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LUBRICANT AND PROCESS OF MAKING THE SAME

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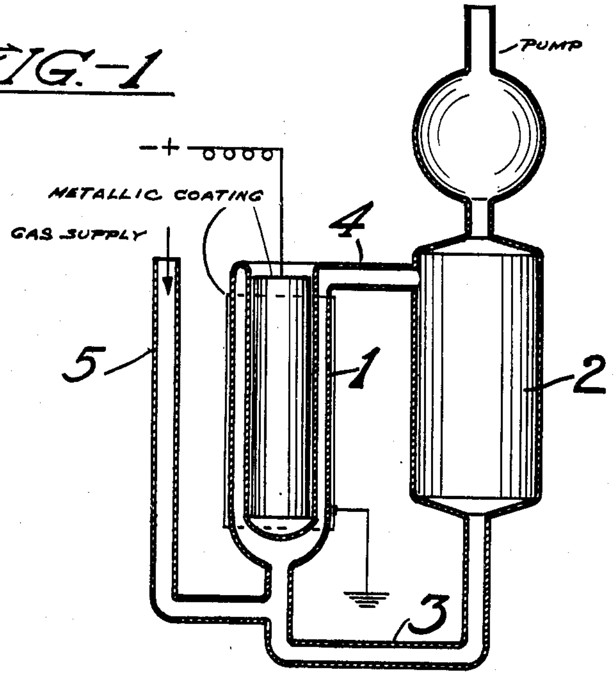
FIG.-1



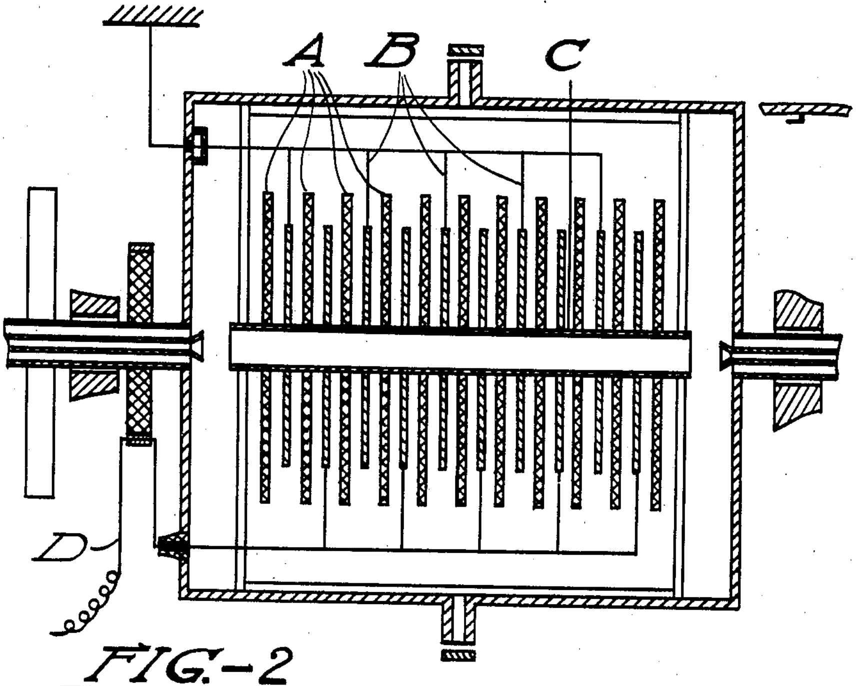


FIG.-2

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LUBRICANT AND PROCESS OF MAKING THE SAME

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8 Claims. (Cl. 87—9)

The present invention is concerned with the production of lubricants, more particularly with the production of substances which are either good lubricants themselves or which are valuable improving agents for other lubricants.

We have found that particularly valuable lubricating oils are obtained by subjecting the said paraffin waxes or similar waxes rich in hydrogen or mixtures containing the same, for example mixtures with hydrocarbon oils rich in hydrogen (petrolatum) or with fats, fatty oils, other waxes, high molecular alcohols or esters or acids, such as stearic acid, palmitic acid or oleic acid, to condensation by means of the action of silent electric discharges. The condensation products thus obtained may also be employed with advantage as additions to lubricating oils. They have the effect of improving the properties of the latter; in particular the pour point of the lubricating oils is lowered to an appreciable degree. By the term paraffin wax we mean paraffin wax from any origin, as for example from mineral oils or from brown coal, as well as waxes consisting of solid isoparaffins (by which we mean paraffinic hydrocarbons having branched carbon chains), as for example Palembang wax, or dehydrogenated paraffin waxes, which may be dehydrogenated by heat-treatment, such as, preferably slight, cracking or by introducing into the initial paraffin wax an exchangeable substituent, such as a halogen or sulphur or oxygen, and subsequently splitting off the hydride of the said substituent at an elevated temperature, preferably in the presence of a catalyst.

The said treatment of paraffin waxes or similar waxes with silent electric discharges is hereinafter referred to as "voltolization".

We have further found that by suitable modifications or special modes of proceeding the results arrived at by the said voltolization may be considerably improved.

Careful investigation of the phenomena occurring in the voltolization of hydrocarbon materials has led us to the conclusion that products having particular advantages for the purposes hereinbefore described are obtained by subjecting to the voltolization initial materials having certain well defined characteristics not inherent in the other members of the aforesaid class of initial materials used for the treatment with silent electric discharges.

Thereafter we found that also initial materials which do not possess the aforesaid characteristics, on being suitably pretreated, and then subjected to voltolization will yield the same valuable results as when employing the said peculiar initial materials.

We further found that the products obtained by the voltolization treatment of any hydrocarbon materials often contain constituents which more or less substantially impair their properties, and we developed processes for what may be termed "immunization", i. e., the removal or otherwise rendering harmless of the said obnoxious constituents contained in the voltolization products.

We further discovered that by carrying through the voltolization treatment under quite specific conditions products may be obtained possessing one or the other quite peculiar characteristic which therefore are particularly valuable under certain circumstances.

The properties of the voltolization products obtained according to the present invention vary to a more or less substantial extent with the nature of the initial materials subjected to voltolization, with the conditions employed for the voltolization treatment and also with the nature of the further treatment of the crude products resulting from the treatment with silent electric discharges. In view of these varying properties the products obtained according to our present invention may be used as lubricants, i. e. lubricating oils or greases, or when being less suitable for direct use as lubricants, they are highly valuable agents for improving other lubricants, imparting to the latter particularly valuable properties. Our present invention is also concerned with such compositions containing voltolization products as improving agents.

Before we now proceed to explain in detail the several features or modifications of our present invention, it is thought convenient first to explain briefly how the voltolization of hydorcarbon materials may be carried out. While apparatus for effecting a treatment with silent electric discharges are well known in the art, the following explanations of the apparatus will facilitate the understanding of our present invention.

A very suitable form of apparatus for carrying through the voltolization consists of a comparatively narrow glass-tube inserted within a wider glass-tube so that a double walled, or jacketed tube is formed; the space within the inner tube is filled with a conductor liquid for which purpose water is very suitable. The whole apparatus is surrounded by a bath of conductor liquid, preferably water. The electric poles are arranged in the two bodies of conductor liquid whereas the jacket space between the inner and outer glass tubes serves for the electrical treatment of the initial hydrocarbon material. The jacket space should preferably be quite narrow in order to facilitate the passage of the silent discharge. Since the initial material subjected to the voltolization treatment is usually a highly viscous or even solid body, it is usually advisable to heat the conductor liquid, surrounding the apparatus and that in the inner tube. Apparatus of this type are well known in the trade as Siemens ozonization. Of course instead of surrounding the apparatus and filling its inner portion with a conductor liquid, metallic coatings may be provided over those surfaces of the glass tubes as otherwise would be in contact with the water or other conductor liquid, such as mercury, weak acids or bases. The glass tubes provided with a metallic coating may also be replaced by metal tubes. The jacket tube is filled up to about half its height with liquefied initial hydrocarbon material. When switching on the electric current the hydrocarbon material is converted into a state of foam and in that state forms a very thin layer. The said foam rises in the jacket tube and then is passed by means of the specifically heavier hydrocarbon liquid present in a vessel communicating with said jacket tube through a suitable pipe into this vessel connected to the jacket space and there is reconverted into the coherent liquid state so that the material can be reintroduced into the treatment space thus establishing a circulation of the treated hydrocarbon material. If the foam evolved is not sufficient for passing through the said pipe connecting the jacket space with the vessel communicating therewith the formation of foam may be facilitated by passing small amounts of a gas through the jacket tube. The gases evolved are withdrawn, for example by suction, from a suitable place of the said vessel. The apparatus described will be further understood by reference to Figure 1 of the accompanying drawing showing in a somewhat diagrammatic manner a vertical section of the vessels through which the treated hydrocarbon material is continuously passed. In this drawing numeral **1** denotes the jacket tube in which the hydrocarbon material is exposed to the action of silent electric discharges. The foam evolved by these electric discharges is passed by way of pipe **4** into the vessel **2** from which the hydrocarbon material is conveyed as a liquid into jacket tube **1** by way of pipe **3**. Numeral **5** denotes the pipe for supplying the gas facilitating the formation of foam in tube **1**.

A thin layer of the hydrocarbon material under treatment may also be produced in the treatment space by arranging the glass tubes horizontally and continuous rotation of the inner tube or the whole apparatus whereby a thin film of the hydrocarbon material is produced on the outer surface of the said inner tube.

The voltolization treatment may also be carried through in apparatus construed after the type of condensers with a plurality of plates. A vertical section of such condenser apparatus is shown in Figure 2 of the accompanying drawing. For example a plurality of glass plates denoted in Figure 2 by letter A may be arranged in a reaction vessel with a metal sheet B between each pair of glass plates so that there is an interval between each glass plate and its neighboured metal sheets. The metal sheets are then alternately connected to the terminals of a source D of high frequency current while the remaining metal sheets are grounded. The glass plates A may be rigidly connected to a central axle C so that they may be rotated by turning the axle. Also in this case a formation of foam takes place during the treatment whereby a thin layer of hydrocarbon material is produced, which is highly desirable. For the treatment of large batches of hydrocarbon material an apparatus is preferred which consists of a large number of electrode sheets, each being separated from the others by means of a dielectric sheet, such as glass. Both the electrodes and the dielectric sheet are immersed in the hydrocarbon material under treatment. A thin layer of this material is then produced by means of pumps, scoops or the like which cause the hydrocarbon material to flow downwardly over the surface of the metal sheets. The horizontally arranged voltolization drum may for example be filled up to half its height with the hydrocarbon material to be treated; by the rotation of the dielectric glass plates a thin layer of the hydrocarbon material is continuously maintained. If the dielectric glass plates do not dip into the hydrocarbon liquid or if only a small part of their surface dips thereinto the formation of the thin layers is effected by means of scoops or spraying devices or similar means as mentioned above. The glass plates or the metal sheets may also be fastened together by means of an outer frame in which case no difficulties as to insulation are encountered. The drum and likewise the set of glass plates may also be fixedly arranged in which case only a wheel provided with scoops is rotated.

Instead of using glass as a dielectric, use may also be made of, for example, porcelain, earthenware, vulcanized fibre, artificial resins such as coumarone resins or Bakelite, or the material known in the trade as "Pertinax", which is an insulating material prepared by means of natural or artificial resins. Also the metal sheets may be coated with these or with other insulating materials.

Another method of procedure is the following. A longitudinal closed tube, which is provided at either end with an electrode, is evacuated. The initial hydrocarbon material is then introduced, if desired in a finely divided state, into the tube whereupon the current is switched on. In order to produce a thin layer of the hydrocarbon material it is preferable to maintain the tube in motion during the electric treatment. The tube is advantageously heated in order to keep the treated materials readily mobile. This is especially the case when starting from very viscous materials. The hydrogen split off during the operation is sucked off at any suitable place.

We now come to the detailed explanation of the several specific features or modifications of the process in accordance with the present invention.

As has been pointed out above we have found that it is desirable to subject to the voltolization treatment such initial materials as possess certain well defined characteristics.

A very suitable kind of initial materials consists of paraffin hydrocarbons having a molecular weight above that of hard paraffin wax. By this expression we mean paraffin hydrocarbons having a molecular weight of preferably more than 350. As such initial materials may be mentioned paraffin waxes having so high a molecular weight or still higher molecular substances which boil preferably above 300° in a high vacuum below 2 millimeters mercury gauge, as for example ceresine and ozokerite. Substance of this kind may also be prepared synthetically, as for example by electrolytic treatment of fatty acids or by a destructive hydrogenation of waxy substances followed by a condensation in the presence of condensing agents, such as aluminium chloride.

In the treatment of the said initial materials with silent electric discharges in Siemens ozonization tubes or other discharge apparatus it is preferable to employ a diluent, as for example hard or soft paraffin wax, paraffin oil, illuminating oil and the like. In this case it is preferable to add the diluents after at least the first two-thirds of the duration of the electric treatment have passed. Thus for example when the initial materials have been exposed to the silent electric discharges for about 20 hours the resulting products are mixed with a diluent and then treated again for a shorter time, for example from 3 to 8 hours. When employing paraffin wax or paraffin oil as a diluent it is possible that also the diluent becomes condensed to some extent. However, since in the above described treatment the diluent is exposed to the silent electric discharges for a considerably shorter period the degree of condensation is a considerably lower one than with the initial materials and therefore the condensed initial materials may be easily separated from the diluents at the end of the operation. Also other solvents, for example those containing halogens, such as dichloroethane, tetrachloroethane, tetrachlorobenzene, or also aniline may be employed as diluents, the diluent is removed from the condensation product after the treatment by distillation or with the aid of a solvent as hereinafter more fully described. Furthermore it is advantageous to separate the unchanged initial material from the condensation product by treatment with a suitable solvent or by distillation as will be set forth below.

The method of treating initial materials of the said kind will now be explained further by way of two specific examples.

Example 1

Ceresine having a melting point of 73° is treated at temperatures above its melting point, as for example at from 80° to 100°, in a Siemens ozonization tube under a pressure of from about 5 to 10 millimeters (mercury gauge) with electric discharges at about 7000 volts and 1000 cycles for from 25 to 30 hours, the same amount of hard paraffin wax having a melting point of 50° being added as a diluent after from 20 to 22 hours. The resulting mixture is then subjected to a vacuum steam distillation up to 280° whereby the added paraffin wax and any products of low boiling point formed are distilled off.

Valuable products are likewise obtained by exposing such paraffin hydrocarbons having preferably, a boiling point of more than 300° in a high vacuum, in admixture with hard or soft paraffin wax or with hydrocarbon oils rich in hydrogen, i. e., those containing more than 13, preferably more than 14.5 parts of hydrogen for each 100 parts of carbon, and containing considerable amounts, as for example 10 per cent or 30 per cent or more, of these waxes, such as petrolatum, crude paraffin wax, petroleum jelly, and crude lubricating oils containing paraffin wax, or with other oils, such as paraffin oil, spindle oil, machine oil, tar oil, cylinder oil, hydrogenated naphthalenes, high boiling products preferably rich in hydrogen obtained by the destructive hydrogenation of carbonaceous substances of the nature of coals, tars, mineral oils and the like, or aromatic oils or oxygen-containing derivatives such as montan wax, to the action of silent electrical discharges under such conditions that the hard or soft paraffin wax or other admixed products rich in hydrogen are also completely or to the greater part converted.

As initial materials may be mentioned paraffin wax or oils rich in hydrogen containing wax in considerable amounts and which by nature contain constituents having a molecular weight of more than 350. They may also be prepared by mixing. The content of paraffin hydrocarbons or their oxygen derivatives, having a molecular weight exceeding 350, such as ceresine, ozokerite, neftgil, hatchettine, mineral fat or even tallow, wool grease, fish oil or train oil, or the content of montan wax or other waxes, as for example beeswax, may amount for example to 5, 10, 25 per cent or more, as for example 80 or 90 per cent. Moreover, alcohols of a molecular weight above 200, such as ceryl alcohol, or acids of a molecular weight above 200, such as cerotic acid, or esters, the acid component of which has a molecular weight above 200, as for example the glycerides of fatty acids, such as stearic acid, palmitic acid, oleic acid or lauric acid, may be employed. The said hydrocarbons of high molecular weight may also be prepared synthetically, as for example by electrolytic treatment of fatty acids, in the manner referred to above.

The voltolization of the said mixtures may be carried out in the presence of gases or vapors, such as hydrogen, nitrogen, hydrogen halides, halogens or gaseous saturated or unsaturated hydrocarbons, or waste gases from the destructive hydrogenation or coke oven gases or natural gas. These gases or vapors have the effect of facilitating the formation of foam during the electric treatment and of simultaneously promoting the condensation action. The employment of foam-forming agents, such as saponine, sulphonic acids and their salts and fatty acids of high molecular weight, such as oleic acid, is also of advantage. Moreover, other substances promoting the condensation may be present, such as active carbon and active silica, or metal oxides, such as zinc oxide, cadmium oxide, molybdenum oxide, tungsten oxide or chromium oxide, or halogen compounds of non-metals, such as sulphur, phosphorus or boron, or of metals, such as of copper, silver, magnesium, titanium, vanadium, molybdenum, tungsten, chromium, nickel and cobalt, or metal halides, in particular iodides or organic halogen compounds, such as those of benzene, toluene, xylene, or naphthalene, or methyl, ethyl, methylene or ethylene chloride, iodide or bromide. The said halides, in particular the iodides as well as the metal oxides have the effect of improving the color of the final products.

Aromatic hydrocarbons, as for example naphthalene, or tetrahydro- or decahydro-naphthalene, may also be added to the initial materials before the treatment in cases when they are not already contained therein. It is preferable to select aromatic hydrocarbons of high molecular weight, as for example anthracene or phenanthrene; condensation or polymerisation products of unsaturated hydrocarbons of low molecular weight may also be added.

It is also advantageous to carry out the treatment of the paraffin hydrocarbons in the presence of diluents, such as paraffin oil or illuminating oil, which, in order to avoid any substantial participation in the reaction, are added only during the reaction and are subsequently separated again.

The following examples will further illustrate this feature of the present invention.

Example 2

A mixture consisting of 80 parts of hard paraffin wax and 20 parts of ceresine is treated at 80° in a Siemens ozonization tube under a pressure of from 5 to 10 millimeters (mercury gauge) with a silent electric discharge of about 7000 volts and 4000 Hertz for 10 hours. The resulting mixture is subjected to a vacuum steam distillation at 280°, a small remainder of incompletely converted paraffin wax and any products of low boiling point formed being thus distilled off.

Another way of producing valuable voltolization products consists, as has been pointed out above, in subjecting initial materials containing paraffin hydrocarbons, more particularly of the nature of soft or hard paraffin wax, to a preliminary treatment by which they are rendered suitable for giving valuable voltolization products.

One method of carrying out this modification of the present invention consists in subjecting the initial materials of the said kind to a preliminary distillation whereby the paraffin waxes or the oils containing paraffin wax are divided into fractions having a different mean molecular weight. The distillation is preferably carried out in vacuo, for example between 10 and 20 millimeters mercury gauge and at a temperature between 200° and 300°, advantageously between 260° and 290°. It is also of advantage to employ steam or other gases or vapors during the distillation, as for example hydrogen or nitrogen or carbon dioxide or benzine vapors. By this distillation the lower molecular fractions are obtained as distillate while the higher molecular fractions remain as residue in the still. If these two fractions are separately subjected to a treatment with high voltage currents, preferably of high frequency, the higher molecular fraction yields a product which very effectively improves the properties of lubricating oils.

Another method of improving initial materials of the said kind and rendering them suitable for the voltolization treatment consists in subjecting them to a preliminary hydrogenation by the action of hydrogen or gases containing hydrogen at elevated temperatures, preferably under superatmospheric pressures so as to obtain products which are particularly rich in hydrogen. In this manner also high molecular paraffin waxes or other waxes, which contain less than 14.5 parts of hydrogen for each 100 parts of carbon may be satisfactorily made use of for the purposes of the present invention. It is preferable to carry out this hydrogenating treatment in the presence of hydrogenating catalysts, preferably of compounds of metals belonging to groups 2 to 8 of the periodic system, as for example the oxides or sulphides of copper, zinc, tin, vanadium, molybdenum, tungsten, chromium, uranium, rhenium, manganese, cobalt or nickel. The temperatures employed range from 100° to 500° C. preferably from 100° to 350° C. Pressures of 10, 20, 50, 100, 200, 500 or 1000 or more atmospheres come into question. The conditions are preferably so selected that no substantial conversion into lower molecular compounds takes place.

Another pretreatment may be effected by subjecting the initial materials to extraction. To this end the initial materials are preferably treated with liquefied gaseous hydrocarbons, in particular ethane or propane or mixtures thereof or with liquefied sulphur dioxide, or phenol, nitrobenzene, aniline, furfurol, ketones, ketonic acids or mixtures of cyclohexane with methanol. In this manner a separation into fractions rich in hydrogen and those poor in hydrogen takes place. By the voltolization of the resulting fractions rich in hydrogen products having a very high viscosity may be produced without the other properties being affected in an undesired way.

This method of working will be further explained by the following examples.

Example 3

A topped residue of a Mid-Continent oil is mixed with four times the amount of liquefied propane. At ordinary temperature the asphalt-like and resinous bodies remain undissolved. The solution is freed from these bodies and then cooled to 35° C. below zero C. whereby a mixture of paraffin wax and a high molecular oil rich in hydrogen separates out. This is removed from the solution of liquefied propane and represents a purified product which may be subjected with advantage to voltolization.

Example 4

A crude black ozokerite having a melting point of 80° C. is dissolved at about this temperature in 10 volumes of liquid propane. A black tar amounting to about 3 per cent of the original ozokerite is precipitated leaving a dark brown colored wax in solution. This black tarry material is separated from the solution. The clear solution is then heated up to a temperature of about 90° C. whereupon a portion of the wax is precipitated and carries with it a substantial proportion of the dark colored material. This precipitated material is removed. The refined material is then subjected, if desired after a purification with bleaching earth, to a voltolization treatment.

A further improvement is also attained if the initial materials are treated with agents having a refining action, such as sulphuric acid, bleaching earths, aluminum chloride, zinc chloride, boron fluoride, iron chloride or chromic acid. In this way the portions poor in hydrogen as well as other constituents impairing the quality of the voltolized products are removed.

This embodiment of the present invention will be further illustrated by the following example.

Example 5

Petrolatum is treated at from 80° to 100° C. while stirring with 10 per cent of its weight of aluminum chloride. The aluminum chloride is then allowed to deposit together with the condensation products at the bottom of the reaction vessel, the constituents rich in hydrogen thereupon being separated from the deposit and voltolized in the aforedescribed manner.

The aforesaid initial materials may also be dissolved in suitable solvents, the different constituents then being separately precipitated from the solution. Thus the initial material may be dissolved in ether, whereupon the high molecular fraction is separated by the addition of acetone. This precipitation may be effected by the addition of the precipitant in stages. The stepwise precipitation may also be facilitated, or even be effected, by a change of the temperature, for example by lowering the temperature. Similar results are obtained by first dissolving in ether and then precipitating by alcohol or by dissolving in chloroform and precipitating by alcohol or by dissolving in chlorinated ethylene and precipitating by acetone or by employing similar solvents and precipitants.

The following example will further explain this feature of the present invention.

Example 6

A paraffin wax obtained from mineral oil and which has a molecular weight of 330 is dissolved at 20° C. in the double amount of ether. To this solution acetone is added in an amount half that of the ether whereby a paraffin wax having a melting point of 57° C. and a molecular weight of 370 is precipitated in an amount of 45 per cent of the initial paraffin wax. This paraffin wax is then freed from the solution by filtration. From the solution ether and acetone are distilled off, a paraffin wax having a melting point of 45° C. and a molecular weight of 300 which represents 55 per cent of the initial paraffin wax remaining as distillation residue. Both fractions of paraffin wax are then treated with high voltage high frequency electric currents. The voltolization product from the precipitated paraffin wax has a greater efficiency as pour point depressant than the voltolization product of the paraffin wax remaining dissolved in the mixture of ether and acetone.

When using initial materials entirely composed of solid constituents, as for example paraffin wax or montan wax or other waxes, fractions having different melting points or different molecular weight may also be obtained by fractional crystallization from a solvent by cooling in stages to successively lower temperatures. The initial materials may also be precipitated as a whole from their solutions by strongly cooling, for example to a temperature of 40° below zero C., the single fractions then being obtained from the precipitate by subjecting the latter to stepwise sweating out at successively increased temperatures. If a pure initial material is to be worked up this may be separated into fractions of different molecular weight, melting point or other characteristics simply by sweating without preliminarily dissolving it in a solvent. The aforesaid methods of separating the initial materials into fractions may also be combined with each other.

This modification of the process according to the present invention will be further illustrated by the following example.

Mixtures consisting of solid paraffin wax or another wax and a liquid hydrocarbon product rich in hydrogen, as for example a hydrocarbon oil, are preferably subjected to a mild cracking at temperatures between 450° and 550° C., care being taken that at the most a small part (up to about 20 per cent) of the high molecular components, in particular the paraffin wax or the other wax is converted into lower boiling constituents. This may be regulated by a suitable selection of the speed of flow of the materials subjected to the cracking conditions. It is also preferable to carry through the heat-treatment in the presence of hydrogen, preferably under pressure, as for example of 50, 100, 200 or 500 atmospheres. It is of advantage to employ catalysts having a dehydrogenating action in the said heat-treatment, as for example copper, molybdenum, vanadium, tungsten, iron, nickel, aluminum or titanium or the oxides or sulphides of these metals. The products resulting from this heat-treatment are then cooled, if desired, while dissolved in a diluent such as benzine, illuminating oil, ketones, alcohol, chlorinated alcohols or mixtures of these liquids, to a temperature of 10° or 5° or 0° C. or 20° below zero C. or even lower, as for example 30 or 40° below zero C., the resulting precipitate then being separated from the body of the solution by mechanical means, as for example by centrifuging or filtering. The paraffin wax thereby obtained is then treated in the manner aforedescribed. If desired, the paraffin wax recovered in this way may be separated into different fractions.

The said method of procedure will be further explained by the following example.

Example 7

Petrolatum consisting of 40 per cent of paraffin wax and 60 per cent of oil are distilled, while slightly cracking, at a temperature between 475° and 500° C. The distillate is then mixed with the same amount of benzine and cooled to 10° below zero C., whereby 35 per cent of paraffin wax, which may be readily separated and then voltolized, are precipitated.

Still another method of preliminarily treating initial materials to be subjected to the voltolization treatment consists in separating high quality solid paraffin wax from petrolatum or similar products by mixing the initial material with light benzine, especially a light benzine containing more than 5 but less than 9 carbon atoms, cooling the mixture to low temperatures and filtering or centrifuging, if desired in several stages. If desired, the paraffin wax thus separated may be freed from gums or asphalts, preferably by distillation in vacuo. With paraffin wax separated in the manner described, this is comparatively easy.

As light benzines may be mentioned fractions boiling between about 30° and 100° C. which may be obtained for example from mineral oil by distillation or by the destructive hydrogenation of coals, tars, mineral oils or by cracking tars or mineral oils, fractions boiling within the said limits but within a narrower range may also be employed. Aliphatic light benzines, in particular those rich in hydrogen, have an especially advantageous action.

In order to carry out the process according to this invention, petrolatum (crude paraffin wax) is preferably mixed with from 2 to 8 times its amount of light benzine, cooled to low temperatures, preferably below 10° below zero C., for example to 25° below zero C., and the paraffin thus separated filtered or centrifuged off. It is advantageous to carry out the cooling and the separation in several stages, as for example at zero and 25° below zero C. respectively. The paraffin wax thus obtained is then subjected when necessary to a distillation in vacuo at temperatures up to about 400° C., if desired while employed scavenging gases, in order to remove gums or asphalts.

The paraffin wax obtained according to the aforesaid method has the valuable property of yielding a product when treated with high voltage, preferably high frequency, electric currents, which considerably lowers the setting point of lubricating oils. In many cases it is advantageous to carry on the electric treatment until the product has a viscosity of 10° Engler at 99° C. or still higher, as for example from 15° to 50° Engler at 99° C.

As has been pointed out above we have also found that the products resulting from the voltolization treatment can often be improved by subjecting them to an after-treatment more particularly with a view to "immunize" obnoxious constituents which are mostly present in these products. They often contain more or less substantial amounts of paraffin hydrocarbons of the order of those present in ordinary soft or hard paraffin wax or of a still higher order. We have therefore attempted to improve the crude products by removing therefrom such paraffin wax hydrocarbons, for example by freezing them out. It has been found, however, that while such treatment often leads to a very substantial improvement of the crude voltolization products it does not render them free from objectionable matter in all cases. Further investigation has revealed the fact that during the voltolization treatment comparatively large quantities of products of middle oil character are formed and that it is due to such constituents of middle oil character that the voltolization products hitherto known and often also those obtained as hereinbefore described do not meet all requirements of practice. We have therefore found it necessary to "immunize" not only paraffin wax hydrocarbons but also middle oils either by removing both kinds of substances or by removing only the constituents of middle oil character and otherwise rendering harmless the paraffin hydrocarbons.

By the presence of these substances in the voltolization products the high quality of the latter (the tests of which are much better than those of the natural or synthetic lubricants hitherto known) is appreciably affected. The voltolization products are impaired by the said substances in particular as regards their flash point, their setting point, their viscosity and their capacity of forming films. If, however, the voltolization products are subjected to the aforesaid "immunization", products having excellent properties are obtained; for example the films formed therefrom are only difficultly broken even if two parts of a machine are pressing with a high pressure against each other. The said after-treatment is also of particular advantage in case the voltolization products are to be employed for improving other lubricating oils since the effect attained by a certain amount of such product is considerably greater than the effect obtained by the same amount of a voltolized product which has not been subjected to the said after-treatment, in particular as regards the lowering of the pour point, the improvement of the viscosity index and the capacity of forming films.

The said "immunization" may be effected for example by subjecting the crude products to distillation. This is preferably effected under reduced pressure and most suitably with the aid of scavenging gases such as water vapor or the like. In order to prevent valuable constituents of the crude voltolization products from being removed during such distillation temperatures of 280° C. should as a rule not be exceeded.

When employing scavenging gases, such as steam, hydrogen, nitrogen, carbon dioxide, benzine vapors, waste gases from the destructive hydrogenation or coke oven gases, the distillation temperature may be lowered by from 20° to 30° C. By this manner of working the noxious constituents are distilled off, while the improved voltolization product remains in the still. The distillation may be effected in the presence of absorbing agents, such as bleaching earth. These absorbing agents may be removed from the distillation residue for example by dilution with a solvent, as for example benzine or illuminating oil and subsequent filtration or centrifuging. The voltolization product may then be freed from the solvent by distillation or by precipitating it from the solution by means of a suitable precipitant as for example acetone or alcohol when dissolving in ether.

This feature of the present invention will be further illustrated by the following example.

Example 8

A voltolization product prepared by treating paraffin wax in an ozonization tube for 40 hours with electric currents of 6000 volts and 2000 Hertz is heated in a still to 180° C. and then mixed with 5 per cent of finely ground bleaching earth while stirring. The resulting mixture is then distilled while passing through steam at 250° C. under a reduced pressure at 15 millimeters of mercury gauge. In this manner 10 per cent of the voltolization product are first passed over as a fraction of the boiling point range of middle oils whereupon further 40 per cent are carried off as unchanged paraffin wax. The product remaining as distillation residue is dissolved in the same amount of benzine and separated by filtration from the bleaching earth. The final product remaining after distilling off the benzine is a light yellow oil having a viscosity of 45° Engler at 99° C. With lower viscous products the distillation residue may be filtered without adding a diluent, at about 150° C.

The "immunization" or removal of the obnoxious substances present in the crude voltolization products may also be effected by means of an extraction process in which hydrocarbons gaseous at ordinary temperature which have been liquefied by cooling and/or the application of elevated pressure are preferably used as extraction agents.

For this purpose the voltolization product is mixed with from 4 to 6 times the amount of liquefied gaseous hydrocarbons as for example methane, ethane, propane, butane, ethylene, propylene or mixtures thereof. It is preferable to employ propane or ethane or mixtures of propane and ethane. The said treatment is effected in a vessel capable of withstanding elevated pressures whereby a pressure prevails which is equal to the vapor pressure of the particular liquefied hydrocarbon or of the particular mixture of liquefied hydrocarbons at the working temperature, which is either ordinary or slightly reduced temperature. In this manner the lower molecular constituents present in the voltolization product are dissolved by the solvent while the valuable portion of this product remains undissolved. The two layers formed are then separated. By lowering the temperature stepwise, products having different characteristics may be precipitated from the solution in the liquefied hydrocarbons.

It is also possible to dilute the crude voltolization products with lower molecular hydrocarbons such as gasoline or kerosene or the like, then to cool the mixture and to remove the substances, in particular the paraffin waxes which have been separated out.

In this case the voltolization product is preferably diluted with benzine or illuminating oil or with halogenated hydrocarbons such as trichloroethane, then cooled to a temperature between 8° and 30° below zero C. whereby the paraffin wax contained in the crude product is precipitated, the latter then being filtered or centrifuged. The solution containing the valuable constituents of the voltolization product and the low boiling constituents thereof is then freed by distillation from the diluent and from the said low boiling constituents. This product may also be first freed from the low boiling constituents and from the bulk of the paraffin wax and then subjected to the aforesaid cooling operation. The paraffin wax separated from the voltolization product may again be supplied to the voltolization treatment. If the cooling operation is carried out stepwise the paraffin wax may be obtained in the form of single fractions.

We have also found that the crude voltolization products may be dissolved in solvents as for example ether or kerosene, whereupon such substances as acetone are added whereby the valuable constituents of the crude product are precipitated out.

This operation may be carried out as follows:—The crude voltolization product is dissolved in a solvent, as for example ether, whereupon the pure voltolization product is precipitated by means of a precipitant, such as acetone. This treatment may also be effected in stages, whereby pure voltolization fractions having different viscosity may then be employed for improving lubricating oils while the fraction having the lower viscosity may be used as such as a lubricant. The said precipitation may also take place at a subatmospheric temperature, in which case the temperature may be lowered in stages. In this manner the paraffin wax present in the crude voltolization products is precipitated, after the precipitation of the valuable constituents of the said products, if desired in the form of two or more fractions having a different mean molecular weight, while the low boiling constituents formed during the voltolization remain dissolved in the solvent. The voltolization product may also be dissolved in other solvents and precipitated by other precipitants. Thus it may be dissolved in ether and precipitated by alcohol or dissolved in trichloroethane and precipitated by acetone.

A purification of the crude voltolized product may also be effected by hydrogenation. To this end the said product is treated at elevated temperatures of between 100° and 450° C. with hydrogen, preferably at elevated pressures, as for example 20, 50, 100, 200, 500 or 1000 atmospheres, in the presence of a catalyst having a hydrogenating action, preferably an oxide or sulphide of a metal belonging to groups 5 or 6 of the periodic system or of nickel or cobalt. The said hydrogenation may, if desired, be carried out in the presence of a diluent, as for example a heavy oil or illuminating oil, rich in hydrogen, preferably containing more than 15 parts of hydrogen for each 100 parts of carbon and free from asphalts. The duration of treatment is so selected that no substantial amounts of the voltolized products are split up into lower molecular compounds. By the said hydrogenation the iodine number of the voltolization product is improved. If desired, the final hydrogenated product may be subjected to a distillation or purified by dissolving it in a solvent and subsequently precipitating it therefrom.

The following example will further illustrate this purification by hydrogenation.

Example 9

100 parts of a crude voltolization product obtained as described in Example 2 are passed in the liquid phase together with hydrogen at 200° C. and under a pressure of 200 atmospheres over a catalyst consisting of tungsten sulphide which is rigidly arranged in the reaction vessel. By subsequent fractional condensation the middle oils formed during the voltolization are separated from the higher boiling portions. The latter are then subjected to a distillation in the presence of steam at a reduced pressure of 15 millimeters mercury gauge, unchanged paraffin wax thereby being carried off. The residue represents an excellent voltolization oil having a low iodine value and a good color.

It is often also advisable to immunize the constituents of middle oil character and the paraffin wax hydrocarbons by combining several of the aforesaid refining treatment. For example the crude voltolization products may be first subjected to distillation and the resulting residue be subjected to extraction or other removal of the paraffin wax hydrocarbons.

The crude voltolization products may also be subjected first to distillation, the distillation residue then being subjected after the addition of a diluent, to a cooling treatment. The residue may also be dissolved and then precipitated, if desired in stages, by means of a precipitant. Still another method consists in first hydrogenating the crude product and then subjecting it to a cooling operation, or first to dissolve the crude product, then precipitating it by means of a precipitant and finally purifying the precipitate thus obtained by dissolving it in a solvent and then precipitating it by cooling the resulting solution.

The product obtained by the aforedescribed purification operations may subsequently be treated with adsorbing agents, such as Florida earth. The adsorbing agents may also be present during the distillation of the crude voltolization product. Thus bleaching earth may be added before the distillation, the distillation residue then being freed from the adsorbing agent by the addition of a solvent and subsequent filtration or centrifuging.

These methods of operation may be further explained by the following example.

Example 10

A crude voltolization product is subjected to distillation in the presence of 15 per cent of finely ground Florida earth at 280° C. and under a reduced pressure of 15 millimeters mercury gauge while adding steam, middle oil and paraffin wax thereby being distilled off. The distillation residue is then dissolved in benzine and filtered or centrifuged. The oil freed from Florida earth has a viscosity of 12° Engler at 99° C. and a molecular weight of 1100. This oil is then dissolved in twice the amount of ether and has subsequently added thereto acetone in an amount half that of the ether in three portions, the products precipitated in the first two stages and the oil remaining in the solution being isolated by distilling off the solvent. In this manner 3 portions of oils are obtained having a viscosity at 99° C. of 23° Engler, 6° Engler and 4° Engler respectively and a mean molecular weight of 1500, 900, and 700 respectively.

The paraffin wax hydrocarbons may also be immunized without removing them from the voltolization products by the addition of substances which are known to have pour depressant properties, for example by the addition of a product obtained by the condensation of halogenated paraffin wax with naphthalene in the presence of aluminum chloride. It is, however, preferable first to subject the crude product to a distillation. The crude voltolization product may be mixed, preferably after separation of the middle oil formed during the voltolization, with an amount of from 0.5 to 2 per cent of the said condensation product.

The said condensation product may also be added, for example in an amount of about 5, 10 or 20 per cent or more, to the initial material before voltolizing it.

In order to prepare a very effective improving agent for lubricating oils and pour point depressants the said condensation product may be subjected as such to voltolization or the voltolization products obtained according to the present invention may be subjected to a condensation with aluminium chloride or similar condensing agents. If for example such condensation product having a viscosity of from 25° to 30° Engler at 99° C. is voltolized so that the final product has a viscosity of 100° Engler at 99° C., the efficiency of the said condensation product as pour point depressant is increased by 30 per cent.

The nature of the reaction products varies not only with the nature of the initial materials used and the after-treatments applied but also with the conditions used for the voltolization treatment itself. As will be apparent from the above description, the voltolization treatment may be carried through in the presence of gases such as hydrogen, nitrogen, carbon monoxide, halogen hydrides, halogens, carbon dioxide, waste gases from the destructive hydrogenation, coke oven gases, benzine vapors or natural gas, and catalysts as for example metal powders, such as molybdenum, tungsten, vanadium, or copper, or metal oxides, in particular the oxides of the last mentioned metals, or organic halogen compounds, such as methylene chloride or ethylene chloride or the corresponding bromides or iodides, or halogen substitution products of benzene or of toluene, or pulverulent carbon, or bleaching earth such as Florida earth or active silica may also be added. The nature of the products varies also with the frequency of the alternating current and the time for which the initial material is exposed to the silent electric discharges. The frequency may be for example 50 or 200 or 500 or 1000 or 10,000 or 50,000 or even more cycles per second. The time required for the treatment depends not only on the degree of condensation or polymerization which is to be attained but also on the frequency of the current. It may be noted that in order to obtain the same degree of condensation or polymerization the time required is the lower the higher the frequency. For example, when working with the same tension and increasing the frequency to 10 times its original value, the time required for the treatment is reduced to $\frac{1}{10}$ of that originally necessary. The nature of the products may also vary with the tension used. Generally speaking it is preferable when working with tube apparatus such as Siemens ozonization tubes, to use tensions between 7000 and 8000 volts, the vacuum applied ranging preferably between 1 and 10 millimeters mercury column. In the case of large apparatus tensions between 4000 and 5000 volts or more are preferably used and the vacuum applied should preferably range between 5 and 10 centimeters mercury column.

The products obtained according to the process of the present invention are either valuable lubricating oils or greases themselves or they are with great advantage used as pour depressants or for improving the temperature-viscosity curve of other lubricating oils.

A specific kind of substances suitable for improving other lubricants is obtained in the form of a highly viscous, oily product by carrying out the voltolization in the presence of condensing agents.

As condensing agents may be mentioned for example aluminum chloride, boron fluoride and zinc chloride. For example from 10 to 20 per cent or more of aluminum chloride may be added to the substance to be polymerized or condensed. The reaction temperature is preferably between 20° and 200° C., the yields of the highly viscous, oily product being greater with increasing temperature. In this treatment, it is advantageous to add from 10 to 50 per cent or more of cyclic hydrocarbons, especially naphthalene.

Similar products are obtained in small yields by carrying out the voltolization in the absence of condensing agents at temperatures between 200° and 300° C. The products thus prepared may also be satisfactorily employed for improving the color of lubricating oils.

As will be apparent from the foregoing description of our process of carrying through the voltolization and working up the crude reaction products, the products may vary widely in their properties.

Generally speaking it may be said that the voltolization products are mostly characterized by the following properties:

They have a viscosity index of between about 120 and 150, more particularly between 130 and 150, in preferred cases between 140 and 150. The viscosity at 99° C. ranges between 3 and 150° Engler or is even higher, as a rule between 9 and 80° Engler and more usually between 12 and 60° Engler; the molecular weight determined in benzene ranges between 500 and 10,000, as a rule between 600 and 5,000 and more usually between 800 and 2,500; the specific gravity is about 0.86. The products contain between about 16 and 16.3 parts of hydrogen for each 100 parts of carbon, they have a Conradson carbon test of between 0.6 and 0.05, more usually between 0.4 and 0.1, a flash point between 280° and 330° C., and in any case above 300° C. if the viscosity at 99° C. is higher than 5, and a tar value below 0.4. Their color is from light yellow to dark yellow.

Thus for example a voltolization product which may be directly employed as a cylinder oil has a molecular weight between 800 and 1,000, a viscosity between 5° and 10° Engler at 99° C., a viscosity index between 130 and 150, a carbon test between 0.4 and 0.5 and contains 16.4 parts of hydrogen for each 100 parts of carbon.

The voltolization products which may be added to lubricating oils for improving their properties as a rule have a molecular weight above 900, for example between 900 and 2,000 or even higher and a viscosity, at 99° C., between 12° and 80° Engler, as for example 40° or 60° Engler. But also less viscous products having for example a viscosity between 4° and 10° Engler at 99° C. may be employed for the said purpose. The amount of the voltolization products added to the lubricating oils depends on the properties of these products and on the viscosity index to be imparted to the lubricating oil to be improved.

Crude voltolization products which are only freed from the low boiling constituents formed during the voltolization have the consistency of fats. When lubricating greases are to be prepared directly by the voltolization the treatment is continued until a viscosity at 99° C. of between 30° and 80° Engler or higher, such as of 50° Engler is attained. The resulting products have a solidification point of between 30° and 35° C. and a dropping point of about 30° C. These products may also be employed in admixture with other lubricating greases.

We now come to the explanation of the use of the voltolization products for improving other lubricants. Generally speaking the voltolization products substantially improve the pour point of lubricants when added thereto in small amounts, and the temperature viscosity curve, i. e., the viscosity index when added in comparatively large amounts.

Dealing first with the property of the voltolization products of reducing the pour point of lubricants, we have found that the products obtained by employing paraffin hydrocarbons having a molecular weight above that of hard paraffin wax, have the valuable property, as additional agents for lubricating oils, gear oils, and greases and the like, of improving their properties even when added in very small amounts, by considerably lowering the setting or pour point of ordinary lubricating oil. For example by an addition of from 0.05 to 10 per cent, preferably 0.1 to 3 per cent, the pour point of lubricating oils may be lowered by from 10° to 40° C.

The following example will further illustrate this feature of our invention.

Example 11

By adding the voltolization product described in Example 1 to an oil having a setting point of zero C., an addition of 0.3 per cent lowers the setting point of the oil to 25° below zero C.

We have further found that excellent lubricating oils are obtained by adding to lubricating oils which by reason of their containing no or only small amounts of paraffin wax have an unsatisfactory temperature-viscosity curve, as for example asphaltic base or naphthenic lubricating oils, paraffin wax or other waxy substances, in order to impart to them a favourable temperature viscosity curve, and in addition thereto an amount of a voltolization product in order to lower the pour point increased by the content of paraffin wax. Also oils originally containing appreciable amounts of paraffin wax and which have afterwards been freed therefrom to a smaller or larger extent in order to render them marketable but which still contain some paraffin wax as for example 5 per cent or more, may be employed for lubricating purposes after addition of a voltolization product. Also in this case the advantage of a favourable flat temperature-viscosity curve is combined with that of a low pour point.

The said method of operation will be further illustrated by the following example.

Example 12

A Columbia lubricating oil is first treated with sulphuric acid of 66° Bé. strength and then filtered over clay. The resulting product has the following properties:

Specific gravity	0.910
Viscosity at 38° C	13.3° Engler
Viscosity at 99° C	1.74° Engler
Viscosity index	50
Pour point	18° below zero C.
Flash point	210° C.

If 8.5 parts of this oil has added thereto 1 part of a petrolatum having a specific gravity of 0.872 and a viscosity of 1.4° Engler at 99° C., the resulting mixture has the following properties:

Specific gravity	0.908
Viscosity at 38° C	12.2° Engler
Viscosity at 99° C	1.7° Engler
Viscosity index	60
Pour point	15° C.

While the viscosity index has been raised by 10 points also the pour point is raised by 33° C. If 0.5 per cent of the voltolization product prepared as described in Example 1 is added to this mixture a final product having the following characteristics is obtained:

Specific gravity	0.908
Viscosity at 38° C	12.2° Engler
Viscosity at 99° C	1.7° Engler
Viscosity index	64
Pour point	below 23° below zero C.

Similarly, the products obtained from mixtures of the aforesaid paraffin hydrocarbons with products rich in hydrogen under strong conditions have valuable properties as additions to lubricating oils, gear oils and lubricating greases and are capable, even in quite small amounts, as for example from 0.3 to 10 per cent or in some cases more, of improving their properties, as for example of lowering quite considerably the setting point of ordinary lubricating oils and flattening the temperature-viscosity curve. This will be further illustrated by the following example.

Example 13

If the polymerization product described in Example 2 be added to an oil in the amount of 0.7% which sets at zero C., the setting point of the oil is lowered to 25° below zero C.

In addition to having the aforesaid properties, the products obtained from the said mixtures, especially from paraffin waxes of high molecular weight or their derivatives with hard or soft paraffin wax or oils rich in hydrogen containing the same, by voltolization treatment are excellent solid lubricants by themselves and it is not necessary to separate the unconverted or only partially converted substances from the crude voltolization products.

Turning now to the improvement of the viscosity index of lubricants by the addition of voltolization products, we have found that polymerization products prepared in the said manner and having a viscosity of more than 10°, preferably more than 12° Engler at 99° C. are particularly valuable in that by the addition even of small amounts thereof to lubricating oils having an unsatisfactory temperature-viscosity curve, a considerable improvement in the same is effected.

As initial materials for the preparation of the said voltolization products to be added may be mentioned semi-solid and solid paraffinic hydrocarbons from any source or hydrocarbons containing the same in considerable amounts, i. e. preferably more than 20 per cent. They may be obtained by distillation from petroleum or extraction from brown coal or by the destructive hydrogenation of coals, tars, mineral oils and the like. Furthermore unsaturated hydrocarbons, such as olefines, of low molecular weight, which are polymerized into products of high molecular weight, or substances of high molecular weight prepared by the treatment of hydrocarbons of low molecular weight with high-frequency electric currents, may also serve as initial materials.

The condensation or polymerization of the said initial materials is carried out in the liquid phase in apparatus of the kind referred to above. It is important, however, that the electric treatment should be carried on for a sufficiently long period of time to produce a viscosity greater than 12° Engler at 99° C. As will be understood already from the above, the duration of the treatment depends on the electrical energy employed. Thus for example when employing 7000 volts and 1000 Hertz, a duration of treatment of from 30 to 50 hours is chosen.

It is preferable to employ polymerization products the viscosity of which is considerably higher than 12° Engler at 99° C.; for example products having viscosities of from 20° to 60° Engler at 99° C. are eminently suitable for the process according to this invention.

Amounts of from 0.1 to 10 per cent, preferably from 0.1 to 5 per cent are sufficient as the addition.

The advantage of this modification of our present invention resides in the fact that the improvement in the temperature-viscosity curves of any lubricating oils, especially of those having steep temperature-viscosity curves, is very considerable even by the addition of small amounts of the highly viscous condensation products. With large amounts of addition, there is only a slight further increase in the improvement.

These highly viscous products may also be prepared from a voltolization product of low viscosity by dissolving the latter in a solvent and then precipitating from the solution the higher viscous portion. The highly viscous voltolization product may also be mixed in any proportion with mineral or tar oils or fractions thereof or with products obtained by the destructive hydrogenation of carbonaceous materials of the nature of coals, tars or mineral oils or also with alcohols or esters, in particular those of high molecular weight. Products are also of value which are obtained by mixing very highly viscous voltolization products, for example those having a viscosity of from 30° to 100° Engler at 99° C., with lower viscous products obtained by subjecting to silent electric discharges paraffin wax or hydrocarbon oils rich in hydrogen or fatty acids or esters. These mixtures are added to the oils to be improved in such amounts that the highly viscous part thereof having a viscosity of more than about 12° Engler at 99° C. is incorporated with the said oils in an amount of from 0.1 to 10 per cent. Thus for example a highly viscous voltolization product may be mixed with a lubricating oil having a good viscosity index in the ratios 1 to 2, 1 to 3, 1 to 4, or 1 to 6, the mixture then being employed as pour point depressant or for improving the viscosity index, the amount of the mixture added to the lubricant to be improved being dependent on the content therein of voltolization product.

The following examples will further illustrate this feature of our invention.

Example 14

Hard paraffin wax is fused and exposed at 7000 volts and 1000 Hertz in a Siemens ozonization tube to silent electric discharges for 50 hours. A product is obtained which consists to the extent of from 60 to 65 per cent of a cylinder oil having a viscosity of 43° Engler at 99° C. and to the extent of from 35 to 40 per cent of unchanged paraffin wax. This is distilled with steam in a vacuum of 15 millimeters (mercury gauge) whereby a cylinder oil free from paraffin wax is obtained.

The cylinder oil thus obtained is added in an amount of 1 per cent to a lubricating oil having a viscosity index of 0 which has been obtained by distilling German mineral oil. By the said addition, the viscosity index of the lubricating oil is increased to 22. An addition of 1.5 per cent of the condensation product to the lubricating oil is increased to 22. An addition of 1.5 per cent of the condensation product to the lubricating oil increases the viscosity index to 30.

Thus by the addition of small amounts of the synthetic product, an oil of medium quality is obtained from an oil of bad quality.

Example 15

A lubricating oil obtained by the destructive hydrogenation of a Pennsylvanian cylinder oil having the following properties:

Specific gravity	0.863
Viscosity at 38° C	15.35° Engler
Viscosity at 99° C	2.22° Engler
Viscosity index	114
Flash point	264° C.
Pour point	8° below zero C.
Conradson carbon test	0.03

is mixed with 5 per cent its weight of an oil produced by the voltolization of paraffin wax and having a viscosity at 99° C. of 112° Engler. The resulting mixture has the following properties:

Specific gravity	0.863
Viscosity at 38° C	21.6° Engler
Viscosity at 99° C	2.84° Engler
Viscosity index	125
Flash point	265° C.
Pour point	18° below zero C.
Conradson carbon test	0.03

Example 16

A voltolization product obtained from crude scale wax and having the following characteristic

A. P. I	31.8
Viscosity at 38° C	107° Engler
Viscosity at 99° C	9.6° Engler
Viscosity index	124
Flash	600
Pour	22° C.
Carbon	0.657%
Color	1¼ Robinson
Yield	53 per cent

is blended in a proportion of 15 parts to 85 parts of a lubricating oil termed "Hydrolube S. A. E. 30." The inspections of these two oils are as follows:

	Hydrolube S. A. E. 30	85% hydrol. S.A.E. 30 15% voltolized product
A. P. I	29.3	29.8.
Viscosity at 38° C	15.5° Engler	18.2° Engler.
Viscosity at 99° C	1.9° Engler	2.3° Engler.
V. I	101	120.
Flash	485	490.
Pour	15	0.
Carbon	0.035 percent	0.12 percent.
Color	17½R	10R.

Also the voltolization products obtained from paraffin wax which has been separated from petrolatum in the manner described above have the valuable property of flattening the temperature-viscosity curve of lubricating oils when added thereto in amounts of from 0.5 to 10 per cent or more.

The following example will further illustrate the effect of an addition of a voltolization product obtained from a material containing paraffin wax together with liquid hydrocarbons.

Example 17

A petrolatum consisting of 60 per cent of paraffin wax and 40 per cent of lubricating oil fractions is treated with high voltage high frequency electric currents in an apparatus as described above consisting of a longitudinal closed tube which at either end is provided with an electrode, until the voltolized product adopts a viscosity of 12° Engler at 99° C. This product is then freed from paraffin wax and lower boiling constituents by distillation in vacuo while passing through steam and thereupon added in an amount of 10 per cent to a machine oil having a viscosity of 11.7° Engler at 38° C. and 1.6° Engler at 99° C., a viscosity index of 40 and a pour point of 15° below zero C. The resulting mixture has a viscosity of 13° Engler at 38° C. and 1.8° Engler at 99° C., a viscosity index of 87 and a pour point of 30° below zero C.

When separating paraffin wax or other waxes from hydrocarbon products containing the same, such as mineral oils, tars, products obtained by the extraction of coals or tars or by the destructive hydrogenation of carbonaceous materials of the nature of coals, tars and mineral oils, difficulties are often encountered in the mechanical separation of the precipitated constituents since the precipitate constitutes a smeary mass from which the solid portions can be separated only with difficulty. By the addtion of small amounts of the voltolization products obtained as hereinbefore described the said solid portions may be easily separated from the body of oil.

The following example will further illustrate this method of working.

Example 18

100 parts of lubricating oil fraction of a German mineral oil which boils between 200° and 350° C. in vacuo (15 millimeters mercury gauge) and which contains about 22 per cent of paraffin wax are mixed with 100 parts of illuminating oil, and to the resulting mixture is added 0.5 per cent (calculated with reference to the lubricating oil fraction) of a voltolization product as prepared according to Example 1. The mixture is then cooled to 15° below zero C. The paraffin wax thus separates in such a form that it may be filtered off without difficulty whereas without employing the additional substance the precipitated wax is a slimy mass which can be filtered only very badly. The filter cake and the filtrate obtained are treated separately with steam in order to remove the illuminating oil. The final products obtained are about 80 parts of machine oil and about 20 parts of paraffin wax having a melting point of from 45° to 50° C.

Also oils for coating, protecting and impregnating purposes may be improved by the addition of voltolization products. For these purposes especially tar oils containing paraffin wax or extraction products thereof, in particular those obtained by treating tars with solvents, such as alcohols, may be used.

An addition of voltolization products proves valuable not only when added to lubricants having a high pour point due to the presence of paraffin wax, but also in the case of hydrocarbon mixtures which contain crystallizable cyclic hydrocarbons which are soluble in oil.

Also in this case, the oil obtains a good mobility even at low temperatures. As initial oils may be mentioned for example tar oils or fractions thereof, especially coal tar oils containing naphthalene, anthracene and carbazole which crystallize out at low temperatures thereby rendering their employment troublesome. We have found that this crystallization is prevented by the said additions.

We have also found that the highly viscous, oily product described above considerably improves the color of lubricating oils when it is added thereto. Furthermore the other properties of the lubricating oils, as for example the setting point and viscosity, may also be improved by the addition. An addition of a few tenths of one per cent is sufficient to impart to a non-fluorescent lubricating oil a strong fluorescence such as is frequently required in commerce. Of course also greater amounts of the said resinous products may be added if so desired.

An addition of voltolization products proves valuable also in the case of lubricating greases (also known as consistent greases) as for example those used for driving gear, differential gear and similar apparatus, which in some cases become hard and stiff at comparatively low temperatures.

We have found that the plasticity and mobility of such lubricating greases at low temperatures is considerably improved by adding thereto synthetic products of the aforesaid kind, obtained by the treatment of hard or soft paraffin wax or derivatives thereof or montan wax, or substances containing the said products in considerable amounts, such as petrolatum, crude paraffin wax, petroleum jelly or crude lubricating oils containing paraffin wax or high molecular alcohols or esters, if desired in admixture with paraffin wax, with high voltage, preferably high frequency, electric currents.

Generally speaking it is preferable to add from 0.5 to 5 per cent of the synthetic products to the lubricating grease to be improved, but larger amounts, as for example 10 or 20 per cent or more may be employed. In the case of lubricating greases which are not to be used under extreme conditions an addition of less than 2 per cent, as for example 1 per cent is sufficient in some cases.

The synthetic products may be added to the lubricating greases either alone or in admixture with metal soaps, as for example lead, sodium or ammonium oleate or stearate, or with other substances, such as condensation products of organic acids of high molecular weight, or oxidized oil distillates of high boiling point.

The lubricating greases thus prepared have at low temperatures a better mobility, a smaller resistance to friction, a greater lubricating action, may be more readily pumped and cause a better engagement of the gears than the original grease. When employing the greases as gear greases, the gears are less worn and the temperature of the gear housing is not unnecessarily increased.

The following example will further illustrate this feature of our invention.

Example 19

200 grams of hard paraffin are fused and treated in a vacuum of 5 millimeters (mercury

gauge) with silent electric discharges of 7000 volts and 4000 Hertz. After a treatment for 9 hours, a soft product similar to petroleum jelly is obtained which consists to the extent of 70 per cent of a highly viscous lubricating oil. The remainder is unchanged paraffin wax which is expelled from the oil. 5 per cent of the said lubricating oil are mixed with a lubricating grease for gears. In this manner the grease remains soft or liquid at lower temperatures, the lubricating action thus being increased and the engagement of the gears facilitated.

If a mixture of hard paraffin wax and ceresine in the ratio of 1:1 be employed as the initial material for the electrical treatment, and the product be worked up as described, an addition of 2 per cent to the said gear grease suffices to produce the same effect.

The voltolization products may also be very useful when added to lubricants in conjunction with other addition agents.

Thus we have found that oils containing hard or soft paraffin wax, especially lubricating oils, gear oils, lubricating greases and gear greases, are much improved by adding thereto small amounts of high molecular hydrocarbons which, even in small amounts, increase the viscosity and also such voltolization products as are capable of lowering the setting point. It has been found that the additions exerting effects in the different directions are not mutually injurious and in most cases the setting point, which is not influenced or only slightly influenced by the additions increasing the viscosity when added alone, is much improved and the viscosity index favorably influenced.

As oils containing paraffin wax may be mentioned especially those which have a high flash point, as for example Mid-Continent oils, Pennsylvanian oils, lubricating oils, still containing hard or soft paraffin obtained by destructive hydrogenation, or oils containing paraffin wax which have been treated with liquefied hydrocarbons which are gaseous at room temperature, with phenols, with sulphur dioxide or with other solvents or extraction agents.

In order to increase the viscosity and improve the temperature-viscosity curve, hydrocarbons having a molecular weight of more than 1000, preferably of more than 2000, are added to the said oils; these added hydrocarbons should have the property of exerting a favorable effect in this direction even when added in small amounts.

Substances suitable for this purpose are for example hydrogenated rubber or hydrogenated polymerization products of diolefines, in particular of butadiene, cyclo-caoutchouc, hydrogenated resins soluble in oil, hydrogenated balata or gutta percha, polymerized styrene, hydrogenated polymerized styrene, polymerized indene, oil-soluble cellulose derivatives, as for example cellulose laurate, and their hydrogenation products, oil-soluble polymerization products of olefines, such as of isobutylene, preferably those which are prepared at low temperatures, if desired in the presence of volatile halides. These substances are added to the oils in an amount of from 0.5 to 10 per cent, preferably of from 1 to 5 per cent.

According to this feature of our invention there is also added to the improved oils a small amount, as for example from 0.5 to 10 per cent, of a voltolization product which lowers the setting point, most suitably such as is obtainable by the voltolization of hard or soft paraffin wax (as for example petrolatum) or of paraffins or of acids of high molecular weight, preferably in the presence of cyclic hydrocarbons.

In this way oils can be obtained which have a low setting point and a viscosity index far above 100. Lubricating oils treated in the said manner may, by reason of their flat temperature-viscosity curves and their good mobility at low temperatures, be employed both in summer and in winter.

The following example will further illustrate this feature of our invention.

Example 20

1 per cent of a hydrogenated rubber and 1 per cent of a substance capable of lowering the setting point and prepared as described in Example 1 are added to a machine oil containing paraffin wax derived from German crude oil by distillation and having a viscosity index of 70, a viscosity of 1.8° Engler at 99° C. and a setting point of 3° C. The resulting mixture has a viscosity index of 107, a viscosity of 2.4° Engler at 99° C. and a setting point of 25° below zero C.

If, instead of the hydrogenated rubber, 30 per cent of a natural or synthetic cylinder oil having a viscosity of from 8° to 10° Engler at 99° C. and a setting point of from 5° to 8° below zero C., be added, the resulting mixture has the same viscosity, a viscosity index of about 100 and a setting point of only 1° below zero C.

An addition of voltolization products also offers great advantages when adding the said substances to hydrocarbon mixtures other than lubricating oils, as for example to benzines, gas oil, illuminating oil and paraffin wax.

The advantages of the process in the case of liquid hydrocarbons consist in the facts that their viscosity is increased and a better capacity for being pumped and a smaller consumption are ensured. Furthermore when adding the said voltolization products to motor fuels the valves in the combustion space of the motor are continually lubricated and the piston rings are more tightly connected with the cylinders. In the case of paraffin wax the viscosity of its melt is increased and after cooling no cracks appear or, in cases when they do appear, they rapidly disappear again.

The amount of the substances to be added may amount to from 0.5 to 10 per cent, preferably from 0.5 to 5 per cent.

Example 21

Paraffin wax, which exhibits cracks and white crystal centres and is therefore unsuitable for the preparation of candles, has added thereto 2 per cent of the product obtained according to Example 2 while it is in the fused condition. By cooling the mixture, a paraffin wax free from cracks is obtained.

Voltolization products may also be used for special purposes, as for example when for the operation of aeroplane engines, highly sensitive automobile engines and the like, lubricating oils having a viscosity index of more than 120, a flash point of more than 230° C., a Conradson coke test of less than 1, a viscosity of from 2° to 3.5° Engler at 99° C. and in some cases a setting point of lower than 10° below zero C., are required. The preparation of such lubricating oils is, however, very troublesome and expensive by the usual methods.

We have found that lubricating oils having the said properties are obtained in a comparatively simple manner by adding to lubricating oils obtained by the destructive hydrogenation of paraffin basic mineral oils or fractions thereof of high boiling point, the condensation products obtainable by the voltolization of hard or soft paraffin waxes.

As the first-mentioned component may be mentioned especially destructive hydrogenation products of Pennsylvanian, and also, if desired, of Mid-Continent, oils especially their lubricating oil fractions. For example lubricating oil fractions having a viscosity index of from 80 to 110, especially from 100 to 110, a viscosity of from 2° to 8° Engler at 99° C., especially of from 2.5° to 6° Engler at 99° C., a coke test of more than 0.5, especially of more than 1, and a flash point of from 200° to 320° C., especially of from 230° to 290° C., may be subjected to destructive hydrogenation. In this way a lubricating oil is obtained having a viscosity of from 2° to 3° Engler at 99° C., a viscosity index of from 100 to 120, advantageously from 110 to 120, a coke test of from 0.05 to 0.5 and a flash point of from 200° to 300° C., especially of from 220° to 300° C. To such a lubricating oil, one of the said voltolization products is added in an amount of from 2 to 30 per cent by weight, especially of from 5 to 15 per cent if they have a viscosity of from 6° to 100° Engler at 99° C., especially of from 10° to 60° Engler at 99° C., a viscosity index of from 125 to 150, especially of from 130 to 140, a flashpoint of 280° C., or more, especially of from 280° to 320° C. and a coke test of from 0.3 to 0.1.

These products may also be employed in admixture with hydrogenation products of rubber or of polymerization products of diolefines, such as butadiene, or of cyclo rubber or resins free from oxygen or of polymerization products of olefines, such as isobutylene.

The following example will further illustrate this feature of our invention.

Example 22

If there be mixed with a lubricating oil obtained by destructive hydrogenation 10 per cent of a condensation product obtained from ordinary paraffin wax by means of silent electric discharges and 1 per cent of a substance capable of lowering the setting point and obtained by treatment of a paraffin wax having a mean molecular weight of 400 with high voltage frequency electric currents an excellent motor oil having the following characteristics is obtained:

Specific gravity at 20° C.	0.860
Viscosity at 99° C.	2.8° Engler
Viscosity index	125
Flash point	270° C.
Conradson coke test	0.1 per cent
Setting point	23° below zero C.

The voltolization products together with the paraffin wax contained in the crude product or after separation thereof may be employed in admixture with a white oil of any desired viscosity, for example with paraffinum liquidum, for pharmaceutical or cosmetic purposes. In this case the said products may also be stirred with small amounts of water or preferably purified before use.

The voltolization products may also be employed together with water as lubricants.

It should be noted that whenever in the foregoing examples we have spoken simply of parts, what we mean thereby is parts by weight.

This application is a division of our copending application Ser. No. 651,802, filed January 14, 1933.

While in the foregoing we have explained our invention by reference to specific examples, we wish it to be understood that our invention is not in any way limited to these specific examples, the scope of our invention being defined in the appended claims.

What we claim is:

1. An improved lubricant comprising a mineral lubricating oil and a condensation product of paraffin wax, having a molecular weight above 350, said product having a viscosity of at least 3° Engler at 99° C., being soluble in hydrocarbon lubricating oils and being highly effective in depressing the pour point of waxy lubricating oils when added thereto in small amounts, said product being obtained by subjecting said wax to the action of a silent electric discharge for a time sufficient to increase the viscosity of the wax to the said extent.

2. Lubricant composition according to claim 1 in which the said wax is selected from the group consisting of ceresine and ozokerite.

3. Lubricant composition according to claim 1 in which the said wax is a petroleum wax having a molecular weight above 350 and a melting point of at least 57° C.

4. Lubricant composition according to claim 1 in which the said wax comprises a mineral wax having a molecular weight above 350 and a melting point above 57° C.

5. An improved lubricant comprising a mineral lubricating oil and a condensation product of paraffin wax, having a molecular weight above 350, said product having a viscosity of at least 10° Engler at 99° C., being soluble in hydrocarbon lubricating oils and being highly effective in depressing the pour point of waxy lubricating oils when added thereto in small amounts, said product being obtained by subjecting said wax to the action of a silent electric discharge for a time sufficient to increase the viscosity of the wax to the said extent.

6. An improved lubricant comprising a mineral lubricating oil and a condensation product of paraffin wax, having a molecular weight above 350, said product having a viscosity of at least 40° Engler at 99° C., being soluble in hydrocarbon lubricating oils and being highly effective in depressing the pour point of waxy lubricating oils when added thereto in small amounts, said product being obtained by subjecting said wax to the action of a silent electric discharge for a time sufficient to increase the viscosity of the wax to the said extent.

7. An improved lubricant comprising a mineral lubricating oil and a complex condensation product of paraffin wax, having a molecular weight above 350, and an aromatic hydrocarbon, said product having a viscosity of at least 3° Engler at 99° C., being soluble in hydrocarbon lubricating oils and being highly effective in depressing the pour point of waxy lubricating oils when added thereto in small amounts, said product being obtained by subjecting said wax to the action of a silent electric discharge for a time sufficient to increase the viscosity of the wax to the said extent.

8. An improved lubricant comprising a mineral lubricating oil and a complex condensation product of paraffin wax, having a molecular weight above 350, and an organic oxygen-containing compound selected from the group consisting of

alcohols and acids, having a molecular weight above 200, and esters of such acids, tallow, wool grease, fish oil, train oil, montan wax and beeswax, said product having a viscosity of at least 3° Engler at 99° C., being soluble in hydrocarbon lubricating oils and being highly effective in depressing the pour point of waxy lubricating oils when added thereto in small amounts, said product being obtained by subjecting said wax to the action of a silent electric discharge for a time sufficient to increase the viscosity of the wax to the said extent.

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