

UNITED STATES PATENT OFFICE

2,236,897

LUBRICATING OIL

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No Drawing. Application April 18, 1940,
Serial No. 330,370

13 Claims. (Cl. 252—45)

Our invention relates to improved lubricating oils and more particularly to lubricating oils having exceptionally high viscosity indices.

This application is a continuation-in-part of our co-pending application, Serial No. 230,660, filed September 19, 1938.

Two general methods of obtaining high viscosity index oils have been described in the literature of the art, namely, the production of synthetic or synthetically treated oils with high viscosity index and the addition of various materials to ordinary or low viscosity index oils to improve them. Our products are of the first type and are intended to be used directly as lubricating oils.

In the prior art of synthesizing oils of lubricating properties, various processes have been employed as well as various starting materials. For example, lubricating oils have been prepared by the action of polymerizing reagents such as aluminum chloride, ferric chloride, phosphoric acid and phosphates, boron fluoride, and the like on lower olefins such as ethylene, propylene, butylenes, and higher olefins such as hexene, octene, and even cetene, $C_{16}H_{32}$. Various mixed olefins have been polymerized such as cracked gases, cracked paraffin wax and the like.

Synthetic lubricating oils have been prepared by various condensation reactions. For example, the condensation of halogenated wax or other petroleum fractions with aromatic hydrocarbons or other aromatic compounds such as naphthalene, diphenyl ether and the like.

The products of our invention are more cheaply and easily made than other synthetic lubricating oils. They have higher viscosity indices than any previously reported. Furthermore, we utilize non-lubricating fractions of petroleum to produce these high quality lubricating oils. Our products are, like the so-called white oils, extremely stable toward oxidation and sludging which is not true of ordinary lubricating oils. By our processes, we convert materials of low economic value into products of greatly enhanced value.

One object of our invention is to provide lubricating oils having extremely high viscosity indices.

Another object of our invention is to utilize non-lubricant petroleum fractions to produce improved lubricating oils.

A further object of our invention is to synthesize materials which may be used to improve the characteristics of ordinary lubricating oils.

A still further object of our invention is to convert materials of low economic value into

valuable products by a commercially feasible process.

Other objects of our invention will appear in the course of the following description.

Briefly our invention consists in the production of mixed cyclic and alkyl ethers of the type RXR' in which R is a high molecular weight, aliphatic radical having at least 13 carbon atoms, such as may be obtained, for example, from paraffin wax and R' is an organic radical containing a carbocyclic or heterocyclic nucleus which may or may not bear various alkyl or other substituting groups. It is necessary to have at least 13 carbon atoms in the aliphatic radical in order to obtain as products lubricating oils having viscosities of at least 50 seconds Saybolt at 100° F. In the above formula, X stands for an atom of an element of the right hand side of group VI of the periodic table, that is, oxygen, sulfur, selenium, or tellurium.

While ordinary lubricating oils have viscosity indices from as low as -40 for naphthenic oils to 90 or 100 for Pennsylvania oils, the products of our invention have viscosity indices of not less than 90.

The aliphatic radicals of our products may be derived from any source and may be of various degrees of purity, that is, freedom from other types of radicals. For example, cetyl chloride is a suitable source of the cetyl radical. We may utilize paraffin hydrocarbons of various petroleum fractions as sources of aliphatic radicals including hydrocarbons of the heavy ends of ordinary gasoline, kerosene, gas oil, paraffin wax and higher paraffin hydrocarbons from natural or synthetic sources. One preferred source of aliphatic radicals of the type described is a relatively pure monochlor paraffin wax, dichlor paraffin wax or the like.

In the prior art, references are made to monochloroparaffin, dichloro paraffin, trichloro paraffin, and the like. It is usually considered that the product of direct chlorination is the compound represented by the total chlorine content and therefore the desired compound. We have found that these products of chlorination are very crude mixtures of the chlorinated hydrocarbons and contain unchlorinated hydrocarbons and the mono-, di-, and polychloro derivatives. The whole mixture cannot be considered the desired compound. For example, a so-called "trichloro paraffin wax" containing 24 per cent chlorine, which corresponds very closely to the percentage of chlorine in the trichloro compound, was separated by means of crystallization from acetone at

low temperatures. The least soluble portion consisted of unchlorinated wax. The next least soluble portion consisted of a mixture of monochloro wax and unchlorinated wax. The percentage of unchlorinated wax in the original mixture, supposedly "trichloro paraffin wax," was found to be 7.2 per cent. Thus, even a "trichloro paraffin" as so-called in the prior art, because of the total chlorine content, was in fact a crude mixture containing as much as 7.2 per cent of unchlorinated wax and quantities of mono- and di-chloro waxes, as well as trichloro wax and more highly chlorinated waxes. Its use would not give the same results as a trichloro paraffin free of higher and lower chlorinated paraffin, since the products will contain unhalogenated paraffin hydrocarbons and mixed derivatives.

Even though the appropriate amount of chlorine is introduced in the wax to form a monochloro wax, we have found that the crude chlorination mixture contains, in addition to small amounts of chlorine and hydrogen chloride and the desired monochloro wax, also unchlorinated wax and more highly chlorinated waxes. When dichlor and higher chlor wax is the desired product, the crude chlorination mixture will contain in addition to chlorine and hydrogen, less highly chlorinated waxes.

In contrast to the use of of such a mixture, we have found it possible, as fully described below, to obtain a relatively pure monochloro compound free from unchlorinated hydrocarbon and free from more highly chlorinated compound. We may thus prepare (1) monohalogenated hydrocarbons substantially free from unhalogenated hydrocarbons and more highly halogenated hydrocarbons; (2) dihalogenated hydrocarbons substantially free from unhalogenated hydrocarbons and monohalogenated hydrocarbons, as well as from halogenated hydrocarbons containing more than two atoms of halogen per molecule; and (3) trihalogenated hydrocarbons free from halogenated hydrocarbons containing fewer or more than three halogen atoms per molecule and free from unhalogenated hydrocarbons. We refer in this specification to these materials as relatively pure monohalogen compounds, relatively pure dihalogen compounds, etc.

The chlorination of most petroleum hydrocarbons lowers their melting points and, up to a certain point, the greater the extent of chlorination; that is, the more chlorine atoms per molecule, the lower the melting point. The decrease in melting point is stepwise, and this permits us to separate the unchlorinated hydrocarbons from the monochlorohydrocarbons and the monochloro hydrocarbons from the dichloro and higher chlorinated hydrocarbons. We can, for example, separate the unchlorinated wax from the airblown mixture by filter pressing at such temperatures that all of the chlorinated waxes are largely liquids, while the unchlorinated waxes are largely solid. The temperature for the pressing operation will depend, of course, on the character of the wax used initially and will vary considerably depending on this factor. For example, at a temperature of from 80° F. to 90° F. the monochloro product formed by the chlorination of wax having a melting point of 120° F. will be liquid, while the unchlorinated wax will be solid, enabling a ready separation to be effected.

Other methods of separation, as for example, sweating, selective solvent extraction at various temperatures, the use of diluents followed by chilling and settling or filtering, and the like,

may be employed for separating solid unchlorinated wax from chlorinated portions, and for separating the monochloro wax from the more highly chlorinated portions, and so on. In separating relatively pure monochloro, dichloro, etc., hydrocarbons from such sources as the heavy ends of gasoline, kerosene and the like, we preferably use chilling only as a method of separation since in solution extremely low temperatures are required. Solvents may be used here, of course, but it is more convenient to depend simply on differences in melting point. It will be obvious to those skilled in the art that in these cases it is not practicable to employ differences in boiling point since the halogen derivatives of the lower hydrocarbons will have the same boiling range as unhalogenated higher boiling hydrocarbons in the same fraction of starting material.

The unchlorinated wax separated from the crude chlorination mixture may be recycled to the chlorination step to obtain further quantities of chlorinated waxes. It does not represent refractory material, and the same proportions of chlorination products are obtained from it as from fresh wax.

The liquid chlorinated waxes after separation of unchlorinated hydrocarbons consist largely of monochloro and dichloro waxes when approximately 10 or 20 per cent chlorine respectively is introduced into a starting wax, of, say, from 115° to 130° F. melting point, but some polychloro wax may be present. These mono- and dichloro waxes may be separated from each other by crystallization from acetone, using a solvent-chloro wax ratio of from 1 to 1 to 20 to 1. In preparing the solution, an elevated temperature may be employed to insure that the chloro waxes are completely dissolved in the solvent. The solution is then chilled to a temperature of between minus 15° F. and minus 20° F. when a paraffin wax of 115° to 130° F. melting point is used for the initial chlorination. The monochloro waxes are precipitated out nearly quantitatively, while the dichloro and polychloro waxes will remain in solution. The precipitated monochloro waxes may be readily separated by settling, filtering, or centrifuging.

We have also used other crystallization solvents such as methyl-ethyl ketone, acetone, benzene, methylene chloride, various other halogenated solvents as well as liquid propane or butane. Mixtures of two or more solvents may be used. The use of a particular one or combination of these solvents requires the experimental determination of the proper proportions and temperatures necessary to obtain the desired separation of the crude chlorination mixture into the various stages of chlorine contents. Halogenated solvents serve to aid in the precipitation of unchlorinated wax, while benzene and hydrocarbon solvents increase the solubility of the more highly chlorinated materials.

After removing the monochloro wax, the solution may be chilled to a lower temperature or concentrated by distillation or evaporation of the solvent or both to precipitate the dichloro waxes which may then be separated. A further separation of the remaining liquid may be accomplished by repetition of these processes. In this manner, the crude chlorination mixture may be separated into unchlorinated wax, monochloro wax, dichloro wax and polychloro wax. We proved the homogeneity of our monochloro wax, for example, by chilling until approximately half of the sample had solidified. Solid and liquid portions were

separated by a filtration and contained 12.1 and 11.4 per cent chlorine respectively. In the case of the wax which had the 120° F. melting point, batches showed chlorine contents of 10.2, 10.3 and 10.5 per cent. These values are very close to the theoretical of 10.0 per cent. Thus, our relatively pure monochloro wax is substantially free from unchlorinated wax and more highly chlorinated waxes. We may prepare according to our invention similarly pure di- and polychloro waxes free from unchlorinated wax and more highly chlorinated waxes.

Our paraffin hydrocarbons are preferably obtained from petroleum, though it is to be understood that any source rich in hydrocarbons of the paraffin series may be used as starting materials in practicing our invention. Our method is particularly applicable to the higher paraffin hydrocarbons such as represented by ordinary paraffin wax, but it is to be understood that it may be practiced on paraffin hydrocarbons of higher and lower molecular weight including all those paraffin hydrocarbons whose monochloro derivatives melt lower than the hydrocarbons themselves. While the product of the preferred embodiment of our invention is a mixture, the monochloro derivatives prepared according to our invention are free from unchlorinated and more highly chlorinated material. The dichloro derivatives are free from unchlorinated hydrocarbons, monochlorinated hydrocarbons, and more highly chlorinated hydrocarbons. The purity of the final product with respect to homologues is determined by the purity of the starting hydrocarbon. It is understood, of course, that when a pure hydrocarbon is employed, a correspondingly pure halide is obtained.

Having selected the hydrocarbon in accordance with the desired final product, we chlorinate the hydrocarbon until approximately that amount of chlorine is absorbed which will produce the monochloro compound when that is the desired product, or approximately that amount of chlorine which will produce the dichloro compound when that is the desired product, etc.

In the case of paraffin hydrocarbons having from 18 to 24 carbon atoms per molecule, that is, a material having a melting point of approximately 120° F., about 10 per cent added chlorine will produce substantially the equivalent of the monochloro product. The amount of chlorination may vary between 9 per cent and 12 per cent without being disadvantageous. The percentage of chlorine introduced into the hydrocarbon just described will be approximately 17 per cent when a dichloro product is desired. The amount of chlorine introduced will be less in the case of the high molecular weight, higher melting hydrocarbons, and more in the case of the lower molecular weight, lower melting hydrocarbons, for a given number of chlorine atoms per molecule. The chlorination may be accomplished in any suitable manner. We prefer to heat the hydrocarbon to a temperature at least that of its melting point and pass chlorine gas through the melted hydrocarbon. Agitation increases the efficiency of chlorine absorption but is not essential. The chlorination reaction is exothermic and the heat of reaction is ordinarily ample to maintain the mixture in the liquid state without the addition of other heat. Large quantities of hydrogen chloride gas are evolved which are conducted from the reaction chamber, together with unreacted chlorine. The material being chlorinated is constantly weighed while the chlorina-

tion is in progress, in order to determine the extent of chlorination as indicated above. Samples may be removed from time to time, and the specific gravity of these be determined in order to follow the chlorination process. If desired, chlorine analyses may be conducted on samples of the material being chlorinated. After sufficient chlorine has been introduced, we blow the mixture with air or an inert gas, such as carbon dioxide, until the hydrogen chloride and free chlorine, if any, are substantially removed. While it is not essential, the chlorination mixture or the separated relatively pure halogenated hydrocarbons may be given a stabilizing treatment with dilute aqueous solutions of sodium sulfite, sodium bisulfite, sulfurous acid, potassium permanganate, sodium hypochlorite, or the like.

As an example of the manufacture of a relatively pure chlorinated hydrocarbon, we describe here the manufacture of a relatively pure monochloro wax which contains approximately 26 carbon atoms per molecule. We started with 723.4 parts of a hydrocarbon wax having a melting point of 120° F. The wax was chlorinated until 72.5 parts by weight of chlorine had been absorbed. The chlorinated wax was airblown to remove hydrochloric acid and uncombined residual chlorine, and then pressed at 85° F. The unchlorinated wax was reserved for further chlorination. The liquid portion was then dissolved in acetone, 350 parts of crude chloro wax being dissolved in 3,226 parts of acetone. The solution was chilled to minus 18° F. and 185 parts by weight of solid monochloro wax containing 10.3 per cent chlorine was precipitated. Monochloro wax from this paraffin wax contains theoretically 10.0 per cent chlorine. The monochloro wax was normally liquid at room temperature.

Dichloro waxes and polychloro waxes prepared according to our method are suitable for use in any of the applications described in the prior art, where such dichloro waxes and polychloro waxes are required. Since they contain no unchlorinated wax or lower chlorinated waxes, they are particularly efficient in these applications and are a distinct improvement over the prior art which used crude chlorination mixtures of approximately the proper chlorine content but which consisted of unchlorinated wax and more highly chlorinated wax.

While chlorine has been referred to above almost exclusively, it is to be understood that any of the halogens are suitable to make halogen derivatives of the paraffin hydrocarbons according to our method. Thus bromine, iodine, and fluorine may suitably be used to obtain the corresponding bromides, iodides and fluorides. For some purposes to which the halides are to be put, the bromine compounds are much to be desired over the chlorine compounds, since they are considerably more reactive. Where this is the case, we halogenate with bromine, using a halogen carrier, such as halides of antimony, phosphorus, iron, various metals, and the like, and separate the brominated mixture into its components as described above in the case of the chlorine compounds. The iodine compounds of the paraffin hydrocarbons may be prepared by direct iodination or by an indirect method. By the indirect method, the above described separation of mono-, di-, and polyhalogen derivatives may be employed in any step of the process. Thus we may separate a relatively pure mono- or dichloro paraffin and convert it to the corresponding iodine compound, or we may convert

the crude halogenated mixture into a crude iodinated mixture and then separate into the various stages of halogenation. Fluorine may be introduced into paraffin hydrocarbons directly or indirectly by analogous methods. For most purposes, however, we prefer to use the chlorine compounds because of the cheapness and availability of chlorine above all the other halogens.

In preparing the lubricating oils of our invention, we use these relatively pure monochlor waxes or dichlor waxes and treat them with metal derivatives of cyclic compounds of the type $R'XH$ in which X is an atom of an element selected from the right hand side of group VI of the periodic tables that is, oxygen, sulfur, selenium and tellurium, and R' is an organic radical containing at least one cyclic nucleus. We prefer to use the cheap sodium derivatives but other alkali, alkaline earth and heavy metal derivatives of the $R'XH$ compounds may be used. These cyclic compounds may be monocyclic, bicyclic or polycyclic, such as phenol, cresols, xlenols, phenylethyl alcohol, naphthols, hydroxydiphenyls, di- and triphenyl carbinols, phenyl cyclohexanol, methyl cyclopentanol, thionaphthols, selenophenol and the like. Even heterocyclic phenols such as 8-hydroxy quinoline may be used. It appears to be particularly advantageous to have at least one alkyl group attached to the ring as in p-tert.-butylphenol, octadecylphenol, pentacosylphenol, amyl cyclohexanol, and the like. Other substituting groups may be present as in p-nitrophenol, p-hydroxybenzaldehyde, amyl salicylate, p-hydroxyacetophenone, o-hydroxybenzophenone, phenol sulfonic acid, its salts, esters and amides, vanillin, eugenol, thymol, mesitol, carvacrol, o-chlorophenol, tri-iodophenol, pentachlorophenol, nitrochlorophenols, o-methylaminophenol, picramic acid, m-hydroxyazobenzene, thiophenol, selenocresol, resorcinol, hydroquinone monomethyl ether o-chlorobenzyl alcohol, phenylethyl alcohol, cinnamyl alcohol, and the like.

The reaction whereby our lubricating oils are produced proceeds at satisfactory rates at about 200° C. with most of the ring $R'XH$ compounds and most of the halogenated aliphatics, but temperatures between 100° C. and 300° C. may be used, provided the reaction is not too slow or provided the product is not converted to dark colored products of relatively low viscosity index.

It will be obvious that our relatively pure wax and metal derivative must be substantially dry in order to carry out this reaction. We may use purchased dry metal phenolates or alcoholates or they may be prepared and treated with the halogen compound in the same reaction vessel. We mix the solid metal derivative with the halogen compound and keep the mixture agitated during the reaction. Usually the mixture is more difficult to agitate at first than after the reaction has proceeded for a time.

We add water to the reaction mixture and wash out metal halide and excess metal derivative from our synthetic oil. Usually the oil needs only to be dried and this may be accomplished in any suitable manner. For example, we may use a vacuum dehydrator.

The following examples are given as illustrations and not as limitations:

Example 1

A mixture of 94 parts of phenol and 44 parts of sodium hydroxide in 300 parts of toluene was heated. The condensate was separated, discarded-

ing the water and returning the toluene to the reaction chamber. When no more water was separable from the distillate, 200 parts of our relatively pure monochlor wax was added and the toluene removed by distillation. Reaction temperature was held at 160-180° C. for two hours. Mixture was cooled and water added. Oil was washed several times with water, then with dilute acid and finally steamed to remove any phenolic odor. The dried oil had a viscosity (S. S. U.) of 70.6 seconds at 100° F.; 37.9 at 210° F. and a viscosity index of 91.

Example 2

A mixture of 108 parts of o-cresol and 44 parts of sodium hydroxide were melted together and heated at 110-140° C. for two hours, poured out on a cold surface and pulverized. It was substantially water-free. To this solid was added 200 parts of our relatively pure monochlor wax and the mixture was heated at 160° C. and then at 160-190° C. for one hour. Mixture was cooled, washed, steamed, and dried. It had a viscosity of 89.4 at 100° F. and 40.2 at 210° F. The viscosity index was 160.4.

Example 3

As an intermediate, a tetra- "waxyated" phenol was prepared as follows: To a mixture of 94 parts of phenol and 1,550 parts of our relatively pure monochlor wax was added 50 parts of anhydrous aluminum chloride at about 65° C. The temperature was raised to 120° C. during 20 minutes and then to 175° C. in 90 minutes. The mixture was cooled, decomposed by the addition of dilute hydrochloric acid, washed thoroughly with dilute acid, water, and dried.

A mixture of 900 parts of the tetra- "waxyated" phenol, 34 parts of potassium hydroxide and 3,000 parts of toluene were heated as described in Example 1 until no more water was formed. Then 232 parts of our relatively pure monochlor wax was added and, after removing the toluene, the mixture was heated at 190-200° C. for two hours. The oil obtained from the mixture as described in Example 1 was chlorine-free and had a viscosity of 233.1 at 100° F. and 56.3 at 210° F. The viscosity index was therefore 148.1.

Example 4

A mixture of 868 parts of the product of Example 1 and 773 parts of our relatively pure monochlor wax in 2,500 parts of carbon bisulfide was heated with 270 parts of anhydrous aluminum chloride for about 2½ hours. The mixture was heated for ½ hour with dilute hydrochloric acid and the organic product extracted with benzene. After removing the solvent, the residual oil had a viscosity of 80.0 at 100° F. and 40.0 at 210° F. The viscosity index of this oil is 187.4.

Example 5

A blend of 40 per cent by volume of the product of Example 2 with 59 per cent of a Mid-Continent neutral oil (viscosity 225 at 100° F.) and 1 per cent of a mixture of 75 per cent bright stock and 25 per cent of a naphthalene-chlorowax condensation product had a viscosity of 141.3 seconds at 100° F. and 43.1 seconds at 210° F. The viscosity index of the pale oil was 85 while that of the blend described was 110.7.

Example 6

We may condense 130 parts of the anhydrous

sodium derivative of benzyl alcohol with 200 parts of a relatively pure monochlor wax and follow the procedure of the preceding examples to obtain another product of our invention.

Example 7

The mixture of 1,845 parts of the anhydrous calcium derivative of o-chlorobenzyl alcohol with 2,000 parts of our relatively pure monochlor wax when treated by the procedure of the preceding examples gives another product of our invention.

Example 8

The condensation product of 1,300 parts of sodium cresolate with 1,260 parts of our relatively pure dichlorowax gives another product of our invention.

Example 9

The condensation product of the sodium derivative of cyclohexanol with our relatively pure monochlor wax gives another product of our invention.

It is to be understood that any or all of these reactions may be carried out under atmospheric, subatmospheric, or superatmospheric pressure. Furthermore, various other factors and details may be changed within wide limits within the spirit of our invention. Our invention lies primarily in providing an application of a known chemical reaction using our relatively pure halogen compounds to manufacture lubricating oils having extremely high viscosity indices. While we do not wish to claim the old processes, we do wish to claim all novelty inherent in our processes as broadly as the state of the art permits.

If desired, our product may be prepared in such a manner as to leave some residual halogen. This halogen will remain in the aliphatic part of the ether molecule. For example, we may condense one molecular proportion of a relatively pure dichlorowax with 1 or 1.5 molecular proportions of a metal phenolate or alcoholate. Or we may cause the condensation to proceed so as to remove halogen completely from the aliphatic part of the ether but use a halogen-bearing aromatic hydroxy compound such as p-chlorobenzyl alcohol, o-chlorophenol or the like. If desired, a halogen-free condensation product may be halogenated to obtain a halogen-bearing lubricating oil. Any of these halogen-bearing products have superior lubricating properties, particularly in film strength as compared to the halogen-free lubricating oil.

Other elements such as sulfur, nitrogen or phosphorus may be present in our lubricating oil molecule. For the former purpose we may use substituted reagents in the condensation such as p-nitrophenol, 2-chlor-3 amino-pentacosane, 1-mercaptanaphthyl disulfide, hydroxyphenyl diphenyl phosphate, o-hydroxyphenyl diamylphosphine and the like. The finished lubricating product may be so made that it will contain from 0.2 to 20% by weight of one of the halogens, sulfur, nitrogen, phosphorus or combinations of two or more of these. Generally quantities ranging from only 0.2 to 5.0% of these elements are contained in the lubricant. We may add from 0.5 to 20% of other oxygen bearing organic compounds, halogen-containing or halogen-free, such as diphenylene oxide, chlorodiphenylene oxide, chlorinated diphenyls, methyl dichlorostearate, benzyl sulfide, tricresyl phosphate, tri (2-ethylhexylphenyl) phosphite, benzyl sulfone, sulfurized methyl linoleate, diamyl

xanthate, lauryl thiocyanate and the like. Furthermore, we may add various metallic compounds such as chromium oleate, tetra-phenyl lead, aluminum naphthenate, calcium cetyl 3-isopropyl-6-methyl-3, 6-endoethylene-4-tetrahydro phthalate, tin octadecyl phthalate, and the like. Examples of some of these blends are:

Example 10

	Per cent
10 Condensation product of Example 2-----	90.0
Sulfurized methyl linoleate (10% S)-----	10.0

Example 11

Condensation product of Example 2-----	98.0
15 Triphenyl phosphite-----	1.0
Chlorodiphenylene oxide-----	1.0

Example 12

20 Condensation product of sodium thiocresolate and monochlor wax-----	99.0
Methyl dichlorostearate-----	1.0

Example 13

Condensation product of Example 2-----	97.8
25 Solution of 25 per cent naphthalene-chlorowax condensation product in 75 per cent of bright stock-----	1.5
Sulfurized methyl esters of corn oil acids---	0.5
Tin phenylstearate-----	0.2

Example 14

Cresoxy wax (condensation product of Example 2)-----	75.0
35 Condensation product of sodium thionaphtholate and monochlor wax-----	25.0

Example 15

Cresoxy wax-----	18.0
40 Condensation product of sodium 8-hydroxyquinolinate with dichlor wax-----	80.0
Sulfurized methyl linoleate-----	0.2
Methyl dichlorostearate-----	1.8

It will be seen that we have accomplished the purpose of our invention; namely, to utilize petroleum hydrocarbons of low economic value to produce high viscosity index lubricating oils of great economic value.

It will be understood that certain features and sub-combinations are of utility and may be employed without reference to other features and sub-combinations. This is contemplated by and is within the scope of our claims. It is further obvious that various changes may be made in details within the scope of our claims without departing from the spirit of our invention. It is, therefore, to be understood that our invention is not to be limited to the specific details shown and described.

Having thus described our invention, we claim:

1. A lubricating oil having a viscosity index of over 90, comprising principally an ether of the type RXR' where R is a high molecular weight aliphatic radical having at least 13 carbon atoms, R' is an organic radical containing at least one cyclic nucleus, and X is an atom of an element selected from the right-hand side of group VI of the periodic table.
2. A lubricating oil having a viscosity index of over 90, comprising principally an ether of the type RXR' where R is a high molecular weight aliphatic radical having at least 13 carbon atoms, R' is an organic radical containing at least one cyclic nucleus, and X is an atom of an element selected from the group consisting of oxygen, sulfur, selenium and tellurium.

3. A lubricating oil having a viscosity index of over 90, comprising principally a thioether of the type RSR' where R is a high molecular weight aliphatic radical having at least 13 carbon atoms, and R' is an organic radical containing at least one cyclic nucleus.
4. A lubricating oil having a viscosity index of over 90, comprising principally a seleno-ether of the type RSeR' where R is a high molecular weight aliphatic radical having at least 13 carbon atoms and R' is an organic radical containing at least one cyclic nucleus.
5. A lubricating oil having a viscosity index of over 90, comprising principally a telluro-ether of the type RTeR' where R is a high molecular weight aliphatic radical having at least 13 carbon atoms and R' is an organic radical containing at least one cyclic nucleus.
6. A lubricating oil having a viscosity index of over 90, comprising principally a mixed cyclic-aliphatic thio-ether with at least 13 carbon atoms in the aliphatic radical.
7. A lubricating oil having a viscosity index of over 90, comprising principally an ether of the type RXR' where R is a high molecular weight aliphatic radical having at least 13 carbon atoms and R' is the radical of a cyclic compound of the type $\text{R}'\text{XH}$ in which X is an atom of an element selected from the right-hand side of group VI of the periodic table.
8. A process for the production of lubricating oils having viscosity indices of over 90, comprising the steps of halogenating paraffin hydrocarbons whose monochloro derivatives melt lower than the hydrocarbons themselves, separating the mono-, di-, and polyhalogenated hydrocarbons from each other and from unhalogenated hydrocarbons and separately replacing the halogen of each of the said relatively pure halogenated hydrocarbons by means of a metal derivative of a cyclic hydroxy compound of the type $\text{R}'\text{XH}$ in which R' is an organic radical containing at least one cyclic nucleus and X is an element selected from the right-hand side of group VI of the periodic table.
9. A process for the manufacture of lubricating oils having viscosity indices of over 90, comprising the steps of halogenating paraffin hydrocarbons whose monochloro derivatives melt lower than the hydrocarbons themselves, separating the mono-, di-, and polyhalogenated hydrocarbons from each other and from unhalogenated hydrocarbons and separately replacing the halogen of each of the said relatively pure halogenated hydrocarbons by means of a metal thio-phenolate.
10. A process for the production of lubricating oils having viscosity indices of over 90, comprising the steps of halogenating paraffin hydrocarbons whose monochloro derivatives melt lower than the hydrocarbons themselves, separating the mono-, di-, and polyhalogenated hydrocarbons from each other and from unhalogenated hydrocarbons and separately replacing the halogen of each of the said relatively pure halogenated hydrocarbons by means of a metal derivative of an aromatic thioalcohol.
11. A process for the production of lubricating oils having viscosity indices of over 90 comprising the steps of halogenating paraffin hydrocarbons whose monochloro derivatives melt lower than the hydrocarbons themselves, separating the mono-, di-, and polyhalogenated hydrocarbons from each other and from unhalogenated hydrocarbons and separately replacing the halogen of each of the said relatively pure halogenated hydrocarbons by means of a cyclic thioalcohol.
12. A lubricating oil having a viscosity index of over 90, comprising principally an ether of the type RXR' where R is a high molecular weight aliphatic radical having at least 13 carbon atoms and R' is an organic radical containing at least one aromatic nucleus and X is an element selected from the right-hand side of group VI of the periodic table.
13. A lubricating oil having a viscosity index of over 90, comprising principally an ether of the type RXR' where R is a high molecular weight aliphatic radical having at least 13 carbon atoms, R' is an organic radical containing at least one aromatic nucleus, and X is an element selected from the group consisting of oxygen, sulfur, selenium, and tellurium.

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