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HYDROCARBON HYDRAULIC OIL

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ABSTRACT OF THE DISCLOSURE

A hydrocarbon hydraulic oil having a pour point below —40° F. coupled with stability at high temperature and a flash point above 430° F., suitable for use over the wide range of temperatures encountered in high altitude aviation service, comprised of linear paraffin hydrocarbon chains of 20 to 30 carbon atoms interrupted by a phenylene group positioned at least six atoms from the end of the chain.

This invention relates to a novel hydraulic oil and power transmission oil useful particularly in aircraft and missiles, and other machinery operating over a wide temperature range, and to the method of its manufacture. This novel hydraulic oil is a synthetic hydrocarbon oil of unique chemical composition which provides physical and chemical properties heretofore impossible or extremely difficult and expensive to obtain with petroleum fractions. More particularly, the invention relates to a hydrocarbon hydraulic oil having the desired physical and chemical properties to an enhanced degree, such as high flash point, high average boiling point, high thermal stability and high viscosity index in combination with a low pour point and relatively low viscosity.

In the operation of aircraft, especially at high altitudes and high speeds over a wide range of geographic conditions, it is essential that the oil have fluidity at very low temperatures and provide adequate viscosity and lubricity at high temperatures in the neighborhood of 250 to 450° F. Also, it is highly desirable for the oil to exhibit minimum volatility at the highest operating temperatures in order to avoid excessive losses from vaporization and to reduce the danger of fires and explosions in the event of leakage onto hot surfaces during operation. Thus the oil must have a high flash point. Furthermore, the oil must be extremely resistant to oxidation and capable of operating for long periods of time at elevated temperatures without sludging or other changes in properties which would be detrimental to the functioning of the hydraulic system. While missiles generally do not operate for a considerable length of time, nevertheless the physical properties of the oil over a wide temperature range may be extremely critical in this service.

The limitations of petroleum fractions in the production of hydraulic fluids for advanced aircraft are well known. A combination of drastic refining, including fractionation, acid and solvent refining, and/or hydrogenation (hydrofining), either preceded by or followed by conventional dewaxing, can be made to give oils from paraffinic crudes which have good physical properties at temperatures above

about 0° F. To obtain a pour point and fluidity at the temperatures considered necessary for military aircraft (about —70° F.) and supersonic commercial aircraft (about —40° F.) additional dewaxing of a drastic and expensive nature is required. Such deep refining and dewaxing are currently being practiced with relatively low viscosity oils in the range of 75 to 100 sec. Saybolt Universal at 100° F. It has not yet been demonstrated commercially that paraffinic oils of higher viscosity can be dewaxed to the necessary pour points required for military aircraft. A substitute for the deep dewaxed paraffinic oils that has been considered is a drastically refined naphthenic base oil from a substantially wax-free crude. Such naphthenic oils as are available are limited in viscosity-temperature susceptibility, showing a maximum viscosity index of about 75. Naphthenic stocks which yield oils of higher viscosity index contain excessive wax, making the oils inoperative at the necessary low temperatures. An even greater disadvantage exhibited by the naphthenic base hydraulic fluids is their lower boiling range and greater volatility for a given viscosity at 100° F. as compared to the paraffinic oils.

The synthetic hydrocarbon oil of this invention possesses both a high viscosity index and a low pour point, and in addition shows a higher boiling range and less volatility for a given viscosity than even the paraffinic oil. The chemical composition and methods of synthesis of the novel hydraulic fluid are shown hereinafter.

Many attempts have been made in the past to use various synthetic hydrocarbon oils as the base component for aircraft hydraulic fluids, but none of the synthetic fluids produced in the past have been satisfactory. Low molecular weight isobutylene polymers do not have sufficient thermal stability and generally exhibit only fair temperature-viscosity characteristics. The heavy residues produced in the manufacture of gasoline alkylate (as, for example, alkylation of isobutane with butylene using either H_2SO_4 or HF catalyst) have also been found unsatisfactory. When alkylated beneze (commonly called "polypropyl benzene" or "dodecyl benzene") became commercially available as a raw material for the manufacture of water soluble detergents, it was thought that the high boiling residues from the alkylation reaction might provide suitable base oils for the manufacture of hydraulic fluids, but such residues were not found useful for this purpose. Such detergent base hydrocarbons have been commonly produced by alkylating benzene with polymers of propylene containing lesser amounts of ethylene and butylene polymers. In preparation for the alkylation, the propylene polymer is fractionated to give on the average, 9 to 15 carbon atoms per molecule, depending on the desired properties of the alkylate. In commercial operations, the alkylation of benzene with the polypropylene fraction is conducted with the aid of either $AlCl_3$ or HF catalysts.

With either alkylating agent, a small portion of the reaction product boils above the range acceptable in the water soluble detergent base. Such residues have been used successfully in the manufacture of secondary plasticizers for vinyl resins, and as raw material for sulfonation to produce oil soluble sulfonates. These heavy residues, and fractions therefrom, exhibit fairly good thermal stability

but their outstanding deficiency as regards their use as hydraulic fluids is their exceptionally poor viscosity temperature characteristics as illustrated by viscosity indexes generally less than zero. Also, their volatility for a given viscosity is quite high and appears to be in keeping with their low viscosity index.

It is generally believed that synthetic oils produced by polymerizing olefins such as butylene, consist of highly branched chain structures and are substantially devoid of cyclic structures. Where the polymerized olefin is used to alkylate benzene, regardless of whether the alkylation is conducted with $AlCl_3$ or HF, the side chain has a branched structure. In the course of alkylation, it is apparent that some of the olefin polymerizes further before the alkylation actually takes place, with the result that high boiling residues are formed. It also appears that some of the high boiling residues are the result of polyalkylation giving di or tri alkyl benzenes. In any case, the side chains have a branched structure.

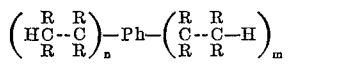
We have now discovered that oils having the characteristics desired in hydraulic oils to a high degree not heretofore found in hydrocarbon oils, can be made with hydrocarbon structures in which a linear paraffin chain is interrupted with a phenylene group. The preferred paraffin chain is from 20 to 30 carbon atoms in length, and the preferred number of carbon atoms in the hydraulic oil molecule is from about 26 to 36, with an empirical formula of C_nH_{2n-6}. A typical hydraulic oil having this chemical structure has the following properties:

Viscosity—SSU at 100° F.	141
Viscosity index	103
Boiling point—50% at 10 mm., ° F.	500
Distillation range—5–95% ASTM, ° F.	<61
Pour point, ° F.	—40
Flash point, ° F.	440
Specific gravity, 60/60° F.	0.864
Aniline point, ° F.	168

Oils having the desired phenylene interrupted paraffin structure may have the phenylene group positioned at various points along the chain from the 6th to the 15th carbon atom. The following structure formulas illustrate the composition of our new hydrocarbon hydraulic oils:

1. Generic formula

R=Hydrogen.



n=number of carbon atoms from 6 to 15 within the parenthesis.

m=number of carbon atoms from 14 to 24 within the parenthesis.

Ph=the phenylene group C_6H_4.

$n+m$=20 to 30

2. Specific example (a):

$$CH_3—(CH_2)_{12}—CH_2—C_6H_4—CH_2—(CH_2)_{12}—CH_3$$

3. Specific example (b):

$$CH_3—(CH_2)_{12}—CH_2CH_2—C_6H_4—CH_2—(CH_2)_{12}—CH_3$$

The synthesis of the phenylene interrupted straight chain hydrocarbons above described is illustrated in the following examples:

Example 1

Mono alkyl benzene was prepared by alkylating benzene with a C_6 to C_9 alpha olefine using HF as the alkylating agent and an excess of benzene of about 200% theory. The olefine employed was a fraction from the thermal cracking of paraffin wax and had a boiling range of about 140–300° F. After removal of unreacted benzene by distillation, the monoalkyl benzene was re-alkylated with an alpha olefin having 16–20 carbon atoms. After removal of unreacted olefin and HF, the finished alkylate had the properties shown in Column 3 in the table. This oil was subjected to laboratory tests to determine its suitability as hydraulic fluid and was found satisfactory.

Example 2

Benzene in excess, was alkylated with essentially a propylene dimer having an average carbon content of approximately 6 carbon atoms per molecule with essentially a straight chain structure. HF was used as the alkylating agent. After removing catalyst, unreacted propylene dimer and benzene were removed by distillation. The mono hexyl benzene obtained was then re-alkylated with a C_{16} to C_{20} alpha olefine using HF as the catalyst. The unreacted olefin and HF were removed and the finished alkylate showed the properties listed in Column 4 of the table. The oil was subjected to laboratory tests and found to be a suitable hydraulic fluid.

Example 3

Benzene was alkylated with a straight chain alpha chlorinated paraffin having 12–14 carbon atoms per molecule, using $AlCl_3$ as the catalyst. The catalyst was removed and the reaction product was distilled to separate unreacted benzene, monoalkyl and dialkyl benzene. Additional chloroparaffin was then added to the monoalkyl fraction and reacted in the presence of more $AlCl_3$ catalyst. The product was then neutralized to remove the catalyst, and distilled to recover the dialkyl benzene from higher boiling residue and monoalkyl benzene. The characteristics of the dialkyl benzene product are shown in Column 5 of the table. Note particularly the low pour point of —55° F. in combination with a flash point of 430° F.

Example 4

A petroleum fraction from a paraffin base crude such as Pennsylvania oil, boiling in the heavy naphtha range, was fractionated on a molecular sieve of the alumino silicate type, recovering the normal or straight chain hydrocarbons. Other types of molecular sieves can be used, such as urea crystals, preferably in combination with methanol. The normal hydrocarbons were chlorinated, primarily in the alpha position, employing an excess of hydrocarbon to avoid as much as possible, dichlorination. The monochlor paraffin thus obtained was reacted with benzene or with monoalkyl benzene, to yield dialkyl benzene in presence of a Friedel-Craft catalyst, such as HF, BF_3 or $AlCl_3$. The product of this reaction, which is a di-normal alkyl benzene or long chain paraffin hydrocarbon interrupted with a phenylene group, had a dark red color and other characteristics shown in Column 5 of the table. It was treated at ordinary temperature with 20 percent by volume of oleum (25% SO_3), neutralized with sodium hydroxide, washed and extracted with sec. butyl alcohol to remove sulfonated products. The treated oil was nearly colorless and was characterized by the test data given in Column 6 of the table.

Example 5

The oil shown in Column 7 of the table, was a long chain, linear alkyl benzene having only one alkyl group. It was prepared in the same way as the dialkyl oils just described, but employing a higher molecular weight alpha olefine, giving an oil with about the same viscosity at 210° F. Note that the viscosity index is quite high but that the pour point is also high, making it entirely unsuitable for most uses of hydraulic oils. Structurally, this oil is a paraffin hydrocarbon containing a phenyl group and contains no phenylene group.

Example 6

Thermal stability. The nearly colorless oil described in Column 6 of the table was sealed in a glass bomb tube without air and heated by submerging the tube in a bath of melted lead held at 650° F. for six hours. The oil remained colorless and suffered only a small reduction in viscosity.

	1	2	3	4	5	6	7
	Conventional petroleum hydraulic oil (130 neutral)	Branched chain dialkyl benzene	Linear chain dialkyl benzene from cracked paraffin		Linear chain dialkyl benzene from chlorparaffins molecular sieve		Linear chain mono-alkyl benzene
			(1)	(2)	Untreated	After 20% oleum treat	
Gravity °API at 60° F	30.9	30.0	32.1	32.3	28.9	31.9	
Viscosity at 100° F., SSU	137.0	158.0	140.9	126.8	146.0	135.4	80.3
Viscosity at 210° F., SSU	42.03	40.55	42.68	41.35	42.81	42.40	38.23
Viscosity index	92	−28	103	93	97	104	130
Pour point, ° F	+10	−45	−40	−25	−55	−75	+35
Flash point, ° F.C.O.C	390	345	440	410	430	430	415
Aniline Pt. (50/50) ° F	209	125.5	168.5	164.0	143.5	165.0	151
Boiling Range, 760 mm.:							
5%	684	624	690	693	708	688	
10%	686	636	694	695	710	694	
20%	693	640	706	700	712	698	
50%	740	661	715	712	721	708	
70%	733	678	721	722	725	711	
90%	757	700	736	740	733	723	
95%	760+	710	751	754	744	727	

Although we have decribed our invention by reference to specific examples thereof, we intend to include the following modifications and variations thereof. Thus, when alkylating benzene with monochlor paraffin, we find it difficult to exclude dichlor paraffin entirely and in fact the monochlor paraffin may include 5 to 10% of dichlor paraffin which, when reacted with benzene, yield polyphenylparaffin hydrocarbons of undesirable characteristics in hydraulic oil. When such polyphenyl paraffins are present, usually in the proportion of about 2 to 10%, they can be removed by refining with concentrated H_2SO_4, usually 10 to 25% by volume of oleum.

When preparing olefins for our process by cracking paraffin wax, it is desirable to employ thermal cracking at high temperature of about 900–1100° F. for short times of 10 seconds to 2 minutes. The cracked product is fractionated to obtain those fractions described hereinabove. Thus, an olefine fraction having about 10 to 14 carbon atoms has been found useful for the manufacture, through benzene alkylation, of water soluble detergents for household uses. The lighter and heavier olefins are then employed to alkylate benzene as described above for hydraulic oils of 25 to 35 carbon atoms.

Another source of alpha olefines for making our hydraulic oil is the natural fats which are all of a straight chain or normal structure. Thus we can hydrogenate olein or stearin to stearyl alcohol, employing a Raney nickel catalyst with hydrogen under high pressure. The alcohol is converted to the alpha chlor paraffin by treatment with PCl_5, $POCl_3$, HCl or other chlorinating agent. The resulting stearyl chloride, having 18 carbon atoms in normal arrangement, is then employed to alkylate benzene to form the phenylene interrupted paraffin hydrocarbon hydraulic oil of this invention. Lighter fats such as those found in palm oil, castor oil and coconut oil can be used to make hydraulic oils by this method.

Alpha chlor paraffins can also be made from unsaturated hydrocarbons by the oxo process in which an olefine is reacted with carbon monoxide and hydrogen to produce a primary alcohol having one more carbon atom. Conversion of the alcohol to the halide and alkylation of benzene as above described, then produces the dialkyl benzene or phenylene interrupted paraffin hydrocarbon which is the unique base of our hydraulic oil.

We prefer to compound our base hydraulic oil with various additives to improve resistance to oxidation, improve viscosity index, reduce wear, or for other purpose. Thus we can add an antioxidant in the amount of 0.1 to 1% and for this purpose we prefer to use a hindered phenol such as ditertiary butyl para cresol. Aromatic amines, amino phenols, phenothiazine, zinc dithiophosphate, etc. can also be used under some conditions. As antiwear agents, tricresyl phosphate in the amount of 0.5 to 5% has been found satisfactory. Viscosity index improvers of the polymethacrylate type such as the various grades of "Acryloid" made by the Rohm & Haas Company can be employed. We prefer to use the poly olefines, particularly the poly butenes, made by Standard Oil Co., New Jersey, under the name "Paratone N," or the polybutene made by Chevron Chemical Co. identified as No. 24 (840 M wt.), No. 32 (1200 M wt.) or No. 128 (1500 M wt.). These viscosity index improvers are fully compatible with the synthetic phenylene paraffin oil of this invention and are usually employed in the amount of 1 to 10% by weight.

Having thus described our invention, what we claim is:

1. A hydrocarbon hydraulic oil for high altitude aircraft and missiles characterized by a narrow boiling range of less than 61° F. between 5% and 95%, ASTM, a viscosity within the range of 80 to 200 Saybolt Universal at 100° F.; an average boiling point of about 500° F. at 10 mm. pressure; an A.P.I. gravity of about 28 to 33 at 60° F.; a pour point below −40° F., a flash point above 430° F., and a viscosity index of about 95 to 125, said hydrocarbon having the following formula:

$$R_1—Ph—R_2$$

wherein Ph is a phenylene group, R_1 is a linear chain paraffin hydrocarbon group having 6 to 15 carbon atoms and R_2 is a linear chain hydrocarbon group having from 12 to 22 carbon atoms, the total number of carbon atoms in said R groups being from 20 to 30, said linear chains consisting of un-branched chains of carbon atoms substituted by hydrogen.

2. The hydraulic oil of claim **1** wherein said phenylene group is an ortho phenylene group.

3. The hydraulic oil of claim **1** wherein said phenylene group is a para phenylene group.

4. The process of preparing the hydraulic oil of claim **1** which comprises the following steps:

(1) fractionating a petroleum distillate to obtain a fraction of 6 to 22 carbon atoms boiling in the range of about 150 to 600° F.;

(2) separating said fraction into linear and non-linear hydrocarbons by selective adsorption of linear components in a molecular sieve followed by desorption of said linear components;

(3) fractionating said linear hydrocarbon mixture into a series of narrow boiling fractions, each having a boiling range of less than 50° F.;

(4) Chlorinating said narrow fractions with not more than half the molar equivalent of chlorine, thereby producing preponderantly alpha monochlor paraffins;

(5) fractionally distilling each chloroparaffin fraction into a lower boiling, un-chlorinated hydrocarbon fraction, a monochlor paraffin fraction and a higher boiling polychlor paraffin residue;

(6) discarding the said polychlor paraffin residue and recycling the unchlorinated fraction to step (4) of the process;

(7) alkylating benzene with said monochlor paraffin fraction by the action of excess benzene in the presence of a Friedel-Craft catalyst;

(8) separating the resulting alkylated benzene by frac-

tional distillation into dialkyl benzene, mono alkyl benzenes and heavier polyalkyl benzene.

(9) realkylating the mono alkyl benzenes with monochlor paraffin, thereby producing further amounts of dialkyl benzenes for use in hydraulic oil.

5. The process of claim 4 wherein the lower boiling mono alkyl benzene fractions from step (8) are alkylated with the higher boiling monochlor paraffin fractions from step (5), thereby producing dialkyl benzenes with preponderantly unlike alkyl groups.

6. The process of preparing the hydraulic oil of claim 1 comprising the following steps:

(1) alkylating benzene with propylene dimer, and a Friedel-Craft's catalyst, thereby producing monohexyl benzene,

(2) separating by fractional distillation, said monohexyl benzene from unalkylated benzene and polyalkyl benzene,

(3) alkylating said monohexyl benzene with an alpha-chlor linear paraffin hydrocarbon of 14 to 22 carbon atoms,

(4) separating by fractional distillation the resulting monoalkyl, hexyl benzene from lower boiling unreacted hexyl benzene and from higher boiling residue;

(5) recycling the unreacted hexyl benzene fraction separated in step (4) to step (3) of the process.

7. The process of claim 4 wherein the dialkyl benzenes from steps 8 and 9 are treated with concentrated sulfuric acid, thereby removing contaminating polyphenyl hydrocarbons resulting from alkylation with polychlor paraffins incompletely separated in step 5 of the process.

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