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WATCH OIL

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This invention relates to a lubricating oil particularly designed for bearings and that particular type of bearing used in watches.

The lubrication of bearings of the type used in watches is becoming an increasingly difficult problem as the size of the watch is constantly being reduced. The actual contact of the bearing with the pivot is over an extremely small area. The application of the lubricant to the bearing is made at stated intervals which may be anywhere from a few months to years. It is necessary, therefore, that such a lubricant possess qualities which while desirable are not necessary in lubricating other types of bearings. The lubricating qualities should be such as to assure the efficient performance of the watch.

The oil should be only slightly volatile within ordinary range of temperatures; it must not spread to other parts of the watch but must remain in the position to which it applied even though the position of the bearing constantly changes, that is with relation to the force of gravity; it should not oxidize or become gummy under ordinary temperatures which should run from 10° below zero to 80° above 0° F.; it should not be corrosive; it should not solidify within the range of temperatures as suggested above; it should retain chemical stability throughout its life.

The cost of producing such an oil need not be taken into consideration as the quantity produced is exceedingly small and as the application to each individual watch is never more than two or three drops, the individual cost per watch is practically negligible. It is, therefore, seen that while cost and economy does not enter the picture, the above described physical properties are essential and in addition the oil should be one whose properties can be maintained to close tolerances so that the behavior of the oil can be predicted and relied upon.

Fatty and mineral lubricants possess varying, spreading properties which leave considerable room for improvement. In order to eliminate the dependency on these oils as timepiece lubricants, this invention pertains to the development of an oil made from purified natural and synthetic organic chemicals and have proved their value in the final spread test. Many factors such as dusty atmosphere, perfumes, perspiration and evaporation contribute to the spread of watch oils and fatty oils are particularly susceptible to these. It has been found by experiment that the true

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synthetic oil produces a favorable reaction when compared with the fatty oils.

In order to establish a basis for comparison certain oils were subjected to a spread test as here outlined. Nine drops of oil spaced uniformly on a square, three to a side with the center of the drops .125 inch apart, are placed on freshly greyed low carbon steel slugs and inserted in an oven at 140° F. At the end of two hour and four hour intervals they are observed and the condition of the droplets noted. Where the nine individual drops remain with the surface not wetted between the drops, the result and conclusion is "Non-Spread." Where nine drops remain with small wetted areas around one or more drops but with no wetted areas touching, the conclusion is termed "Little Spread." Where nine drops remain with wetted areas merged between two or more drops, the conclusion is "Spread." Where there are less than nine drops but more than one drop remaining, "Much Spread." Where there is one drop remaining, the result is termed "Very Much Spread" and where there are no drops remaining, the tabulation "Complete Spread" is given. This renders six classifications which we will use hereinafter in the table below to compare the present oil of this invention with known types.

Material	Spread Rating on Steel
Diethylene glycol mono ethyl ether meta-xylyl stearate.	Non-spread.
Porpoise Jaw Oil	Complete spread.
Neat's-foot Oil	Non-spread.
Olive Oil	Little spread.
Tricresyl Phosphate	Non-spread.
200 Second S U V Mineral Oil	Complete spread.
Silicone Oil	Do.

The only functional method of comparison between the oil which is the subject matter of this invention and known oils is its relative performance during certain tests. These tests are, therefore, included in the description of the invention to set forth the comparative merit of this new oil over other oils. The following test is used to determine the coefficient of friction of different watch lubricants and was devised in connection with the development of this oil.

This method of test is intended to provide a relative value of the "oiliness" or ability to lubricate, of various watch oils and greases. The control oil for this test shall be Drakeol 180 sec-

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onds Saybolt viscosity white mineral oil for which the coefficient of friction has been determined as – –.096.

A pendulum type oiliness tester of the type used by Mr. G. E. Barker and described in the American Society for Testing Materials Bulletin for March 1946 is used with certain modifications as described below. In our test, the pendulum is pivoted on two ball bearings which roll on a sapphire surface, a type of pivot which can be quickly and readily cleaned and one which furnishes reliable comparative information. A thin film of oil is spread both on the sapphire surface and the ball bearings which have been previously cleaned and highly polished. The pendulum is allowed to swing and the amplitude observed and recorded to the nearest estimated tenth of a degree. The amplitude of each third successive period is likewise estimated and recorded until the twelfth period is reached. This procedure is repeated until five sets of reasonably consistent figures are obtained. The coefficient of friction is calculated as follows:

$$f = \frac{(L \cos \theta)}{r} \frac{Ao - An}{4n}$$

where—

f=coefficient of friction.
L=distance of the center of gravity from the point of suspension of the pendulum.
θ=angle between the vertical and the radius of the ball bearings at their point of tangency with the plane bearing sapphire surface.
r=average radius of the ball bearings.
Ao=amplitude of initial period in radians.
An=amplitude of nth period in radians.
n=period of swing.

Duplicate tests are performed on the different oils and a control test run frequently on the Drakeol white mineral oil. The results of this control test must not deviate more than 3% from the original value of this oil showing that there has been no wear on the bearing surfaces.

The tests for determining the contact angle of the different oils is a test which has long been in use to measure wetting properties of various substance. It consists of measuring height and diameter of drops and calculating the angle of contact made on a given surface from proper trigonometric values. The procedure used by us is described in detail as follows:

1. *Setting-up test.*—A small quantity of the standard dibutylphthalate is placed in the watch glass by means of a clean glass stirring rod. This watch glass and one of the test slides is placed on the block beneath the pin chuck of the hand press. The chuck is then lowered until the pins are about half submerged in the liquid. The pins are then withdrawn and the drops removed by touching the pins to the edge of the watch glass. The pins are again lowered into the dibutyl-phthalate and withdrawn. A few moments are allowed for drops to form on the ends of the pins. These drops are then transferred to the polished surface of the test slide by lowering the chuck until the drops just touch and adhere to the surface. The pins are then withdrawn by raising the chuck. Care should be taken to place the drops as nearly parallel and adjacent as possible to the polished edge. Measurements are taken on these drops as follows:

2. *Measurement of drops.*—The contact angle instrument is first leveled by placing a leveling bulb on the stage, and making the necessary adjustments to the four legs. The bulb is then replaced by the slide on which the dibutylphthalate has been placed. One of the three drops is brought into the center of the microscope field by the horizontal and vertical position adjustors on the stage.

The diameter of the drop is measured with the fixed scale of the filar micrometer eyepiece in the horizontal position. The diameter is then found by moving the movable cross hair from one extremity of the drop to the other. The units traveled are noted on the vernier drum and represent the diameter of the drop.

The height of the drop is measured by turning the eyepiece 90° so that the fixed scale is in a vertical position. The movable cross hair is made to coincide with the horizontal axis of the elliptical image. This cross hair is then moved until it just reaches the top of the drop. The units traveled represent the height of the drop.

This procedure is repeated on the other two drops. The measurements obtained are converted to contact angles according to the equation below:

Let h=height of drop measured by micrometer
Let d=diameter of drop measured by micrometer

then

$$\tan a = h \Big/ \frac{d}{2}$$

or

$$a = 2 \tan^{-1}\frac{h}{d}$$

Presuming that the drop being measured is a perfect arc of a circle then the contact angle is equal to 2 or twice the calculated angle.

The values for dibutyl-phthalate thus obtained should be as follows:

	Degrees
Steel slides	40
Ruby slides	40

The overall average between duplicate tests is taken as the contact angle of the oil under test.

Each test shall be performed in duplicate on both ruby and steel. The variation between the contact angles of the drops on any one slide may not exceed 3°. If it is greater than 3° the test must be repeated. Also the averages of duplicate tests must agree within 3° or the test must be repeated.

Any deviation greater than 3° from these average values indicate that the slides are unfit for the testing of other oils and must be repolished and recleaned.

Experimental oils are tested in exactly the same manner as that just described for dibutyl-phthalate.

For the oxidation corrosion test which is performed upon this material as a qualifying condition for its use, metered moist air is bubbled for 96 hours through a 212° F. heated sample in which are immersed brass and steel slugs. Tests performed upon the oil exposed to these conditions measure gumming, development of acid and effect of the oil upon the metals so named. After the test, the oil shall not show more than 10% increase in viscosity nor exhibit an acid number greater than five (5). In addition, the brass and steel slugs shall not show a weight loss of more than 0.0005 gram.

The table below is included to show the relation of the physical and chemical properties of the new watch oil to other known watch oils.

Average laboratory test results upon various oils used as timepiece lubricants

Laboratory Tests	Diethylene glycol mono ethyl ether meta-xylyl stearate	Porpoise Jaw Oil	Raw Neat's-foot Oil	Commercial Tricresyl Phosphate	200" SUV Mineral Oil	Silicone Oil
Specific Gravity at 25° C	0.95	0.90	0.913	1.18	0.87	0.97
Refractive Index at 25° C	1.490	1.461	1.467	1.560	1.475	1.402
Kinematic Viscosity at 100° F. csts	57	23	45	35	45	170
Viscosity Index	115	70	150	below 0	80	
Steel Spread	Nonspread	Complete Spread	Nonspread	Nonspread	Complete Spread	Complete Spread
Corrosion Steel	none	gum and stain	gum and rust	stain	none	none
Stability (percent viscosity increase)	do	5	15	none	do	Do.
Pour Point (° F.)	minus 50	minus 15	20	minus 15	minus 15	minus 40
Evaporation (percent loss in weight)	2	15	none	none	15	5
Coefficient of Friction (Steel on Sapphire)	0.075	0.08	0.06	0.10	0.09	0.31
Contact Angle on Ruby Slide (degrees)	39	27	40	49	below 25	below 25
Contact Angle on Steel Slide (degrees)	44	24	37	46	do	Do.
Combined Oxidation-Corrosion Increase in Viscosity, Percent	5	200	2000	(¹)	not performed	not performed.
Metal Loss (grams): Steel	0.0003	gain 0.1	0.0001	(¹)		
Brass	0.0003	gain 0.001	0.004	(¹)		
Acid Number Increase	5	25	35	(¹)		

¹ Test results vary according to purchase source of oil.

The preparation of meta-xylyl stearic acid, the ester of which with diethylene glycol mono ethyl ether, is the main ingredient of the oil forming the subject matter of the invention. A low organic acid content olive oil is used as a base in the preparation of meta-xylyl stearic acid. This oil consisting of high percentages of the mono-, di-, and tri-glycerides of oleic acid is converted to the respective methyl esters and vacuum distilled to isolate methyl oleate. The methyl oleate is condensed with meta-xylene by anhydrous aluminum chloride, thereby saturating the organic acid to meta-xylyl methyl stearate. The meta-xylene was previously fractionated from a mixture of the isomers of xylene using a fifty inch still packed with ¼ inch glass helices and equipped with a total reflux-variable take-off head. The C_8H_{10} or meta-xylyl group is attached to the methyl oleate at the #9 and #10 carbon atoms. The meta-xylyl stearic acid which is obtained upon saponification and acidulation is an inseparable mixture of 9- and 10- meta-xylyl stearic acids, and requires only the determination of neutral equivalent and refractive index to confirm its identity before using it in additional syntheses.

The preparation of meta-xylyl stearic acid from olive oil is carried out in five stages, the first of which is the alcoholysis of the olive oil with methyl alcohol in which the olive oil is combined with the alcohol to produce a methyl olive ester.

The second step is the processing of the ester to form a methyl oleate by fractionally distilling the ester under reduced pressure to produce the oleate which should have the following constants: N_D1.4485 to 1.4500, acid neutral equivalent 280 to 282 and a kinematic viscosity of 4.5 to 5.0 centistokes at 100° F.
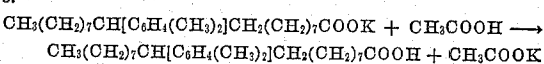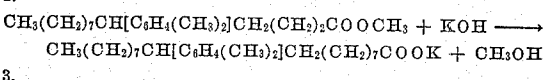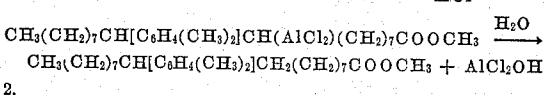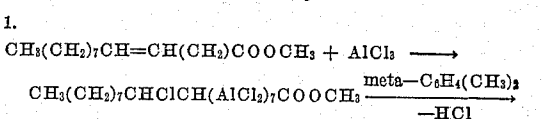
The third step is the condensation of methyl oleate with meta-xylene by anhydrous aluminum chloride.

The fourth stage in the preparation is the purification of meta-xylyl methyl stearate. This is accomplished by repeated washings and filterings, paying particular attention to eliminating acid constituents.

The fifth and final step is the preparation of the meta-xylyl stearic acid by adding to the meta-xylyl methyl stearate an excess of potassium hydroxide for complete saponification and a quantity of methyl alcohol equal to the quantity of meta-xylyl methyl stearate. The methyl alcohol-soap mixture is evaporated to dryness and the soap dissolved with distilled water. Dilute acetic acid is used to liberate the meta-xylyl stearic acid which is then washed with distilled water until the washings are neutral. This meta-xylyl stearic acid is the principal ingredient of the oil forming the subject of this invention. The following equations trace the preparation from the methyl oleate:

In order to provide a graphic account of the synthesis of meta-xylyl stearic acids, the equations below trace its preparation from methyl oleate. For convenience, the meta-xylyl group is pictured on the #10 carbon atom, although as mentioned before, a mixture of 9- and 10-meta-xylyl stearic acids is actually the case.

1.

$$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3 + AlCl_3 \longrightarrow$$
$$CH_3(CH_2)_7CHClCH(AlCl_2)_7COOCH_3 \xrightarrow[-HCl]{meta-C_6H_4(CH_3)_2}$$
$$CH_3(CH_2)_7CH[C_6H_4(CH_3)_2]CH(AlCl_2)(CH_2)_7COOCH_3 \xrightarrow{H_2O}$$
$$CH_3(CH_2)_7CH[C_6H_4(CH_3)_2]CH_2(CH_2)_7COOCH_3 + AlCl_2OH$$

2.

$$CH_3(CH_2)_7CH[C_6H_4(CH_3)_2]CH_2(CH_2)_7COOCH_3 + KOH \longrightarrow$$
$$CH_3(CH_2)_7CH[C_6H_4(CH_3)_2]CH_2(CH_2)_7COOK + CH_3OH$$

3.

$$CH_3(CH_2)_7CH[C_6H_4(CH_3)_2]CH_2(CH_2)_7COOK + CH_3COOH \longrightarrow$$
$$CH_3(CH_2)_7CH[C_6H_4(CH_3)_2]CH_2(CH_2)_7COOH + CH_3COOK$$

The ester of meta-xylyl stearic acid with diethylene glycol mono ethyl ether is the principal ingredient of the oil which is the subject matter of this invention. The foregoing has described the preparation of meta-xylyl stearic acid which will now be combined with diethylene glycol mono ethyl ether and an ester of the two formed according to the following procedure.

To a predetermined weight of meta-xylyl stearic acid, an excess of diethylene glycol mono ethyl ether is added followed by 1% by weight of

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para toluene sulfonic acid. This mixture is re-fluxed for six hours and the water of reaction removed by azeotropic distillation with an excess of toluene.

The crude ester is dissolved in a suitable solvent, preferably diethyl ether, made alkaline with 10% aqueous solium carbonate solution and washed with distilled water until neutral and dried. The solvent is then removed under the vacuum and the ester vacuum distilled using a centrifugal molecular five inch still. The ester thus obtained is tested to meet requirements of viscosity and refractive index. These tests are extremely critical and the results are held to extremely close tolerances. To the ester which successfully meets these requirements, 1% by weight of an oiliness agent of the oxygenated-hydrocarbon type consisting predominately of alcohols, ketones and methyl esters is added thoroughly dissolved and the resultant mixture is filtered. This oiliness agent is Alox 350. Alox 350 is derived from the controlled oxidation of fractions of Pennsylvania petroleum. Alox 350 is one of the methyl esters of straight chain, hydroxy-, keto-, and keto-hydroxy acids of oxygenated hydro-carbons from the controlled oxidation of high molecular weight petroleum fractions. It belongs to a group consisting fundamentally of mixtures of organic acids and their esters ranging from C_5 to C_{35}, but they also contain high-

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molecular weight alcohols, lactones, ketones, and alcohol-ketones. The properties of Alox 350 may be outlined as specific gravity at 158° F. .8927 to .8861 viscosity, Saybolt sec. at 210° F. 68–80, melting point 100 to 110° F., flash point 300 to 340° F., acid no. 15–20, saponification no. 90–115. This resultant mixture is the oil which forms the subject of the invention.

What is claimed is:

1. A lubricant consisting of the ester of diethylene glycol mono ethyl ether and 9- and 10-meta-xylyl stearic acid.

2. A lubricant consisting of the ester of diethylene glycol mono ethyl ether and 9- and 10-meta-xylyl stearic acid containing from 0.05% to 5% by weight of a methyl ester of straight chain, hydroxy-, keto-, and keto-hydroxy acids of oxygenated hydro-carbons from the controlled oxidation of high molecular weight petroleum fractions.

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