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METHOD OF LUBRICATION EMPLOYING SYNTHETIC HYDROCARBON LUBRICANTS

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The present invention relates to a method of lubrication employing synthetic hydrocarbon lubricants. More particularly, the present invention relates to a method of lubrication employing a lubricating material produced by the condensation of a long, substantially straight-chain paraffinic hydrocarbon with an aromatic hydrocarbon, said lubricating material having outstanding low temperature viscosity, pour point and flash properties.

Numerous oleaginous materials have served as lubricants for centuries. With the advent of commercialization of the recovery of petroleum from subterranean formations, various petroleum fractions have been used as lubricants. As is well known, the petroleum lubricants have supplied the major part of the lubricants of commerce. More recently, in order to improve upon the properties of petroleum lubricants attention has been given to the problem of providing synthetic lubricants.

A wide number of physical and chemical tests are used in evaluating the properties of lubricants. Of the physical tests the following are usually reported: color, specific gravity, viscosity, viscosity index, pour point, and flash point. Of these physical properties, the viscosity-temperature relationship is generally regarded as being of primary importance. (The viscosity index is one means of expressing the viscosity-temperature relationship.) However, for certain applications lubricants having low pour points are desirable. In other applications, lubricants having good viscosity properties at low temperatures are desirable. In still other applications, lubricants having high flash points are desirable. In yet still other applications, lubricants having a combination of low pour point, good viscosity properties at low temperatures and high flash points are particularly desirable.

Synthetic lubricants have been developed having improved viscosity and pour point properties as compared to petroleum lubricants. Unfortunately, however, the synthetic lubricants of the prior art have been relatively expensive. It is thus apparent that it would be highly desirable to develop an inexpensive synthetic lubricant having very good viscosity, pour point and flash point properties. The present invention is concerned with a method of lubrication employing such a lubricant.

It is an object of the present invention to provide a method of lubrication employing a lubricating material having good low temperature viscosity, excellent pour point and flash point properties.

It is another object of the present invention to provide a method of lubrication employing a synthetic hydrocarbon lubricating material.

It is a further object of the invention to provide a method of lubrication employing a lubricating composition prepared by the condensation of a long, substantially straight-chain hydrocarbon with an aromatic hydrocarbon.

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Broadly stated, the present invention relates to a method of lubrication which employs a lubricating material produced by the condensation of a substantially straight-chain paraffinic hydrocarbon, generally containing in the range of from about 8 to about 18 carbon atoms, with an aromatic hydrocarbon.

More particularly, the invention relates to a method of lubrication which employs as a lubricating material a bottoms fraction of the product resulting from the condensation of a substantially straight-chain paraffinic hydrocarbon, containing in the range of about 8 to about 18 carbon atoms, with an aromatic hydrocarbon, said bottoms fraction having properties which render it particularly useful as a lubricant.

Description of lubricating material

The lubricating material of our invention is characterized by having extremely low pour point properties concurrently with good viscosity indices and good flash points. Some of the materials of our invention have extremely low pour points concurrently with excellent viscosity indices for hydrocarbon materials and excellent flash points. All of the lubricating materials of our invention have extremely low pour point properties, excellent flash points and good low temperature viscosities.

More specifically, the lubricating materials of our invention always have a pour point of at least -30° F., a viscosity index of at least 70, and a flash point of at least 380° F. In one instance a lubricating material of our invention can have a pour point of at least -50° F., a viscosity index of at least 90, and a flash point of at least 400° F. In another instance, a lubricating material of our invention can have a pour point of at least -70° F., a viscosity index of at least 70, and a flash point of at least 430° F. In general, the preferred lubricants of our invention can have a pour point of at least -70° F., a viscosity index of at least 90, and a flash point of at least 430° F.

While the lubricating materials of our invention have good to excellent viscosity indices, the viscosity index of the material is not entirely indicative of the outstanding quality of the materials. Our lubricating materials have much better low temperature viscosities than is indicated by the viscosity index. As is well known, according to the standard procedure, the viscosity index is calculated from the 100 and 210° F. measured viscosities. Unexpectedly, our materials have a much lower measured viscosity at -40° F. than is obtained by simply determining the viscosity at -40° F. by a straight line extrapolation of the viscosities measured at 100 and 210° F. and plotted on standard ASTM viscosity charts. More specifically, our lubricating materials generally have a -40° F. viscosity of not more than 100,000 centistokes, more usually have a -40° F. viscosity of not more than 35,000 centistokes, and preferably have a -40° F. viscosity of not more than 25,000 centistokes.

The preceding physical characteristics of our lubricating materials can be shown more readily in the following tabular form. It is to be understood that this tabular form is by way of amplification and not by way of limitation of the preceding description.

	Suitable	More Suitable	Preferable
Viscosity index ¹ -----	70	80	90
Viscosity at -40° F., cs. ² -----	100,000	35,000	25,000
Four point, ° F. ³ -----	-30	-50	-70
Flash point, ° F. ⁴ -----	380	400	430

¹ ASTM Method, D-567.

² ASTM Method, D-445.

³ ASTM Method, D-97.

⁴ ASTM Method, D-92.

The lubricating materials of our invention can be characterized generally by chemical constitution. Since these chemical characteristics cannot be determined as accurately as the physical characteristics, they are included more for reason of illustration than by way of limitation.

Usually the major constituent of the lubricating compositions used in our method is a mixture of dialkyl aromatic hydrocarbons. These can be present in amounts in the range of about 25 parts to about 90 parts (by volume), preferably, in the range of about 50 parts to about 95 parts (by volume). A second constituent of the compositions used in our methods is a mixture of diphenylalkanes. Preferably, this mixture of diphenylalkanes is present in amounts in the range of about 5 parts to about 50 parts (by volume), although it can be present in the range of about 0 parts to about 70 parts (by volume). A third constituent of the composition is a mixture of alkyl tetralins, indanes, and other condensed alkyl aromatics. These are present in an amount of less than 25 parts (by volume), preferably less than 10 parts (by volume). Another constituent which is not desirable, but nevertheless usually is present, is a mixture of monoalkyl aromatic hydrocarbons. Preferably, these should be present in an amount of less than 0.5 part (by volume), usually less than 10 parts (by volume), and always less than 30 parts (by volume). The terms "alkyl" and "alkanes" as used hereinbefore refer to those radicals derived from C₈-C₁₈ normal paraffinic starting materials.

Processes of preparing lubricating material

As previously indicated, the lubricating material used in our method is prepared by the condensation of a substantially straight-chain alkylating agent, containing from about 8 to about 18 carbon atoms, with an aromatic hydrocarbon. Preferably, the lubricating material is a bottoms fraction resulting from the condensation reaction. The particular type of alkylating agent used in the condensation reaction is an important feature in the preparation of the lubricating material used in our method. For this reason, the alkylating agent will be described at length.

At this time it is believed well to indicate that a preferred method of preparing the lubricating material used in our method is described in application Serial No. 129,252, now abandoned filed August 4, 1961, and having the same assignee as the present application. For reason of convenience, the specification of Serial No. 129,252 is made a part of this application. Briefly, application Serial No. 129,252 relates to a process of preparing a detergent alkylate wherein the process comprises the following steps, broadly stated: (a) separating a fraction of substantially straight-chain C₈-C₁₈ hydrocarbons from a petroleum distillate substantially free of olefins and containing said straight-chain hydrocarbons together with non-straight chain hydrocarbons, (b) chlorinating said fraction to the extent whereby between about 10 and about 35 mole percent of the straight-chain hydrocarbons present are substantially only mono-chlorinated, (c) alkylating an aromatic compound, selected from the group consisting of benzene, a lower alkyl substituted benzene and mixtures thereof, with the chlorination product of step (b) in the presence of an alkylation catalyst. In application Serial No. 129,252 the desired product is a dis-

tillate fraction obtained from the alkylation reaction mixture. In the present invention, however, the desired product for use in our method is, preferably, the bottoms fraction of the alkylation reaction mixture. In some instances in the forthcoming discussion more detailed reference will be made to the aforementioned application.

The alkylating agent of our invention is substantially straight-chain, contains from about 8 to about 18 carbon atoms, and is characterized particularly as containing either halogen substituents or olefinic bonds, thereby rendering it susceptible to alkylation with an aromatic hydrocarbon. Preferably, the halogen substituents of the alkylating agent are chlorine, bromine, or mixtures thereof. In addition, it is to be understood that trace amounts of other halogens can be included with the preferable halogens.

For convenience in describing a preferred alkylating agent we will refer briefly to those agents derived by chlorination of a mixture of straight-chain hydrocarbons. The mixture of straight-chain hydrocarbons is chlorinated in a manner to produce largely monochlorinated hydrocarbons. A suitable degree of chlorination is in the range of about 10 to about 40 mole percent in order to attain satisfactory selectivity of the mono-chlorinated derivatives. A more suitable degree of chlorination is in the range of about 15 to about 35 mole percent. A preferred degree of chlorination is in the order of about 20 mole percent, which provides a product having a selectivity of above about 90 percent mono-chlorinated product with less than 10 percent of di-, tri-, and poly-chlorinated alkanes. It may be well to note at this time that a chlorination of 40 mole percent provides a selectivity of about 80 percent (mole) mono-chlorinated product; by contrast, a chlorination of 10 mole percent provides a selectivity of about 95 percent (mole) mono-chlorinated product.

In addition to the aforementioned halogenated alkylating agents, olefinic analogs thereof are suitable in the preparation of the lubricating material used in our method of lubrication. The term olefinic analogs refers to that material corresponding to the halogenated material with the exception that a double bond, instead of a halogen atom, is present on the carbon atom. Our olefinic analogs are therefore a mixture of mono- and di-olefins with perhaps a small amount of tri- and higher olefins, but are substantially mono-olefins.

Any of the procedures of the prior art which yield an alkylating agent as described above are suitable for preparing the lubricating material used in our method. A particularly suitable method of preparing the olefinic alkylating agent is by dehydrohalogenation of a halogenated paraffin. It is to be understood, however, that the preferred alkylating agent is the halogenated agent described in application Serial No. 129,252.

Generally, the alkylating agent is prepared by treatment of normal paraffinic hydrocarbons. While normal paraffinic hydrocarbons from any source containing from about 8 to about 18 carbon atoms can be used, from a commercial viewpoint a particularly suitable material is obtained from a petroleum fraction having a high normal paraffin content. A naphtha fraction corresponding to a kerosene cut is a particularly satisfactory source of normal paraffins for use in preparing the alkylating agent used in the preparation of the lubricating material used in our method. The normal paraffins can be obtained from the naphtha fraction either through the use of molecular sieves or by the urea adduction method. Both of these methods are now well known in the art and are described in detail in Serial No. 129,252.

Regardless of the method used for obtaining the normal paraffins, or regardless of the source of the normal paraffins, the substantially straight-chain hydrocarbons used in preparing the lubricating material of our method contain no more than about 10 percent, preferably no more than 5 percent, branched-chain material.

While in general any alkylatable aromatic hydrocarbon can be used for the condensation reaction with the alkylating agent, the more suitable aromatic hydrocarbons are benzene, toluene, the xylene isomers, and naphthalene. Of these, benzene and toluene are preferable in that they are believed to give, generally, improved products. Benzene is still more preferable in that it gives better products.

The reaction between the alkylating agent and the aromatic hydrocarbon can be conducted employing about 1 to 12 moles of aromatic hydrocarbon per mole alkylating agent. Preferably, this ratio is in the range of about 3 to about 10 moles of aromatic hydrocarbon per mole of alkylating agent.

It is to be understood that the process of alkylating aromatic hydrocarbons is not a part of this invention. In particular, the process of alkylating aromatic hydrocarbons employing low mole ratios, e.g., 1:1, is not a part of this invention. This process is the subject of application Serial No. 446,720, filed April 8, 1965.

When employing an olefin as the alkylating agent, any of the more conventional alkylation catalysts (e.g., Hf, BF₃, and H₂SO₄) can be used. However, when the alkylating agent is a halogenated paraffin, a stronger alkylating agent, such as aluminum chloride or aluminum metal plus hydrogen chloride, is required.

It is not considered necessary to describe any of the other conditions of the condensation reaction, such as temperature and residence time, in that anyone skilled in the art having the information provided herein can carry out this reaction.

When the alkylating agent consists of higher hydrocarbons (e.g., C₁₆-C₁₈), the entire alkylate fraction (i.e., after removal of benzene and other lower material boiling below a C₁₄ alkaryl hydrocarbon) can be used as the lubricating composition in certain lubrication methods. Generally, it is desirable to employ only the bottoms fraction. More specifically, the bottoms fraction comprises that material distilling above about 173° C. at 5 mm. Hg pressure. A more satisfactory lubricating material is that material distilling above about 185° C. at 5 mm. Hg pressure. Sometimes it is particularly desirable, in order to obtain a more preferred lubricating composition to remove the upper 20 percent of the bottoms fraction. When this is done the topped bottoms fraction is that material distilling above about 165° C. at 0.1 mm. Hg pressure.

Advantages of our invention

Our method of lubrication has the advantage of being inexpensive in that the lubricating material used in our method can be produced as a by-product in the production of the so-called "biodegradable" detergents.

Our method of lubrication also has the advantage that the lubricating material for our method can be "tailor-made" to give it specific properties, thereby rendering it suitable for special applications. For example, the dialkyl aromatic hydrocarbon content of the material used in our method can be controlled by varying the mole ratio of aromatic hydrocarbon to alkylating agent. Also, the diphenylalkane content of the lubricating material of our method can be controlled by varying the degree of chlorination of the normal paraffins. Still further, the

Yet further, the bottoms can be fractionated to yield lubricants having special properties. As another feature, the carbon content of the alkylating agent can be varied to yield special properties of the bottoms which are used as a lubricating material in our method.

Uses of the lubricating material of our method

The lubricating materials described herein in some instances can be used per se in lubricating methods. Usually they will be used in combination with other materials, i.e., lubricating oil additives, such as detergents, inhibitors, and the like. (It is believed that the use of lubricating oil additives in lubricating oil base stocks, such as that described herein, is so well known to those skilled in the art that further description is not necessary herein.) In addition, the lubricating materials described herein can be used in combination with other lubricants, either natural or synthetic, in methods of lubrication. It is to be understood that, when we refer to a method of lubrication employing the lubricating material described herein, we include any method of lubrication employing lubricating compositions wherein the lubricating material described herein is present in a minor proportion. Preferably, however, the lubricating material described herein is present in a major proportion.

The method of lubrication described herein can be used to lubricate turbojet aircraft engines, automotive engines, steam turbines, and the like. In addition, the method of lubrication described herein is particularly useful for automatic transmissions. In view of the outstanding properties possessed by the lubricating materials described herein for use in our method of lubrication, it will be readily apparent to those skilled in the art that our method of lubrication can be used in a wide variety of specialized lubrication problems, an example of which is the lubrication of aircraft instruments.

The compositions which are used in the method of the subject application are disclosed and claimed in copending applications, Serial No. 446,661, filed April 8, 1965, and Serial No. 529,284, filed February 23, 1966, the second-mentioned application being a continuation-in-part of the first-mentioned application.

Illustrations and comparisons

Lubricating compositions for use in the claimed invention are illustrated herein below and are compared with certain prior art compositions. It is to be understood that this information is for purposes of illustration and not for any purpose of limitation.

I. This illustrates the properties of a bottoms fraction obtained using the procedure of Serial No. 129,252. A C₁₂-C₁₄ normal paraffin fraction was chlorinated at a 20 mole percent level. The resulting chlorinated paraffin was alkylated with benzene using a 3:1 benzene-chlorinated paraffin ratio. The bottoms fraction was that material distilling above 185° C. at 5 mm. Hg pressure. Twenty volume percent of this material was subsequently removed by topping (i.e., the material distilling above 165° C. at 0.1 mm. Hg pressure was removed). The topped bottoms fractions had the following physical properties. The properties of 170 pale oil (a naturally occurring, solvent-refined, Mid-Continent lubricating base stock) are included for comparison.

	Viscosity, cs. at				V.I.	Flash Point ° F.	Pour Point ° F.
	210° F.	100° F.	0° F.	-40° F.			
Topped Bottoms.....	5.95	39.57	1,647	23,000	103	455	-80
170 Pale Oil.....	5.75	38.0	solid	solid	96	410	-5

monoalkyl aromatic hydrocarbon content in the composition of the material used in our method can be controlled by varying the cut-off point for obtaining the bottoms.

The topped bottoms fraction also gave the following results on lubricity tests. Results on 170 pale oil are again included for comparison.

	Topped Bottoms	170 Pale Oil
Timken, OK, lbs. ¹	Less than 5.....	Less than 5.....
Four Ball Wear, MM ²	0.666.....	0.762.....
Falex Wear, at 500 lbs. ³	6 teeth.....	8 teeth.....

¹ This test is conducted to determine the maximum load the lubricant will carry (pounds).

The test is run for ten minutes at successively higher loads until maximum OK and failure loads are determined. The OK load is the maximum weight (pounds) which can be applied without producing scoring on the test block.

² The Four Ball wear measures the permanent displacement of surface material caused by fractional forces on sliding or rolling parts.

The test is run for one hour at 77° F. The points of contact are lubricated by immersion in the cup surrounding the Four Ball assembly. The average diameter of the scars, which is a measure of wear, is determined on the three stationary balls.

³ The Falex wear test is somewhat similar in principle to the Four Ball test. This procedure incorporates two V-blocks loaded against a journal. The prescribed load is applied by an automatic mechanism allowing the wear to be recorded as the number of teeth advanced to maintain the jaw load during the prescribed time.

II. This illustrates the properties of a bottoms fraction similar to I above. In this case a C₁₀-C₁₂ normal paraffin was subjected to chlorination. The bottoms fraction was then subjected to incremental topping (i.e., 15 percent, then 28 percent, then 34 percent, then 40 percent of the bottoms fraction was removed by topping). The various fractions had the following physical properties:

Viscosity, cs. at—	Total	85%	72%	66%	60%
210° F.....	5.06	5.38	5.65	5.93	6.12
100° F.....	31.97	34.68	37.65	40.33	42.91
0° F.....	1,300	1,450	1,610	1,810	1,990
-40° F.....	20,160	22,670	25,340	29,900	34,250
V.I.....	91	97	96	98	95
Pour point, ° F.....	(¹)	(¹)	(¹)	(¹)	(¹)
Flash point, ° F.....	>400	>400	>400	>400	>400
Cut point, ° F.....	>444	>452	>452	>458	>467
mm. Hg. Vac.....	5.0	5.0	5.0	5.0	5.0

¹—70 and fluid.

III. For purposes of comparison, we include here the properties of a typical sample of postdodecylbenzene. Postdodecylbenzene (or, as it is sometimes known, polydodecylbenzene) is a by-product of the manufacture of dodecylbenzene. Dodecylbenzene is the alkylation product of a propylene polymer, having predominantly C₁₂ material, and benzene. Postdodecylbenzene is the bottoms fraction after removing the dodecylbenzene and higher boiling materials. Postdodecylbenzene has a molecular weight which corresponds to the bottoms fraction used in the instant invention. It differs primarily from the material used in the instant invention in that it consists substantially of branched-chain material, whereas the material of the lubricating composition of the instant invention consists substantially of straight-chain material. Typical postdodecylbenzene has the following properties.

Viscosity, cs. at:	Postdodecylbenzene
210° F.....	7.59.
100° F.....	97.37.
0° F.....	Too viscous.
-40° F.....	Too viscous.
V.I.....	4.
Pour point, ° F.....	-20.
Flash point, ° F.....	360.

While particular embodiments of the invention have been described, it will be understood, of course, that the invention is not limited thereto, since many modifications may be made; and it is, therefore, contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

1. A method of lubrication employing a lubricating material produced by the condensation of a substantially straight-chain paraffinic hydrocarbon, containing from about 8 to about 18 carbon atoms, with an aromatic hy-

drocarbon, characterized in that the lubricating material is prepared by a process comprising the steps of:

(a) preparing a substantially straight-chain alkylating agent, containing from about 8 to about 18 carbon atoms of a halogenation product prepared by substantially monohalogenating a paraffinic mixture, containing at least 90 percent straight chain material, to the extent whereby from about 10 to about 40 mole percent of the paraffins are so halogenated and that of the halogenated paraffins from about 80 to about 95 mole percent are monohalogenated;

(b) alkylating the alkylating agent of step (a) with an aromatic hydrocarbon to prepare an alkylation reaction mass;

(c) subjecting the alkylation reaction mass of step (b) to a distillation and recovering therefrom a lubricating material comprising a bottoms fraction distilling above about 173° C. at 5 mm. Hg, said bottoms fraction being characterized further as containing from about 50 parts to about 95 parts (by volume) dialkyl aromatic hydrocarbons, from about 5 to about 50 parts (by volume) diarylalkanes, having a viscosity index of at least 80, a viscosity at -40° F. of not more than 35,000 centistokes, a pour point of at least -50° F., and a flash point of at least 400° F.

2. A method of lubrication as defined in claim 1, characterized further in that the aromatic hydrocarbon of step (b) is selected from the group consisting of toluene and benzene.

3. A method of lubrication as defined in claim 2, characterized further in that the aromatic hydrocarbon of step (b) is benzene.

4. A method of lubrication employing a lubricating material produced by the condensation of a substantially straight chain paraffinic hydrocarbon containing from about 8 to about 18 carbon atoms with an aromatic hydrocarbon, characterized in that the lubricating material is prepared by a process comprising the steps of:

(a) preparing a substantially straight-chain alkylating agent, containing from about 8 to about 18 carbon atoms, by substantially monochlorinating a paraffinic mixture, containing at least 90 percent straight chain material, to the extent whereby about 20 mole percent of the paraffins are so chlorinated and that of the chlorinated paraffins at least above about 90 percent are monochlorinated and less than about 10 percent are selected from the group consisting of dichlorinated, trichlorinated and polychlorinated;

(b) alkylating the alkylating agent of step (a) with an aromatic hydrocarbon to prepare an alkylation reaction mass;

(c) subjecting the alkylation reaction mass of step (b) to a distillation and recovering therefrom a lubricating material comprising a bottoms fraction distilling above 185° C. at 5 mm. Hg, said bottoms fraction being characterized further as containing from about 50 parts to about 95 parts (by volume) dialkyl aromatic hydrocarbons, from about 5 to about 50 parts (by volume) diarylalkanes, less than 10 parts (by volume) condensed alkyl aromatic hydrocarbons, selected from the group consisting of alkyl tetralins and indanes, and less than 0.5 part (by volume) mono-alkyl aromatic hydrocarbons, having a viscosity index of at least 90, a viscosity at -40° F. of not more than 25,000 centistokes, a pour point of at least -70° F. and a flash point of at least 430° F.

5. A method of lubrication as defined in claim 4, characterized further in that the aromatic hydrocarbon of step (b) is selected from the group consisting of toluene and benzene.

6. A method of lubrication as defined in claim 5, characterized further in that the aromatic hydrocarbon of step (b) is benzene.

References Cited by the Examiner

UNITED STATES PATENTS

2,015,748	10/1935	Frolich	252—59
2,189,924	2/1940	Pier et al.	260—671
2,339,493	1/1944	Lieber et al.	260—671
2,688,643	9/1954	Raymond et al.	252—59
3,173,965	3/1965	Pappas et al.	252—59

OTHER REFERENCES

The Petroleum Chemicals Industry by R. F. Goldstein, 1958; E. & F. Spon., second edition, 1958.
 Shell: German printed application, No. 1,096,529, January 1961.

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