers without forming hydrocarbons of lower molecular weight, so as to produce a hydrocarbon product consisting essentially of paraffins and naphthenes and having a pour point of 0° F. and therebelow.

11. A process of treating olefines for the production of saturated liquid hydrocarbon products comprising: contacting a gaseous mixture containing lower aliphatic olefines and substantially free from cyclic olefines and aromatics, with a catalytic agent suspended in a liquid carrier at a temperature below about 250° F. to polymerize said olefines, separating said olefine polymers from the catalytic agent and carrier, fractionating said olefine polymers to produce a fraction having a boiling point range at 10 mm. of mercury of between 450° F. and 650° F., and then subjectingsaid fraction of olefine polymers to a saturating hydrogenation without forming hydrocarbons of lower molecular weight, so as to produce a hydrocarbon product consisting essentially of paraffins and naphthenes and having a pour point of 0° F. and therebelow.

12. A process of treating aliphatic olefines for the production of saturated liquid hydrocarbon products comprising: contacting a gaseous mixture containing lower aliphatic olefines and substantially free from cyclic olefines and aromatics, with a catalytic agent suspended in a liquid carrier at a temperature below about 350° F. to polymerize said olefines, separating said olefine polymers from the catalytic agent and carrier, fractionating said olefine polymers to produce a fraction having a boiling point range at 10 mm. of mercury of between 450° F. and 650° F., and then subjecting said fraction of olefine polymers to a saturating hydrogenation without forming hydrocarbons of lower molecular weight, so as to produce a hydrocarbon product consisting essentially of paraffins and naphthenes having a mean molecular weight of between about 330 and 480 and containing hydrogen and carbon in an atomic ratio greater than 2 to 1.

13. A process of producing substantially saturated liquid hydrocarbon products having a pour point of 0° F. or therebelow and containing hydrogen and carbon in an atomic ratio greater than 2 to 1, comprising: polymerizing a normally gaseous mixture containing polymerizable constituents, said polymerizable constituents virtually consisting of aliphatic mono-olefines of molecular weight no higher than amylene and being substantially free from cyclo-olefines and aromatic hydrocarbons, with a catalyst from the group consisting of anhydrous aluminum chloride and boron fluoride, and at a temperature of below 350° F.; separating the resulting polymers from the catalyst; and then subjecting the resulting separated poylmers to a saturating hydrogenation without the formation of hydrocarbons of lower molecular weight at a temperature of between 100° F. and 450° F. and at a pressure of from 1 to 50 atmospheres.

14. A process of producing from the gases derived from the pyrogenetic cracking of petroleum oil to form motor fuels substantially saturated liquid hydrocarbon products having a pour point of 0° F. or therebelow and containing hydrogen and carbon in an atomic ratio greater than 2 to 1, comprising: polymerizing the said normally gaseous mixture containing polymerizable constituents, said polymerizable constituents virtually consisting of aliphatic mono-olefines of molecular weight no higher than amylene and being substantially free from cyclo-olefines and aromatic hydrocarbons, with a catalyst from the group consisting of anhydrous aluminum chloride and boron fluoride, and at a temperature of below 350° F.; fractionating the resulting polymers; and then subjecting the fractionated polymers to a saturating hydrogenation without the formation of hydrocarbons

of lower molecular weight, at a superatmospheric temperature and pressure.

15. A process of producing gases derived from the pyrogenetic cracking of petroleum oils which are substantially free of hydrogen sulfide and mercaptans substantially saturated liquid hydrocarbon products having a pour point of 0° F. or therebelow and containing hydrogen and carbon in an atomic ratio greater than 2 to 1, comprising: polymerizing the said normally gaseous mixture containing polymerizable constituents, said polymerizable constituents virtually consisting of aliphatic mono-olefines of molecular weight no higher than amylene and being substantially free from cyclo-olefines and aromatic hydrocarbons, with a catalyst from the group consisting of anhydrous aluminum chloride and anhydrous boron fluoride, at a temperature of below about 350° F.; fractionating the resultant polymers and then subjecting the fractionated polymers to a saturating hydrogenation at a superatmospheric temperature and pressure, without the formation of hydrocarbons of lower molecular weight.

16. A process of producing substantially saturated liquid hydrocarbon products having a pour point of 0° F. or therebelow and containing hydrogen and carbon in an atomic ratio greater than 2 to 1, comprising: polymerizing a normally gaseous mixture containing polymerizable constituents, said polymerizable constituents virtually consisting of aliphatic mono-olefines of molecular weight no higher than amylene and being substantially free from cyclo-olefines and aromatic hydrocarbons, with a suitable catalyst of the group of anhydrous aluminum chloride, boron fluoride, ferric chloride and zinc chloride at a temperature of below about 350° F., fractionating the resulting polymers to form a fraction having a boiling point range of between 300° F. at atmospheric pressure and 650° F. at 10 mm. of mercury pressure; and then subjecting the fractionated polymers to a saturating hydrogenation at a superatmospheric temperature and pressure without the formation of hydrocarbons of lower molecular weight.

17. As a new article of commerce, a saturated stable hydrocarbon oil, liquid at normal temperatures, composed of branched chain paraffins in major proportion, having an empirical formula of C_nH_{2n} to C_nH_{2n+2}, and characterized by a pour point of 0° F. or therebelow, freedom from cloud at 0° F., and by a higher viscosity than that of normal acid refined mineral oils of the same specific gravity and of a comparable molecular weight.

18. As an article of manufacture, a liquid hydrocarbon product consisting virtually of hydrogenated and saturated polymerized aliphatic mono-olefines, having a molecular weight of between 200 and 700, containing hydrogen and carbon in an atomic ratio greater than two to one, said product having a pour point of 0° F. and therebelow.

19. As an article of manufacture, a liquid hydrocarbon product consisting essentially of paraffins and naphthenes composed of hydrogenated and saturated polymerized aliphatic mono-olefines, having a molecular weight of between 300 and 500 and containing hydrogen and carbon in an atomic ratio greater than two to one, said product having a pour point of 0° F. and therebelow.

20. A saturated, stable hydrocarbon oil, derived from the mixed gases produced from the pyrogenetic cracking of petroleum oils, liquid at normal temperatures, having a lower specific gravity than ordinary petroleum oils of the same viscosity, said oil having an empirical formula of C_nH_{2n} to C_nH_{2n+2}, a pour point of 0° F. or therebelow, and being composed of branched chain paraffins in major proportion.

21. A saturated, stable hydrocarbon oil, derived from the mixed gases produced from the pyrogenetic cracking of petroleum oils, liquid at normal temperatures, having a lower specific gravity than ordinary petroleum oils of the same viscosity, said oil having an empirical formula of C_nH_{2n} to C_nH_{2n+2}, a pour point of 0° F. or therebelow, and more than 50% of said oil consisting of branched chain paraffins.

22. A stable hydrocarbon oil, derived from the mixed gases produced from the pyrogenetic cracking of petroleum oils, liquid at normal temperatures composed of hydrogenated and saturated polymerized aliphatic mono-olefines, more than 50% of said oil consisting of branched chain paraffins, said oil having a cloud point of 0° F. and therebelow and having an empirical formula of C_nH_{2n} to C_nH_{2n+2}.

23. A stable hydrocarbon oil, derived from the mixed gases produced from the pyrogenetic cracking of petroleum oils, liquid at normal temperatures composed of branched chain paraffins in major proportion, having a cloud point of 0° F. or therebelow and having an empirical formula of C_nH_{2n} to C_nH_{2n+2}.

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