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VOLTOLIZED OILS AND PRODUCTS
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This invention relates to the production of valuable materials by subjecting unsaturated oils and liquid waxes, especially from marine animal oils, such as sperm oil, to the action of silent electric discharge, and to improved lubricating compositions containing such materials.

The materials which it is preferred to use according to the present invention comprise the normally liquid waxes, and oils, such as certain marine animal oils, which contain substantial amounts thereof, and other oils of similar characteristics. Such oils include some unsaturated esters of monocarboxylic acids and monohydric aliphatic alcohols in which either the acid or the alcohol group contains unsaturated ethylenic linkages. This includes oils having an iodine value between about 50 and 200, but those having iodine values between about 70 and 100 are preferred. Unsaturated and saturated esters in which either the acid or the alcohol group or preferably both contain more than 8 and up to 20 carbon atoms per molecule thus constitute preferred liquid wax esters to be polymerized by the action of silent electric discharge. Such oils and liquid wax esters may be obtained naturally or may be prepared synthetically by any suitable means. For example, they may be prepared by a limited oxidation of high molecular weight paraffinic oils and waxes such as highly paraffinic viscous petroleum oils, petrolatum and paraffine wax. Some unsaturated esters are formed directly by such oxidation and others may be formed by suitably esterifying the acids and alcohols in the reaction product or after separation therefrom.

The preferred oils for use according to the present invention are the sperm oils. The crude sperm oil may be used directly as obtained or after separation into any desirable fractions by fractional distillation, solvent extraction, precipitation or other methods adapted to separate the oil into fractions of relatively highly and lower melting point or volatility or degree of saturation or molecular weight or other specified characteristics. For example, the sperm "head oil" and sperm "body oil" may be treated according to the present invention either separately or mixed in any desired proportions. Spermacetic, which consist largely of cetyl palmitate and closely related esters of higher fatty saturated and unsaturated alcohols such as octadecyl and eicosyl alcohols and of lower fatty acids, such as capric, lauric, palmitoleic, myristic, oleic, and stearic acids, in smaller amounts, may be separated from the oil to any desired extent and the completely

or partially dewaxed oil and the wax fractions may be treated according to the present invention. Other marine animal oils of this general class are dolphin oil and porpoise jaw oil which are mentioned merely by way of example and not in limitation of this invention.

The process of voltolization consists in subjecting the material to the action of high tension silent electric discharges, preferably of an alternating current. The treatment is generally carried out under vacuum. The pressure may be varied from .001 mm. to .01 atmosphere, .1 atmosphere, .5 atmosphere, or even as high as .8 atmosphere. The voltage used is preferably in the range of 4,000 to 10,000 volts, although higher voltages such as 20,000 or even 50,000 volts may be used, especially when good dielectrics are available. The frequency of the alternating current may be as low as 60 cycles and as high as 1200, 3000, 10,000 or more cycles.

In the usual voltolization processes, the temperature during the treatment with silent electric discharges is maintained at about room temperature or substantially thereabove. The heat liberated in the reaction zone is frequently sufficient to raise the temperature of the mixture to 100, 200 or even 300° C., so that it is necessary to use some cooling means when high temperatures are undesirable or detrimental. It is usual to provide some external means for either heating or cooling the reaction chamber in which the voltolization is carried out.

The apparatus used in the present process may be of the usual type of tube or trommel design. The tube type of apparatus comprises a vertical tube preferably constructed of a dielectric material such as glass coated on the outside with a conductor electrode, a central electrode disposed in the center of this tube, provision being made for a high tension silent discharge between the electrodes. The trommel type of apparatus comprises a series of insulated plates placed a few millimeters apart and mounted on a rotatable shaft, the entire shaft with its plates being disposed within a horizontal drum maintained approximately half full of the material to be voltolized. The bottom portions of the plates dip into the material to be voltolized, and as the shaft rotates the material drips down over the surface of the plates forming a thin film thereon. The high tension silent discharge occurs between the plates. In apparatus of this type, it is generally preferred to operate at a pressure below about 20 cm. of mercury and preferably at about 2 to 10 cm., and an elec-

trode potential of about 1000 to 10,000 volts or more at a frequency of about 500 to 10,000 cycles or more per second.

The oils and waxes may be voltolized according to the present invention in the pure, commercial or crude state or after being purified by treatment with adsorptive clay or other refining agents, solvent extraction, refrigeration in solution followed by decantation or filtration, or in combination with other materials of the types mentioned above or in combination with petroleum, mineral oils, waxes, shale oils, fish oils, animal oils, vegetable oils, or derivatives thereof. The materials may also be first partially voltolized and then blended with the other materials indicated above. The voltolization treatment may also be carried out in the presence of gases such as hydrogen, nitrogen, carbon monoxide, carbon dioxide, oxygen, air, and the like. It may also be conducted in the presence of sulfur, halogens, selenium, hydrogen sulfide, oxygen, phosphorus, boron fluoride, ketene, and the like.

The products obtained by voltolization of these materials according to the method described will be found to contain materials having molecular weights ranging from 400 to 1500, 5000, 10,000 or higher. These products may be subjected to hydrogenation, heat treatment with reagents such as aluminum chloride, boron fluoride, sulfuric acid, alkali, and the like. They may also be treated or refined with clay, charcoal, acid, and the like. If desired, any free acidic or hydroxyl groups may be esterified or otherwise neutralized.

Products of extremely high molecular weight may be precipitated or extracted from the voltolized product by dilution with solvents such as propane, secondary butyl alcohol, methanol, acetone, carbon tetrachloride, and the like, with or without refrigeration and/or filtration.

The products obtained according to this process may be adapted to a wide variety of different uses. For example, they may be used directly as lubricants, coating compositions, plastics, resins, plasticizers and impregnating agents or they may be used as blending agents in other materials of these types. The amount used may vary from .01% to 1%, to 5%, 10%, 50% or even more.

The products of this process are valuable addition agents to crude petroleum oils, partially or highly treated petroleum oils, white oils, solvent-extracted oils, hydrogenated oils, synthetic oils, as well as to distillation products of tars, lignites, shale, peat, and the like. They are also valuable addition agents to fatty oils, greases, lubricating oils, cable oils, insulating oils, textile oils, industrial lubricants, emulsions, naphthas, Diesel fuels and kerosenes.

The products of this process may be employed in conjunction with materials such as oxidation inhibitors, pour inhibitors, dyes, resins, solvents, thickeners, sludge dispersers, oiliness agents, extreme pressure lubricants, soaps, glycerin, sulfur compounds and the like.

The following examples are presented to illustrate suitable methods for preparing improved products according to the present invention and are not to be construed as limiting this invention in any way.

Example 1

Sperm oil having a Saybolt viscosity of 44.5 seconds at 210° F. was subjected to treatment by silent electric discharge in a trommel type

voltolizer at an absolute pressure of 2 to 4 cm. of mercury and an electric potential of 2,000 to 3,000 volts at a frequency of 10,000 cycles per second, until a product having a viscosity of 600 seconds Saybolt at 210° F. was obtained. A viscous petroleum lubricating oil, having a viscosity of 85 seconds Saybolt at 210° F. and prepared by refining a distillate of a Mid-Continent crude with acid, was gradually added with continuing treatment in the trommel voltolizer until a volume equal to the volume of sperm oil had been added and a voltolized mixture having a viscosity of 1017 seconds at 210° F. was obtained.

Example 2

Sperm oil was subjected to the action of silent electric discharge in a glass tube apparatus at a pressure of two cm. of mercury and an electric potential of 7,000 volts at a frequency of 1,200 cycles per second until a product having a viscosity of 540 seconds at 210° F. was obtained. There was then added gradually, with continuing voltolization of the mixture, a petroleum lubricating oil having a viscosity of 65 seconds and obtained from Pan-handle and deep-sand Reagan crudes, until a volume equal to that of the sperm oil had been added and the voltolized mixture had a viscosity of 2087 seconds Saybolt at 210° F.

It has been found that the unsaturated liquid waxes such as sperm oil may be thickened to much higher viscosities by voltolization without formation of jelly-like insoluble products than is possible even with the glycerides previously preferred as raw materials for voltolization. For example, sperm oil was thickened alone by voltolization to a viscosity above 1500 seconds Saybolt at 210° F. without formation of any insoluble products or jelly, while rapeseed oil, voltolized under the same conditions, developed a content of insoluble jelly-like particles at a viscosity of only 300 seconds. Also, when voltolizing a mixture of sperm oil and mineral oil, no jelly was apparent in products having a viscosity above 2000 seconds, while in treating a similar mixture of rapeseed oil and mineral oil under the same conditions, jelly appeared when the mixture was thickened only to 1000 seconds.

The following examples illustrate the use of the voltolized products of this invention in the preparation of blended lubricating oils.

Example 3

10 parts by volume of the voltolized product obtained in Example 1 was mixed with 90 parts of a petroleum lubricating oil. The viscosity and viscosity indices of the original lubricating oil and of the resulting blend are indicated in the following table:

	Petroleum oil	+ 10% of voltolized sperm oil
Saybolt viscosity seconds—		
At 100° F.-----	522	694
At 210° F.-----	63.8	81.8
Viscosity index-----	95	114

Example 4

The lubricating oil composition shown in Example 3 was subjected to test in the lubrication of a four-cycle internal combustion test engine operating at 390° F., jacket temperature, and with tight clearances, for the purpose of accelerating any decomposition of the oil and of making the lubrication of the parts more difficult

than in ordinary service. Comparative runs under carefully controlled and reproducible conditions were made with the lubricating oil-voltolized sperm oil composition shown in Example 3 and with a composition of the same lubricating oil with 10% of a voltolized rapeseed oil. A blank run was made on a hydrocarbon oil composition consisting of the same base lubricating oil used in the above compositions and thickened by the addition of 1.5% of a polymerized olefin in order to produce a blended lubricating oil having the same viscosity as that of the other two blends. At the end of each run, the engine was dismantled and the parts carefully inspected for condition, wear and carbon deposition, using a decimal system to indicate the extent of degradation. The results of the three runs are indicated in the following table, in which it will be seen that the voltolized sperm oil composition was far superior to the mineral oil in every respect. It was also superior to the voltolized rapeseed oil blend in that the condition of the pistons was substantially better and that no rings were stuck in the run with sperm oil, while two rings were stuck for a total range of 180° in the test with voltolized rapeseed oil.

Oil blend	Demerits		Oil used, pounds	Carbon rings stuck		
	Piston	Crank case		Gms.	No.	Degree
10% voltol from rapeseed oil	1.42	0	0.39	1.12	2	180
10% voltolized sperm oil	1.12	0	0.47	1.46	0	0
1.5% olefin polymer	5.24	2.67	0.63	6.71	3	810

The present invention is not to be limited by any explanations or examples all of which have been presented above solely for purpose of illustration, but is limited only by the following claims in which it is desired to claim all novelty insofar as the prior art permits.

I claim:

1. A composition of matter consisting essentially of a polymerized liquid wax ester, said polymerized liquid wax ester being soluble in hydrocarbon oils and having a viscosity of at least 540 Saybolt seconds at 210° F. obtained by silent electric discharge polymerization of a liquid wax ester which occurs as an ingredient of spermaceti.
2. A composition of matter consisting essentially of polymerized spermacetic soluble in hydrocarbon oils and which has a viscosity of at least 540 Saybolt seconds at 210° F. obtained by a silent electric discharge polymerization of spermacetic.
3. A composition of matter consisting essentially of thickened sperm oil, said thickened sperm oil being soluble in hydrocarbon oils and having a viscosity of at least 540 Saybolt seconds at 210° F. obtained by a silent electric discharge polymerization of sperm oil.
4. A composition of matter for use in an improved lubricating composition consisting essentially of polymerized liquid wax esters, said polymerized liquid wax esters being soluble in hydrocarbon oils and having viscosities in the range of 540 to 2,000 seconds Saybolt at 210° F. obtained by the action of silent electric discharges on a mixture of hydrocarbon lubricating oil and liquid wax ester components of spermacetic.
5. A composition of matter consisting essentially of a polymerized liquid wax ester, said polymerized liquid wax ester being soluble in hydrocarbon oils and having a viscosity of at least 540 Saybolt seconds at 210° F. obtained by silent electric discharge polymerization of a liquid wax ester of a monohydric aliphatic alcohol and a monocarboxylic acid, both of which contain more than 8 and up to about 20 carbon atoms per molecule.

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