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RICINOLEYL LUBRICANTS

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This invention concerns lubricating materials containing the ricinoleyl group and characterized in having a low humidity effect.

Since portable timepieces have been made, the problem of finding suitable lubricants for these mechanisms has been attacked by many people associated with the horological industry. Until the wrist watch came into prominence, satisfactory lubricants had been found among the naturally occurring oils. The best of these were the animal and vegetable oils consisting essentially of glycerides of the fatty acids and blends of these oils with mineral oils to obtain desired viscosity and some measure of resistance to chemical change with time. With the coming of the wrist watch and particularly since fashion has demanded mass production of smaller and smaller watches, the problems have become intensified. Until quite recently efforts to further refine and blend the natural oils have resulted in some improvements but all natural and blended-natural lubricants now available commercially are compromises—none of which is entirely satisfactory, for one or more reasons.

It has long been known that glyceryl tri-ricinoleate (even in the crude commercial form of castor oil) has acceptable lubricating properties under conditions where the high viscosity and the possible presence of moisture can be tolerated. For example, in internal combustion engines which operate at above the boiling point of water and high power is available, castor oil has been used for lubrication.

Many attempts have been made to use it for instrument lubrication but its exceedingly high viscosity has militated against its use in spring-driven machines, particularly where space was so important that small power springs were necessary. These springs do not possess the necessary power to drive through the viscous fluid. For example, where low powers only are available, as in the smaller wrist watches, escapement lubrication is desirable as such watches in commercial runs have low amplitudes of motion in the initial absence of such lubrication; on the other hand, most present lubricants soon disappear from the escapement contact surfaces and the friction constant changes: the instant lubricants have been found excellent and long lasting for escapement purposes. For example, fresh ricinoleic acid soon becomes thicker, and this increase in viscosity may be attributed to the formation of intra and inter esters. Ricinoleic acid has a terminal carboxyl group and a branch hydroxyl group. The reduction of ricinoleic acid to ricinoleyl alcohol by sodium involves the resolution of such esters, with conversion of the carboxyl group to hydroxyl, and the resulting alcohol with terminal and branch hydroxyl groups is known: it exhibits an improved and more stable viscosity behavior, and has been found to have lubricating properties but the ricinoleyl alcohol formed by sodium reduction has a bad humidity or hygroscopic action.

A primary feature of the invention is the provision of improved lubricants for watch escapements; it being recognized that materials satisfactory for such use are also

useful for other watch bearings and on watch mainsprings, and for other instruments, particularly where high unit bearing pressures exist.

Another feature of the invention is the provision of a lubricant comprising a compound which has the ricinoleyl radical coupled through oxygen or sulfur to another group; and characterized by low volatility, and low humidity effect.

Another feature is the provision of a lubricant comprising a compound which has the ricinoleyl radical coupled by oxy or thio ether linkage to another hydrocarbon group or groups; and characterized by low volatility and low humidity effect.

Another feature is the provision of a lubricant which permits operation of timepieces and like devices at very low temperatures, which is of particular value for aircraft instruments and other military instruments in general.

Ricinoleyl alcohol was made and proved to be an excellent watch escapement lubricant. Its high surface tension and medium viscosity are an excellent combination and, coupled with its unctuousness, result in good retention by jewel bearings and the ability to remain in situ on the pallets of the escapement for extended periods during service. The properties of several batches appear in the attached table.

In each case, commercially pure ricinoleic acid was reduced by lithium-aluminum hydride, in the presence of dibutyl ether, by the procedure described hereinafter. "Acid No." indicates the milligrams of KOH required to neutralize 10 grams of the product.

TABLE I

Properties of various batches of ricinoleyl alcohol

Batch No.	Cut No.	Acid No.	Refractive Index
11	Undist.	0.2	1.4671
12	Undist.	0.1	1.4648
13	Undist.	2.6	1.4687
	1	0.55	1.4694
	2	1.16	1.4711
	Undist.	0.82	1.4682
14	Undist.	0.55	1.4691
15	Undist.	0.43	1.4691
16	Undist.	2.72	1.4706
17	Undist.	0.26	1.4702
18	Undist.	0.19	1.4709
19	Undist.	0.31	1.4703
20	Undist.	0.40	1.4695
21	Undist.	0.77	1.4685
22	Undist.	0.41	1.4709
23	Undist.	0.66	1.4697
24			

For batch No. 13, cut (1) was obtained by steam vacuum distillation at 175 to 193.5 degrees C. and a pressure of 2.1 to 2.2 mm. Cut (2) was from a continuation of the steam vacuum distillation at 193.5 to 200 degrees C. at 2.2 to 2.3 mm. pressure.

When ricinoleyl alcohol prepared in either fashion is subjected to an ether-forming reaction, its humidity factor is improved immediately, even before any notable ether formation occurs: possibly from a heat-induced isomerization effect, as infra-red studies indicate that the previously absent trans isomer develops. In particular, it has been found that the trans isomer has greatly improved lubricating effects, as in its absence the motion is low when the ambient temperature is low.

It is further notable that ricinoleyl alcohol prepared from commercially pure ricinoleic acid by the lithium-aluminum hydride procedure does not have the high humidity effect that is shown when the reduction is carried out by means of the known sodium procedure.

Even better lubricants have been obtained in the mono- and di-ethers of ricinoleyl alcohol of so-called "mixed" type (i.e. where one of the two ether groups is ricinoleyl and the other is a different group) and mixtures of these with ricinoleyl alcohol itself. Representatives of these have been prepared and studied with the said other group of the ether selected from the normal branched and phenylated hydrocarbon series with carbon chains from 1 to 11 carbon atoms long. Without exception these materials have possessed desirable characteristics for instrument lubricants. They exhibit surprising resistance to humidity effects and good lubricating properties, and carry these into blends. For example, the presence of 5 percent of mixed mono- and di-oxy ethers in 95 percent of ricinoleyl alcohol provides a liquid which has satisfactory lubricating properties and low humidity effects.

The mixed ethers are composed structurally of a ricinoleyl group, the bonding oxy or thio group or groups, and one or more other groups which may be (*a*) straight or branched saturated aliphatic hydrocarbon chains of 1 to 18 carbon atoms, (*b*) phenyl or (*c*) aralkyl hydrocarbon groups of 7 to 18 carbon atoms. Instances are the mixed ethers in which the ricinoleyl group is joined to (*a*) methyl, ethyl, n-propyl, isopropyl, butyl, iso-butyl, amyl, n-hexyl, ethylhexyl; (*b*) phenyl; (*c*) phenylmethyl, phenylethyl, phenylpropyl, phenylundecyl. Blends of two or more are likewise effective.

The following examples are illustrative of compositions which have been made and tested, in which RA designates ricinoleyl alcohol:

Example I—ricinoleyl alcohol
Example II—di-methyl ether of RA
Example III—di-ethyl ether of RA
Example IV—di-n-propyl ether of RA
Example V—di-isopropyl ether of RA
Example VI—di-n-butyl ether of RA
Example VII—di-isobutyl ether of RA
Example VIII—di-n-amyl ether of RA
Example IX—di-isoamyl ether of RA
Example X—di-n-hexyl ether of RA
Example XI—di-2-ethylhexyl ether of RA
Example XII—di-octadecyl (branched) ether of RA
Example XIII—di-phenylmethyl ether of RA
Example XIV—di-phenylethyl ether of RA
Example XV—mono-phenylpropyl ether of RA
Example XVI—di-phenylpropyl ether of RA
Example XVII—di-phenylbutyl ether of RA
Example XVIII—di-phenylamyl ether of RA
Example XIX—di-phenylhexyl ether of RA
Example XX—di-phenylundecyl ether of RA
Example XXI—di-n-amyl thio ether of RA

Results of tests of specimen ricinoleyl ether, including a comparison with ricinoleyl alcohol, are shown below, where the column headed "Motion" indicates the amplitude of motion (unity being one full turn per cycle) at 1 hour after winding watches lubricated with the material after thorough cleaning, and also the amplitude after 24 hours unwinding, the watch being kept in a dry atmosphere (e.g. below 10 percent relative humidity). The column headed "Escapement" shows the visual appearance of the escapement pallet stones after 24 hours run, at the receiving ("R") and leaving ("L") stones respectively: the notation "W" meaning that the impulse face of the stone was "wet," i.e., a film of lubricant was present; "WT" meaning that there were "wet tracks," i.e. some of the lubricant had been displaced but enough was yet present for adequate lubrication; and "DT" meaning that there were "dry tracks," i.e. the lubricant had been displaced until not visibly present although lubrication effects may still be exhibited. The column "humidity" indicates the change in motion after the watches had been placed in a moisture-saturated atmosphere at room temperature after cleaning, lubrication and winding, and

compares the amplitudes of motion in dry and humid atmospheres, after running 1 hour and after running 24 hours. "RF" designates the "retention factor" measured by the percentage of oil drop diameter left in the bearings after 3 months, under storage conditions at normal conditions at normal temperatures and humidity, and with daily winding.

TABLE II

Results of watch tests on ricinoleyl ether lubricating compositions

Lubricant	Motion		Escapement		Humidity		RF 3 Mos.
	1 hr.	24 hrs.	"R"	"L"	1 hr.	24 hrs.	
Castor oil	1.26	1.06	------	------	−0.03	−0.14	------
Example I	1.59	1.50	W	W	−0.53	−0.71	93
Example XV	1.62	1.50	DT	W	0.00	0.00	70
Example XVI	1.57	1.50	W	W	−0.06	−0.06	78
Example XI	1.51	1.42	W	W	−0.05	−0.09	70
Example VII	1.50	1.37	WT	WT	−0.04	−0.11	90
Example V	1.53	1.38	WT	WT	−0.07	−0.09	------
Example XVII	1.55	1.49	WT	WT	−0.06	−0.13	------
Example XIX	1.53	1.50	------	------	−0.02	−0.15	89
Example XVIII	1.55	1.46	------	------	−0.08	−0.09	92
Example X	1.54	1.50	------	------	−0.13	−0.20	74

It is noteworthy that the ethers exhibit a good motion with very little change during normal unwinding, being comparable with ricinoleyl alcohol rather than castor oil: in almost all cases they maintain place under the severe escapement conditions: having a far less humidity effect than the alcohol: and exhibiting satisfactorily high retention behavior.

Specific examples showing particularly desirable characteristics are described below, including:

Example XXII—di-n-hexyl ether of ricinoleyl alcohol with residual alcohol
Example XXIII—di-2-ethylhexyl ether of ricinoleyl alcohol with residual alcohol
Example XXIV—di-phenylpropyl ether of ricinoleyl alcohol with residual alcohol
Example XXV—mono-phenylpropyl ether of ricinoleyl alcohol with residual alcohol

The mixtures as set forth above in Examples XXII to XXV may be made either by making the essentially pure ether and blending it with ricinoleyl alcohol or by controlling the reaction conditions so that the ether reaction is incomplete. There are several advantages to the latter method even though there is more precise control of the chemical components of the composition when the first method is used. Excellent lubrication results from use of such compositions with all percentages of residual alcohol. As stated above, a few percent of ether effects quite desirable changes in the properties of the mixtures.

When the method of incomplete reaction is used, a mixture of all possible combinations of the end products can be obtained, including unreacted alcohol, mono-ethers, and di-ethers; and actual service tests in watches have indicated that such mixtures are quite desirable.

The thio-ethers are likewise satisfactory. For instance, ricinoleyl di-n-amyl thio-ether (Example XXI) is a good lubricant, as shown by tests as low as minus 65 degrees F. In particular, the presence of the trans isomer of the ricinoleyl group is highly desirable, in that compositions having no trans isomer (as indicated by infra red studies) have much lower motions, corresponding to higher friction values or viscosities, than the compositions having trans isomer present but otherwise chemically the same. The amount of motion appears related to the amount of trans isomer present: such isomerization can be effected by water-vapor-vacuum distillation. The behavior of specimen preparations is given in the following:

TABLE III

Motion vs. temperature of movements lubricated with di-n-amyl thio-ether of ricinoleyl alcohol

Preparation No.	Duration of Test (Months)	Average motion of 10 movements (Grade C.) Room Temp.	0° F.	−35° F.	−50° F.	−65° F.	Transmittance	Percent
1	Original	1.45	1.45	1.36	1.13	0.99	83/40	43
	3	1.55	1.35	1.15	0.98	0.81		
	6	1.38	1.38	0.96	0.75	0.68		
	10.46 (end)	1.43	1.21	0.87	0.74	0.66		
2	Original	1.34	1.30	1.20	1.06	0.84	85/48	37
	3	1.30	1.45	1.35	1.21	1.14		
	6	1.29	1.29	1.20	1.15	0.91		
	9	1.30	1.23	1.08	0.89	0.75		
	12	1.28	1.14	1.04	0.83	0.72		
3	Original	------	1.35	0.93	0.65	0.36	82/66	16
	0.23 (end)	1.39	1.36	0.90	------	0.38		
4	Original	------	1.31	0.84	0.55	0.26	82/75	7
	0.23 (end)	1.46	1.20	0.80	------	0.33		
5	Original	1.49	1.53	1.49	1.38	1.08	82/48	34
	1	1.45	1.59	1.56	1.46	1.15		
	3	1.54	1.56	1.53	1.36	1.05		
	6	1.54	1.55	1.50	1.31	1.04		
	9	1.54	1.60	1.49	1.29	0.96		
6	Original	1.43	1.40	1.07	0.79	0.64	85/68	17
	3	1.52	1.49	1.26	0.83	0.75		
	6	1.48	1.54	1.05	0.86	0.74		

The watches were a test group of ten movements of identical type, size, and grade, so that direct statistical averages could be obtained; having the usual tolerances of adjustment of bearings, escapements, etc., and the lubricant was employed at the several bearings. It may be remarked that when the adjustments are refined to high accuracy, the lubricant is satisfactory regardless of physical state even as low as minus 110 degrees F.; that is, the physical behavior of the lubricant, such as an intervening freeze or pour point, does not prevent lubricating action down to such temperature.

The transmittance is set out as the "dip" of the standardized graph representing the transmission factors at the successive infra-red wave lengths, so that the numbers 83/40 represent a "top" value of 83 on the graph adjacent the wave length at which there is response to the trans isomer form, and a value of 40 for the "dip" at this response wave length: the difference being the value 43 or 52 percent of the "top" value of 83. A difference of ⅓ or 20 percent or more having been found to represent a satisfactory condition for desirable motion amplitudes at the lower temperatures.

In test groups of watches, as described herein, there may be variables as high as 10% due to mechanical

tolerances, strength of springs, etc., at various conditions of test. The averaging results therefore are more representative than the effects of any single movement. It is noteworthy that these variables are not normally effective at room temperature, but come largely into play at temperatures of, say, minus 50 degrees F. and below, so that watches which may appear closely similar at room temperature will have variant conditions at these low temperatures. In each of the examples herein stated, the watches continued to run (unless otherwise stated) at the lowest temperatures marked. It may also be noted that three-quarters of a turn of movement has been acceptable at minus 65 degrees F. heretofore: and one turn at minus 35 degrees F. Accordingly, it is noteworthy that many of these materials are far more satisfactory than required by present specifications.

Preparations Nos. 3 and 4 were not distilled for purification of the ricinoleyl di-iodide; whereas distillation was used with Preparations Nos. 1, 2 and 6. Preparation No. 5 was made by combining residues of Preparations Nos. 3 and 4, and then vacuum distilling with water vapor.

Blends of one or more of the mixed ethers with other lubricants are valuable and included herein. For example, diphenylheneicosanone is a lubricating liquid having excellent surface tension and retentivity to metal and sapphire surfaces, but exhibits a humidity effect: when mixed in equal parts by weight with ricinoleyl-di-n-amyl thio-ether (see Example XXI), the humidity effect of the mixture is so low that no attention need be paid to the condition, and the surface tension lies within the desired range of 29 to 36 dynes per centimeter. It may be noted that when the surface tension is below 29 dynes per centimeter, the material exhibits spreading on brass and ruby; within the range of 29 to 33 dynes per centimeter, the material is "slow spreading" or may be designated as a borderline lubricant; while at about 33 dynes per centimeter and up, the material does not spread in a period of three months or more as noted, in commercial uses in watches, etc.

The following shows the behavior of mixtures in parts by weight containing such ethers, the di-n-amyl thio ether of Example XXI (here abbreviated as ATE) being selected for direct comparison, and employed in mixture with diphenyl-heneicosanone (noted as dPH), whose properties alone and in mixture with phenylstearyl alcohol (noted as PSA) are inserted for the comparison. Dodecyl piperidine stearate is noted as DPS.

TABLE IV

(Ladies' wrist watches, 19 jewel, Grade A)

Example	Lubricant	Atmosphere, dry 1 hr.	Atmosphere, dry 24 hrs.	Atmosphere, 60% R.H. 1 hr.	Atmosphere, 60% R.H. 24 hrs.	Humidity Effect 1 hr.	Humidity Effect 24 hrs.
XXI	dPH	1.350	1.200	1.075	0.925	−0.28	−0.27
	80 dPH: 20 PSA	1.324	1.275	0.974	0.874	−0.35	−0.40
	ATE 50	1.500	1.437	1.387	1.276	−0.11	−0.16
XXVI	50 dPH: 50 ATE	1.500	1.402	1.252	1.126	−0.25	−0.28
XXVII	80 dPH: 20 ATE	1.412	1.287	1.127	1.039	−0.28	−0.25

TABLE IV-A

(Ladies' wrist watches, 19 jewel, Grade B)

Example	Lubricant	Atmosphere, dry 1 hr.	Atmosphere, dry 24 hrs.	Atmosphere, 60% R.H. 1 hr.	Atmosphere, 60% R.H. 24 hrs.	Humidity Effect 1 hr.	Humidity Effect 24 hrs.
XXI	dPH	1.474	1.375	1.324	1.127	−0.15	−0.25
	80 dPH: 20 PSA	1.513	1.425	1.387	1.239	−0.13	−0.19
	ATE	1.604	1.513	1.578	1.474	−0.03	−0.04
XXVI	50 dPH: 50 ATE	1.565	1.500	1.451	1.439	−0.11	−0.06
XXVII	80 dPH: 20 ATE	1.513	1.437	1.437	1.238	−0.07	−0.20

TABLE IV–B

(Ladies' wrist watches, Grade B)

Example	Lubricant	Atmosphere, dry		Atmosphere, 60% R.H.		Humidity Effect	
		1 hr.	24 hrs.	1 hr.	24 hrs.	1 hr.	24 hrs.
XXVIII	50 dPH: 50 ATE (lot 2)	1.565	1.500	1.451	1.439	−0.11	−0.06

TABLE IV–C

(Ladies' wrist watches, Grade B)

Example	Lubricant	Atmosphere, dry		Atmosphere, 60% R.H.		Humidity Effect	
		1 hr.	24 hrs.	1 hr.	24 hrs.	1 hr.	24 hrs.
XXIX	50 dPH: 50 ATE (lot 3)	1.25	1.18	1.13	1.07	−0.12	−0.11
XXX	50 dPH: 50 ATE 0.2 DPS (lot 1)	1.23	1.17	1.13	1.09	−0.10	−0.08

It may be stated that the mixtures of dPH and ATE have higher retention factors than ATE alone, therewith overbalancing for lengthy commercial uses, between relubrications, initially higher motions for the ATE. The other oxy and thio ethers exhibit like behavior in mixtures.

For Example XXX, the material showed a retention factor at 3 months of 89.3 percent; at 6 months, 78.5 percent. The failures of lubrication (20 watches running continuously to failure) were none at 3 months, one at 6 months.

The column headed "Humidity Effect" sets out the change in number of turns due to humidity; and the values are the differences between values in the "Atmosphere Dry" and "Atmosphere, 60% R.H." (60% relative humidity) columns.

Further instances, showing the effect of additives upon the viscosity, the comparison being between the dry composition and the composition after exposure for 5 days at 100 degrees C. to an atmosphere provided by passing air through water at 25° C. to procure saturation and then heating, the resultant relative humidity at 100° C. being about 3 percent, are as follows:

TABLE V

Comparison of watch lubricant additives in their effect upon change of viscosity during corrosion tests

Lubricant	Percent change in Viscosity
Example I	145
Example XXXI	21.1
Example XXXIV	48.6
Example XVI:	
Batch III	140.2
Batch IV	60
Example XXXIII, batch III	21.3
Example XXXIV	3.9
Example XXI	2.35
Example XXXV	0.56

Example XXXI was RA (Example I) with added anti-oxidant (1% 2,6 tertiary butyl p-cresol and 0.2% trithiophenyl phosphate).

Example XXXII was 99% by weight ricinoleyl alcohol and 1% hydroquinone.

Example XXXIII was the ether of Example XVI, with the same anti-oxidant as Example XXXI and in the same amount.

Example XXXIV was 99% by weight of diphenyl propyl ether of ricinoleyl alcohol and 1% hydroquinone.

Example XXXV was the ether of Example XXI, with the same anti-oxidant as Example XXXI and in the same amount.

In the above table, one anti-oxidant employed for the tests was 2,6-tertiary-butyl p-cresol and trithio-phenyl phosphate in a mixture found better than either alone. Other anti-oxidants can be used, such as p-tertiary butyl catechol, triphenyl phosphate, and similar organic compounds such as polyhydroxy phenols and phosphate esters of the phenols. In general, the addition of about 0.1 to 1.5 percent by weight of anti-oxidant is desirable whenever the lubricant is to be used in contact with metals which are subject to corrosion.

It has above been stated that the humidity effect is revealed quickly. To show that the effect occurs before moisture-saturation of the material has occurred, the following sets out the behavior of dried oils in a humid atmosphere. For the tests, clean 10 ml. beakers were weighed and about 5 grams of the stated lubricating oil added: the samples were held in a desiccator over concentrated sulfuric acid until constant weight was reached. The samples of dried oil were then transferred to a closed vessel containing a saturated solution of ammonium sulfate until constant weight was again obtained. The tests were conducted at room temperature. The results were reported as percent (%) of water (by weight) absorbed per gram of the dried oil.

TABLE VI

Humidity tests on oils

Identification	Weight Dry Oil over H_2SO_4	Weight Wet Oil over $(NH_4)_2SO_4$	Gm. H_2O Gained	Percent H_2O Absorbed per gm. dry oil	Num. Days in Wet Chamber to Const. Weight
	G.	*G.*	*G.*	*Percent*	
Commercial "B"	1.8945	1.8982	0.0037	0.195	24
Commercial "C"	3.0046	3.0062	0.0016	0.053	17
Commercial "D"	3.3730	3.3767	0.0037	0.110	17
Castor oil, USP	4.7728	4.8067	0.0339	0.710	72
Example I	[a] 4.75	[1]	[1]	[1]	[1]
Example XII	4.7676	4.8242	0.0566	1.187	86
Example XVI	4.9354	4.9881	0.0527	1.067	21
Example XV	4.7190	4.7747	0.0557	1.180	86
Example XVII	4.7392	4.7940	0.0548	1.156	98
Example XIX	4.5731	4.6214	0.0483	1.056	24
Example XI	4.7057	4.7854	0.0797	1.693	82
Example II	[a] 5.127	[2]	[2]	[2]	[2]
Example VII	[a] 4.76	[3]	[3]	[3]	[3]

[a] Approximate.

[1] Sample never reached const. dry weight. Lost 0.0319 g. in 47 days and gained 0.0036 g. in 74 days later. Kept in dessicator for 122 days.

[2] Never reached dry const. weight. Gained 0.1319 g. in 122 days over H_2SO_4.

[3] Never reached const. weight over H_2SO_4—total gain in 122 days was 0.0022 g.

It may be pointed out that the "humidity effect" is often not directly ascertainable by the percentage of moisture present or by laboratory tests of surface tension. Experimental determinations have been made by carefully cleaning a group of identical good watch movements (e.g. ten), lubricating them with the test material, and then causing them to turn for 48 hours in a desiccated atmosphere of 10–20% relative humidity, and noting the individual levels of motion when fully wound and when 24 hours "down" (i.e. after running 24 hours from the latest winding). The watches are then caused to run in a controlled atmosphere of 50–60% relative humidity (i.e. corresponding to a normal atmosphere in the United States); and the levels of motion are observed as before by winding, noting the motion, running 24 hours, again noting, rewinding, noting, again running for 24 hours, and making a final note of the motion level. The averaged results for the group of watches are closely reproduced when the test is repeated. It is striking that changes in level of motion appear, in a change from a drier to a moister atmosphere, in about 15 minutes; and quick qualitative values can be obtained by partly winding a cleaned and lubricated watch and observing its motion after a couple hours in a dry atmosphere, then immediately transferring it while still running to a moist atmosphere and observing the motion at the end of a half hour.

An outstanding effect of the presence of the ether in such mixtures is in the further reduction of viscosity without an injurious effect on the surface tension, particularly when the ethers contain aryl groups: that is, the liquid is "thinned" without injuriously increasing its volatility.

One of the most difficult points to lubricate, where all of the oils made according to the prior art have failed to provide satisfactory lubrication, is at the contact between the pallets of the lever and the teeth of the escape wheel. This part of the watch permits minute amounts of power to be taken from the mainspring and transmitted to the balance wheel at regular intervals of time. The efficiency at which it operates determines to a large extent how efficiently the power of the mainspring is utilized. It is imperative in small watches that this be utilized quite efficiently in order to provide a satisfactory interval between windings.

During the operation of the escapement, the knife edge of the escape wheel travels across the impulse face of the ruby stone or jewel pin. Each stone is thus "wiped" by a knife edge 2½ times per second in the usual "5-beat" watch. Attempts to calculate logically the unit pressures existing at this point result in an extremely high value; it is generally conceded that the unit pressures in watch escapements are determined by the lowest yield point in compression of the materials in contact. Under the most optimistic reasoning, the pressures are much higher than is consistent with fluid lubrication theory. Thus in this instance there is a condition of boundary lubrication where viscosity plays only a small part in reducing friction and the factors effecting satisfactory lubrication here are as yet but little understood.

The lubricants, being capable of such employment, are also useful for other purposes. For example, they give satisfactory results at the mainspring.

Comparative physical properties and corrosion behaviors of some commercial watch lubricants and the instant ricinoleyl ethers are shown by the following table:

TABLE VII

Physical properties of selected compounds compared with commercial watch oils

Chemical	Density	Surface Tension	Viscosity		Percent Ether (±10% Accuracy)	Percent Change in Viscosity After corrosion (100° F. Based on Original Vis.)	Relative Volatility Percent loss in 120 hours
			100° F.	68° F.			
Synthetic Lubricant "A"	0.920	31.0	29.4	64	----------	----------	----------
Synthetic Lubricant "B"	0.926	[1] 34.0	41.5	120	----------	----------	----------
Synthetic Lubricant "H"	0.894	31.0	47.7	112	----------	----------	----------
Castor Oil (Fisher 10-'49)	0.980	35.1	304.3	1,062.0	----------	483.5	----------
Example I	0.908	34.1	167.0	548	0	292.0	----------
Example II	0.867	30.7	10.6	19.9	70	6662.0	−1.72
Example XII	0.908	34.9	53.1	150	36	121.9	----------
Example III	0.904	32.0	37.6	100	26	----------	−0.08
Example IV	0.890	31.0	51.2	144	22	----------	0.07
Example XVI	0.916	35.1	49.8	137	46	125.2	----------
Example VI	0.925	31.1	79.9	216	70	----------	0.49
Example XVII	0.900	34.4	59.1	171	35	172.5	----------
Example VIII	0.910	32.2	91.1	293	4	----------	0.00
Example XVIII	0.918	33.6	38.1	97	71	22.3	----------
Example IX	0.878	30.4	46.3	128	28	----------	−0.07
Example X	0.890	31.7	72.4	221	8	----------	0.07
Example XIX	0.890	34.2	65.2	193	26	117.9	----------
Example XV	0.910	33.8	63.8	186	----------	137.5	−0.07
Example XXI	0.860	30.6	8.7	14.7	----------	2.35	----------

[1] Minimum.

Like comparisons of the behaviors of lubricants of Table VII, in watch service under close observation and maintenance of a humid atmosphere, are given below in Table VIII.

The columns are headed as before, with parentheses marking specific variant readings obtained. The last two columns show the number of dry jewels found out of 20 (10 watches under test, with 2 jewels each, for each value stated).

TABLE VIII

Results of watch tests of selected compounds compared with commercial watch oils

Chemical	Average Motion (10 Move.)	Escapement, 112 hrs. running		Humidity		Retention		No. Dry Jewels (out of 20) (3 mos.)	No. Dry Jewels (out of 20)(12 mos.)
		L	R	1 hr.	24 hrs.	3 mos.	12 mos.		
Commercial "A"	1.46	Dry track	Dry track						
Commercial "B"	1.54	do	do	−0.06	−0.13	100			
Commercial "C"	1.64	Wet	do	−0.07	−0.07	80			
Castor oil, Fisher 0-'49	1.26	Track—3 min.	Track—3 min.	−0.03	−0.14				
Example I	1.625	Wet	Wet	−0.53	−0.71	93(78) (85)		2(0) (2)	
Example II	1.5	do	Dry	−0.00	−0.33	77		2	
Example XII	1.5	do	do	−0.04	−0.09	63		3	
Example III	1.625	do	do	−0.25	−0.31	58(71)	46	5(1)	8
Example IV	1.625	Dry	do	−0.08	−0.12				
Example XVI	1.625	Wet	Wet	−0.04	−0.05	78	23.4	2	12
Example VI	1.50	Dry	Dry	−0.08	−0.15	67		5	
Example XVII	1.50	Wet tracks	Wet tracks	−0.06	−0.13				
Example VIII	1.50	Wet	Dry	−0.05	−0.20				
Example XVIII	1.55			−0.08	−0.09	92.0		0	
Example IX	1.50	Dry	Dry	−0.00	−0.00				
Example X	1.50	Wet tracks	Wet tracks	−0.13	−0.20	74		3	
Example XIX	1.50	do	do	−0.02	−0.15	88.7	31.9	0	11
Example XV	1.50	do	do	−0.00	−0.00	70	13	2	16

Methods of preparing such compounds will now be described.

PREPARATION A.—RICINOLEYL ALCOHOL

Ricinoleic acid is commercially obtainable, and has been employed in making ricinoleyl alcohol

$$CH_3\cdot(CH_2)_5\cdot CHOH\cdot CH_2\cdot CH{:}CH(CH_2)_8OH$$

To a 12 liter flask equipped with a mechanical stirrer, reflux condenser and opening for a dropping funnel is added 3500 cc. of dried di-butyl ether. To the ether in the flask is then added ¼ lb. (110–120 grams) of lithium aluminum hydride. The slurry is then stirred for several minutes. Then 420–430 grams of dried ricinoleic acid diluted with 3000 cc. of dibutyl ether is added slowly to the slurry while stirring. The rate of addition is governed by the temperature and rate of evolution of hydrogen. The temperature should not exceed 90° C. during this addition. More solvent may be added if the contents of the flask become too thick. The mixture is heated gently for two to three hours after the addition is complete, keeping the temperature between 70–80° C. After this period, the heat is removed and the reaction flask is surrounded with an ice-water bath. About 250 cc. of cold water is then added dropwise: the first few hundred drops should be added one drop at a time, allowing up to half a minute between each drop for the first ten to twenty minutes. The mixture is then hydrolyzed by carefully adding two to three liters of 20% by weight of sulfuric acid. The product is then washed to neutral with distilled water, dried over about one pound of anhydrous calcium sulfate with some anhydrous sodium sulfate. The solvent is stripped by distillation at atmospheric pressure: for a yield of about 99 percent. The alcohol need not be distilled since it can be used in subsequent syntheses.

Di-ethyl ether can be used as solvent, but dibutyl ether is preferred, for its higher boiling point, as this permits a higher reaction temperature with corresponding increased velocity, and with a greater ease of condensing during reflux.

PREPARATION B.—DI-IODO-OCTADECENE

This intermediate

$$(9CH_3\cdot(CH_2)_5\cdot CHI\cdot CH_2\cdot CH{=}CH(CH_2)_8{-}I)$$

(1,12-diiodooctadecene-9), used in the preparation of the thioethers of ricinoleyl alcohol and also in an alternate method for the preparation of the oxyethers of ricinoleyl alcohol, is prepared from ricinoleyl alcohol and phosphorus tri-iodide as follows:

To a three-necked round bottom, two liter flask, equipped with a mechanical stirrer, reflux condenser and dropping funnel is added first 23 grams of red amorphous phosphorus through a powder funnel. Then 375 grams of iodine (resublimed) dissolved by shaking with 300 grams of dried ricinoleyl alcohol, is added through a separatory funnel with no solvent. The first addition is done cautiously. Cooling with ice water is necessary. After this initial reaction subsides, more of the iodine and alcohol are added slowly with stirring. If the reaction does not continue as evidenced by evolution of heat, gentle heating may be necessary. After the addition of the alcohol and iodine is complete, the mixture is heated to about 130–140° C. and held at this temperature for three hours. The heat is then removed and the product allowed to cool slowly and stand overnight. The iodine fumes may be absorbed by a solution of sodium thiosulfate or sodium hydroxide. A trap should be used to avoid sucking back.

The product is then diluted with diethyl ether, washed with three portions of 5% sodium hydroxide followed by several washes with distilled water to neutral. The mixture was then dried over anhydrous sodium sulfate, filtered and stripped of solvent, diethyl ether. The residual solvent was removed by decreasing the pressure at the end of the distillation process. Since it is an intermediate, it was not further purified.

In Preparation B, when the di-iodo-octadecene is distilled by the water vapor-vacuum method, a significant increase in the trans isomer content is noted: and this procedural step can be employed for such purpose.

Infra-red analysis of the product showed the absence of hydroxyls, indicating very pure yields.

PREPARATION C.—RICINOLEYL DI-OXYETHERS FROM RICINOLEYL ALCOHOL

The structural formula for the di-oxyethers of ricinoleyl alcohol (i.e. the ricinoleyl oxy diethers) is:

$$CH_3(CH_2)_5\underset{\displaystyle OR}{\underset{|}{C}}HCH_2CH{=}CH(CH_2)_8{-}OR'$$

where R and R′ may be the same or different groups and where R and R′ are straight or branched chain alkyl or aralkyl groups; it being preferred herein to have the alkyl chains of from 1 to 12 carbons and to have the alkyl chains of the aralkyl groups of from 1 to 11 carbons. This type of compound belongs to the general group of mono-unsaturated-diol ethers where one oxy bond is primary and the other secondary.

The symmetrical ethers (where R and R′ are the same) are more easily prepared than the unsymmetrical.

Though several methods have been employed, the most successful procedure for use in preparing di-ethers with very little or no alcohol in the final product is represented by the following equations:

(1)

$$CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_8OH + 2Na \longrightarrow CH_3(CH_2)_5\underset{\underset{ONa}{|}}{CH}CH_2CHCH(CH_2)_8.ONa + H_2$$

(2)

$$CH_3(CH_2)_5\underset{\underset{ONa}{|}}{CH}CH_2CH{=}CH(CH_2)_8.ONa + 2RHx \longrightarrow CH_3(CH_2)_5\underset{\underset{OR}{|}}{CH}CH_2CHCH(CH_2)_8.OR + 2NaHx$$

(where Hx represents a halogen; and R is the other group for the mixed ether).

In the first equation, the sodium may be combined with other materials prior to reacting it with ricinoleyl alcohol to avoid the use of lumps of metallic sodium, which quite often become coated with the solid alcoholate before the reaction is complete. Sodium methylate can be used. Satisfactory materials are the commercially available sodium dispersions in non-reactive organic liquids, e.g. toluene, where the diameter of the sodium particles is in the range of 1 to 18 microns.

The general procedure for synthesis of the diethers is as follows:

To a three-necked round bottom two liter flask, equipped with a reflux condenser, mechanical stirrer, and dropping funnel is added 0.61 gram atomic weight of sodium in the form of a sodium dispersion in toluene. The dispersion is further diluted by addition of 600 to 700 cc. of toluene (previously dried over sodium). After warming the contents of the flask to 50–60° C., 0.3 moles of dried ricinoleyl alcohol (from Preparation A above) diluted with 200 cc. of dry toluene is added dropwise with constant stirring to the sodium in the flask. Care should be taken to avoid rapid addition of the alcohol in order to avoid forming a complex of alcohol with the alcoholate. After all the alcohol is added, the contents of the flask are stirred for thirty minutes while the solvent is gently refluxing. While still refluxing 0.63 moles of the RHx, diluted with 100 to 200 cc. of toluene, is added dropwise with stirring to the alcoholate. The heat may be reduced if excessive refluxing is encountered on adding with halide. After all the halide is added, the mixture is heated to gentle reflux and maintained at this temperature with continued stirring for ten to twelve hours. The flask contents are then allowed to cool to room temperature with no stirring. The reaction mixture is then separated into a solid and a liquid portion by centrifugation or other means, avoiding contact with moisture insofar as feasible. Separation by laboratory filtration was found very difficult. The solid matter collected is the sodium halide (a reaction product) and unreacted sodium alcoholate of ricinoleyl alcohol. The liquid portion consists of solvent, unreacted halide, and the di-ether of ricinoleyl alcohol. To wash the solid portion to remove as much of the di-ether as possible, the filter cake or solid portion is transferred to a beaker, a small quantity of toluene added to the cake, stirred, and separated again. The liquid portions are then combined and transferred to a separatory funnel. The liquid is then washed with acidulated (HCl) distilled water, then washed with distilled water until the spent wash water has the same pH as the original water (by indicator paper test). The final wash water is drawn off and the reaction product is dried over anhydrous calcium sulfate or anhydrous sodium sulfate. After drying, the solvent is removed by distillation at atmospheric pressure, the last traces of solvent being removed by reducing the pressure at the end of the distillation process. The crude product is then purified by water vapor carrier-vacuum distillation.

In a preparation of diphenylamyl ether of ricinoleyl alcohol, the product had an acidity equivalent of 1.13 mg KOH per gram: and upon test showed presence of 71 percent ether, the residue essentially ricinoleyl alcohol. It may be noted that other preparations of diphenylamyl ether of ricinoleyl alcohol had closely the same properties and behaviors as set out for Example XVIII herein.

PREPARATION D.—RICINOLEYL MONO-OXYETHERS

The formula for the mono-ethers of ricinoleyl alcohol (or ricinoleyl mono-ethers) is as follows:

(1) $CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_8{-}$ OR (primary ether)

and/or

(2) $CH_3(CH_2)_5\underset{\underset{OR}{|}}{CH}CH_2CH{=}CH(CH_2)_8{-}OH$ (secondary ether)

Unless special provisions are made, a mixture of both the compounds represented by the above formula is prepared plus a smaller proportion of the di-ether. Since such precautions are lengthy and expensive, and since mixtures tend to depress the pour and cloud point and in general improve the lubricating qualities, no special precautions need be taken in the preparation of satisfactory mono-ether mixtures for lubricants.

The general procedure for synthesis of the mono-ethers is as follows: to a three-necked round bottom two liter flask, equipped with a reflux condenser, mechanical stirrer, and dropping funnel is added 0.41 gram atomic weight of sodium in the form of a sodium dispersion in toluene. The dispersion is further diluted by addition of 600 to 700 cc. of toluene (previously dried over sodium). After warming the contents of the flask to 50–60° C., 0.4 moles of dried ricinoleyl alcohol (from Method A above) diluted with 200 cc. of dry toluene is added dropwise with constant stirring to the sodium in the flask. Care should be taken to avoid rapid addition of the alcohol with alcoholate. After all the alcohol is added, the contents of the flask are stirred for thirty minutes while the solvent is gently refluxing. While still refluxing, 0.42 mole of RHx, diluted with 100 to 200 cc. of toluene, is added dropwise with stirring to the alcoholate. The heat may be reduced if excessive refluxing is encountered on adding the halide. After all the halide is added, the mixture is heated to gentle reflux and maintained at this temperature with continued stirring for eight to ten hours. The flask contents are then allowed to cool to room temperature. The reaction mixture is then washed first with acidulated (HCl) distilled water, then with distilled water in a separatory funnel until the spent wash water has the same pH as the original water (by indicator test paper). The final wash water is drawn off and the reaction product is dried over anhydrous calcium sulfate or anhydrous sodium sulfate. After drying, the solvent is removed by distillation at atmospheric pressure, the last traces of solvent being removed by reducing the pressure at the end of the distillation process. The crude product is then purified by water vapor carrier-vacuum distillation.

PREPARATION E.—RICINOLEYL THIO-ETHERS

Thio-ethers, such as di-n-amyl, di-n-propyl, di-n-octyl, and the phenyl and branched analogs, are successful lubricants, as illustrated by Example XXI and Table III.

The method stated for preparing these thio-ethers is one which gives a fairly pure compound. Where low temperature properties are desired, an advantage is thus often gained because of the more sharply defined freezing point of compounds as against a gradual thickening and solidifying which takes place as mixtures are cooled to successively lowered temperatures, such thickening being due to components separating out of the solution phase and giving rise to wide freezing ranges, except in the special cases where a eutectic point exists below the desired operating temperature.

The general formula for the thio-ethers of ricinoleyl alcohol (i.e. ethers of di-mercapto-octadecene-9) is as follows:

$$CH_3(CH_2)_5\underset{SR}{\underset{|}{C}}HCH_2CH{=}CH(CH_2)_8{-}SR'$$

where R and R' may be the same or different groups, and where R and R' are straight or branched chain alkyl or aralkyl or aryl groups, the alkyl chains having from 1 to 18 carbons and the alkyl chains of the aralkyl group having from 1 to 11 carbons.

To illustrate this synthesis, the procedure which follows is for the preparation of di-n-amyl thio-ether of ricinoleyl alcohol.

Two equivalent weights (80 grams) of sodium hydroxide were dissolved in the smallest possible quantity of water and diluted with methanol: a solution in methanol of two equivalent weights (208 grams) of n-amyl mercaptan was added through a dropping funnel with stirring. 176 grams of the 1,12-diiodooctadecene-9 from Preparation B above, in methanol, was then added through a dropping funnel with stirring. Further dilution with methanol or toluene may be employed. The mixture was then refluxed for six hours and allowed to cool. The following day, the mixture was transferred to a separatory funnel and the clear aqueous layer withdrawn and discarded. The oil layer was diluted with a solvent such as di-butyl ether; washed with 5% sodium hydroxide solution and then neutralized by washing with distilled water until the efflux pH is that of the entering water; withdrawing the successive water fractions as settled; the oil layer was then dried over anhydrous calcium or sodium sulfate, and stripped of solvent by distillation.

The thio-ether was then purified by vacuum distillation using water vapor as carrier, with vapor temperatures of 200–250° C. at around 10 mm. pressure. The product obtained was a dark amber liquid; and provided a lubricant satisfactory at normal temperatures. On purifying further by chromatography, a pale yellow liquid was obtained. The original color and wide boiling range may be accounted for by the presence of unreacted diiodooctadecene. The behavior of this compound is described herein as Example XXI.

The quantities indicated above include use of sodium hydroxide and mercaptan in large excess over the dihalide compound (of which one equivalent weight is 508 grams) to assure essential exhaustion of the expensive di-halide component before the unreacted materials are separated.

The reactions may be regarded as proceeding:

(1) $$RSH+NaOH \rightarrow RSNa+H_2O$$

(2)

$$CH_3(CH_2)_5\underset{I}{\underset{\cdot}{C}}H{\cdot}CH_2{\cdot}CH(CH_2)_8I + 2(RSNa) \longrightarrow CH_3(CH_2)_5\underset{SR}{\underset{\cdot}{C}}H{\cdot}CH_2{\cdot}CH{=}CH(CH_2)_8SR + 2NaI.$$

Alternative procedures, using differing amounts of the di-halide, and with other purification procedures, have led to the production of the compound: noting that the vacuum distillation with water vapor carrier is effective in assuring a large proportion of trans isomer.

It has been found that the conditions during synthesis may be critical if the best lubricating compositions are to result: although the various syntheses produce lubricants effective at normal temperatures. For example, several of the compounds were synthesized by several procedures: the product by one procedure had a much higher viscosity and a higher surface tension, and gave a poorer motion when used in watches below minus 10 degrees F., as compared with the product by Preparation E. As the viscosity of the former product was not sufficiently high to account for the poor motion thus encountered in watches at low temperatures, it must be concluded that the product does not possess the excellent lubricating properties of the preferred material made in accordance with Preparation E; noting that the former product was low in trans isomer. However, when the former product was then subjected to vacuum distillation with water vapor carrier, to give a high content of trans isomer, it provided a lubricant of light high quality even at the low temperatures.

PREPARATION F.—RICINOLEYL THIO-ETHERS (SECOND METHOD)

An alternative procedure to that of Preparation E is by placing the diiodooctadecene from Preparation B and the mercaptan (here, illustratively, phenylamyl mercaptan) in a flask, with toluene as a diluent. These are heated with refluxing for 30 minutes, and then allowed to cool. It is preferred to use less than the theoretical equivalent amount of the di-halide compound, because of its cost and to assure its total consumption in the reaction: the mercapatn and caustic alkali are each present in proportions of two equivalent weights as before. The sodium hydroxide is dissolved in the least necessary amount of a mixture of equal parts of water and methanol: and introduced dropwise to the flask with stirring. The material is then heated with refluxing for 6 hours. Thereafter, it is cooled, separated, and purified as in Preparation E above.

The reaction may be regarded as illustratively proceeding:

$$CH_3(CH_2)_5{\cdot}\underset{I}{\underset{\cdot}{C}}H{\cdot}CH_2CH{=}CH(CH_2)_8{\cdot}I + 2RSH + 2NaOH \longrightarrow CH_3(CH_2)_5{\cdot}\underset{SR}{\underset{\cdot}{C}}H{\cdot}CH_2CH{=}CH(CH_2)_8SR + 2NaI + 2H_2O$$

where R designates the phenylamyl group in the above example of procedure. Other illustrative groups at the R positions are n-amyl, n-propyl, isopropyl, n-octyl, phenylpropyl.

The products were found to have high retention factors.

Di-phenylamyl thio-ether of ricinoleyl alcohol (Example XXXVI) has a surface tension of 34.03; a viscosity at 68° F. of 46.29 centistokes, at 100° F. of 22.57 centistokes; and behaves (compare Tables IV and IV–A) as follows:

TABLE IX

(Ladies' wrist watches, Grade A)

Lubricant	Atmosphere, dry		Atmosphere, 60% R.H.		Humidity Effect	
	1 hr.	24 hrs.	1 hr.	24 hrs.	1 hr.	24 hrs.
Example XXXVI	1.36	1.21	1.30	1.16	0.06	0.05
(Ladies' wrist watches, Grade B)						
Example XXXVI	1.45	1.30	1.34	1.24	0.11	0.06

The following are illustrative of the behavior of thio-ethers during low temperature tests:

TABLE X

Low temperature watch tests on thio-ethers of ricinoleyl alcohol

Lubricant	Motion at Indicated Temperatures (F.)							
	+75	0	−35	−50	−65	−75	−85	−95
Example XXXVII–*a*	1.35	1.36	1.34	1.29	1.23	-----	-----	-----
Example XXXVII–*b*	1.40	1.43	1.43	1.34	1.24	1.08	0.91	0.66
Example XXXVI	1.43	1.28	0.79	0.21	-----	-----	-----	-----
Example XXXIII	1.50	1.36	1.34	1.29	1.23	-----	-----	-----

Examples XXXVII–*a* and XXXVII–*b* were successive cuts in vacuum distillation, with water vapor carrier, during the purification of di-n-propyl thio-ether of ricinoleyl

alcohol under Preparation E above; Example XXXVII-*a* being the condensate from the boiling range of 114–164° C. at the pressure of 1.0 to 0.9 mm.; and Example XXXVII-*b* the condensate at 164–171° C. at 0.9 to 0.4 mm. Example XXXIII was the di-n-octyl thio-ether of ricinoleyl alcohol, made as in Preparation E above.

The effect of lubricants, under low temperature conditions, upon the rate of watches, can be illustrated as follows, in which the individual variations of each of ten watches (large, grade D) are stated by values representing the gain (plus sign) or loss (minus sign) in seconds during a 5 hour period beginning 3 hours after winding, the values being compared by translation to an 0 rate at plus 75° F.

TABLE XI

Comparison of low temperature lubricants

Lubricant	Temperature, ° F.					
	+75	0	−35	−50	−65	−75
A commercial low temp. oil C	+4.3	−15.6(9)	−523(2)	Stop	Stop	Stop
A commercial low temp. oil L	+7.7(9)	−4.3(9)	−28.8	−114.7(7)	−444.1(7)	(2)
Example XXXIX	+9.8	−7.8	−14.4	−25.6	−94.4	−220.0(9)
Example XXXVII-*b*	+5.8	−5.4(9)	−13.0	−27.0	−57.7(9)	−127.7(9)

In the above table, the numerals in parentheses indicate the number of movements still running at the end of the respective test: e.g. the entry "−523(2)" for lubricant C at −35° F. shows the average of two movements which were still running but having lost 396 and 650 seconds during the 5 hour test. "Stop" indicates that all ten movements had stopped before the end of the test. It is noteworthy that in some instances, one or more movements would stop during test at one temperature, but would operate to the end of test at a lower temperature. Example XXXIX was di-n-amyl thio-ether of RA prepared in two batches without water vapor-vacuum distillation; blended and then subjected to water vapor-vacuum distillation.

It has been pointed out that the di-n-amyl thio-ether of ricinoleyl alcohol has very desirable lubricating characteristics for low temperature applications. It has also been found that when blended with other materials, it imparts many desirable characteristics to them. For example, when used to replace phenylstearyl alcohol in a presently used synthesized watch oil it increases the average motion of the watches and reduces considerably the effect of changes in relative humidity on the motion of the watch. Another change of importance is a reduction of viscosity without unduly decreasing the surface tension (this latter effect is important because of its relation to retention in jewel bearings which controls the interval between necessary servicing). A comparison of these lubricants is given in the attached Tables IV to IV-C for two grades of watch movements. Lubricating compositions are included in these tables.

Mixtures of other thio-ethers are likewise satisfactory.

PREPARATION G.—OXY-ETHERS FROM IODO COMPOUNDS

The 1,12-diiodooctadecene-9 from Preparation B may also be used in making oxy ethers. An equivalent weight of sodium hydroxide is dissolved in the smallest possible quantity of water, diluting with a primary alcohol such as methanol, and then adding an equivalent weight of the alcohol, such as n-amyl alcohol, which is to provide the other ether group. The dihalide from Preparation B is then added to the alcoholic solution with stirring: and the mixture refluxed for six hours and allowed to cool and settle. The aqueous layer is discarded. The oil layer is diluted with a solvent such as di-butyl ether, washed with 5% sodium hydroxide solution, neutralized, dried and stripped of solvent, and purified by vacuum distillation.

In Preparations E, F and G, other di-thio or di-oxy ethers can be prepared by substituting equivalent weights of the corresponding mercaptans or alcohols for the n-amyl mercaptan or alcohol. Similarly the yield is high in mono-ethers when the mercaptan or alcohol is present in half the quantity. Also, mixed ethers may be formed by using mixtures (e.g. in equal amounts by equivalent weights, with the total amount equivalent in SH or OH content to that of the mercaptan or alcohol in Preparations E, F and G); noting that a usual product may comprise both di-ethers (of alcohols or mercaptans R and R') and both di-mixed ethers (with R or R' at the terminal and R' and R at the intermediate coupling), along with one or more of the four mono-ethers; however, when the diiodo component is in defficiency below equivalency by the reaction equations, the essential absence of OH upon infra red study indicates that little mono-ether is present.

PREPARATION H.—RICINOLEYL MONO-THIO-ETHERS

The above procedures for the making of di-thio-ethers can be employed in making the mono-thio-ethers by employing about one-half the equivalent amount of the radical (in mercaptan form) which is to be joined with the ricinoleyl radical: wherewith the caustic hydroxide acts as before to cause coupling of the radical in the mercaptan at one halide position in the ricinoleyl compound from Preparation B, and to effect hydrolysis at the other halide position.

In this preparation, and in Preparation D above, when the quantity of the additive alcohol (or mercaptan) is less than the equivalent to one of the hologen groups of the ricinoleyl compound, and a slight excess of the caustic alkali is present, the product contains little or no di-ether, but usually includes re-converted ricinoleyl alcohol (or mercaptan). When the relative quantity is greater, di-ether is formed, and reconverted ricinoleyl alcohol (or mercaptan) is essentially absent.

PREPARATION I.—RICINOLEYL DI-MIXED ETHERS

When Preparations D and H are prepared, the ether reaction yields two mono-ethers; and if the quantity of caustic alkali is restricted, the ricinoleyl radical retains the other halogen. These mono-ethers may be converted to mixed di-ethers having differing groups attached by ether linkage to the ricinoleyl radical, by repeating the operation with an equivalent amount of the second alcohol (or mercaptan) to be employed in the etherification. Similarly, mixed ethers may be prepared in which one of the additive groups is connected through oxygen and the other is connected through sulfur, by employing first one and then the other of the desired additive radicals in respectively alcohol or mercaptan form.

A present government specification for performance is that the movement will not gain or lose more than 75 seconds at minus 31 degrees F. in 5 hours, compared to its rate at room temperature. Table XI indicates that present materials satisfy such a requirement. In a further series of tests with a group of clocks, which have been run at various low temperatures from time to time over periods of months, with the lubricant of Example XXI (a first batch), it was found that at the beginning some 60% of the clocks remained within the

75 seconds tolerance upon tests at minus 65 degrees F.; but after 16 weeks only 30% passed this test. Upon continuing the tests at minus 50 degrees F., 75% met the 75 seconds tolerance; and after many months, 43% were still within the tolerance at minus 50 degrees F.

In a further series of tests upon the lubricant of Example XXI (di-n-amyl thio-ether of ricinoleyl alcohol), employing this as the sole component (Example XXI), with added oiliness agent (Example XXXV) and with both oiliness agent and a surface tension-increasing agent (Example XXXV-*a*: being Example XXXV with 0.2% of dodecyl piperidine stearate), and with a refined blend (Example XXXIX); and noting the number of watches which stopped (out of the ten movements being investigated; 17 jewels, stem-up position), the results were:

TABLE XII

No. of stoppers in 10 movements of grade 616, 16s, 17 jewels, stem-up position

Temp., ° F.	Example XXI	Example XXXV	Example XXXV-*a*	Example XXXIX
+75	0	0	0	0
−50	0	1	0	0
−65	0	1	0	0
−75	0	1	1	0
−85	1	3	2	0
−100	10	3	4	1

In another test, the movements of Table XII were operated for many months with the indicated lubricants; and were periodically run at the low temperatures indicated. The group was continued on such test as long as the motion was ¾ turn or above. They were fitted with dials and hands, and rated at the various temperatures. No attempt was made to regulate the movements to accuracy at room temperature prior to the test; but the tabulated values have been translated so that each watch is considered at zero rate at room temperature (plus 75 degrees F.). This test is severe, as minus 65 degrees F. is the lowest temperature presently on tentative specification by the Armed Forces. The results in Table XIII show the results for the ten movements, the numerical values in the columns under the examples showing the number of movements which perform with a change in time rate from the actual room temperature rate of less than 75 seconds over a 5 hour period at the stated temperature. Since all four examples of lubricants had the same base, the results of all four have been indicated in a summation column. The values as found were:

TABLE XIII

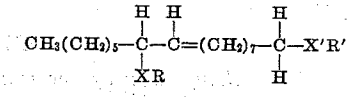
No. of movements whose change in time is less than 75 seconds from the room temperature rate over a 5 hour period

Test Temp., ° F.	Number of movements out of 10 within specification				
	Example XXI	Example XXXV	Example XXXV-*a*	Example XXXIX	Summation
+75	10	10	10	10	40
−50	10	9	10	10	39
−65	10	9	9	10	38
−75	10	9	9	10	38
−85	0	5	6	10	21
−100	0	3	2	0	5

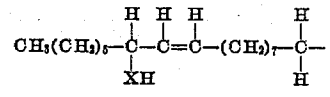
In the foregoing description, the word "ether" has been employed as generically including the oxy-ethers and the thio-ethers.

In the materials used for lubrication, the lubricant according to this invention is provided by a compound containing the ricinoleyl radical combined with radicals selected from the class consisting of hydroxyl, hydrosulfyl, oxy-ether radicals and thio-ether radicals. Preferably, the ricinoleyl radicals are present in the trans isomer form to an extent which exhibits at least a one-fifth reduction of the infrared band intensity for the corresponding compound containing only the cis isomer. Lubricating compositions may consist of such a lubricant, possibly with inclusion of another lubricant such as diphenyl heneicosanone, phenylstearyl alcohol, etc.: and may also comprise an anti-oxidant.

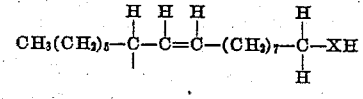
The compounds according to this invention consist of ethers of the general formula:



wherein at least one of the R and R′ radicals is selected from a member of the class consisting of straight and branched saturated aliphatic hydrocarbon chains of 1 to 18 carbons, the phenyl radical, the



radical, the



radical, and aralkyl hydrocarbon radicals of 7 to 18 carbon atoms and the second of the R and R′ radicals from a member of the class consisting of hydrogen, the radicals of straight and branched saturated aliphatic hydrocarbon chains of 1 to 18 carbon atoms, the phenyl radical, and aralkyl hydrocarbon radicals of 7 to 18 carbon atoms, and wherein X and X′ of the above formulas is a member of the class consisting of oxygen and sulfur.

Illustrative of ricinoleyl compounds which may be employed per se or in admixture with the foregoing ethers as a lubricant, is ricinoleyl formal. To prepare this compound, 100 grams of dried ricinoleyl alcohol, 5.3 grams of paraformaldehyde, and 1 gram of p-toluene sulfuric acid are mixed in 500 cc. of toluene and heated with reflux for 2 hours. The solvent is removed by distillation, and then the formal recovered by distillation under increasing reduced pressure. In one preparation, four cuts were separated as follows:

TABLE XIV

Cut No.	Boiling Range, ° C.	Pressure Num. Hg	Volume (ml.)	Weight (gms.)
1	26.5–156	9.5–5.0	15	10.7
2	152 –136	5.0	10	8.5
3	170 –144	5.0	10	10.0
4	140 –159	5.0	18	16.9

The residue was very gummy. Infra-red spectral tests showed strong bands for hydroxyl, ether, and C=C; with unexplained matter represented by terminal

$$CH{=}CH_2$$

grouping rather than a cis or trans —CH=CH— grouping.

The lubricating effects of the compound per se in watch tests are as follows:

TABLE XV

Watch tests on ricinoleyl formal

Test No.	Cut #1		Cut #2		Cut #3		Cut #4	
	1 hr.	24 hrs.	1 hr.	24 hrs.	1 hr.	24 hrs.	1 hr.	24 hrs.
A	1.435	1.34	1.50	1.40	1.52	1.40	1.435	1.40
B	1.35	1.23	1.37	1.24	1.27	1.12	1.27	1.18
C	1.16	1.13	1.26	1.12	1.12	1.08	1.14	1.08
D	−0.19	−0.10	−0.11	−0.12	−0.15	−0.04	−0.13	−0.10
E	1.26	1.14	1.27	1.17	1.26	1.12	1.27	1.16
F	1.16	1.11	1.22	1.14	1.18	1.11	1.17	1.10
G	−0.10	−0.03	−0.05	−0.03	−0.08	−0.01	−0.10	−0.06
	(10 movements)		(4 movements)		(4 movements)		(4 movements)	
H	1.41		1.34		1.25		1.34	
I	0.62		0.62		0.40		0.28 (1)	
J	0.22							
K			0.06				0.125	
L								

Test A states the average motion of 4 movements of grade E.

Test B states the average motion of 10 movements of grade F in a dry atmosphere; test C states the average motion of the same in a wet atmosphere; test D states the humidity effect as the difference of the values for tests B and C.

Test E states the average motion of 10 movements of grade G in a dry atmosphere; test F states the average motion of the same in a wet atmosphere; test G states the humidity effect as the difference of the values for tests E and F.

Test H states the average motion of the stated number of movements of grade E at room temperature; tests I, J, K, L are of the same, respectively at 0° F., minus 25° F., minus 35° F., and minus 50° F. In Test I, (1) indicates that one movement stopped.

Blends of this compound with the above ethers form satisfactory lubricants at the 50:50 ratios and have essentially the behavior of the ether itself, and operate like the blends of the ethers with diphenylheneicosanone referred to in connection with Tables IV to IV–C above.

The foregoing statements of practice are illustrative; and it will be understood that the invention may be practiced in other ways, within the scope of the appended claims.

What is claimed is:

1. A lubricant consisting of di-n-amyl thio-ether of ricinoleyl alcohol.

2. A lubricant consisting of di-n-amyl thio-ether of ricinoleyl alcohol, and characterized by having ricinoleyl radicals in trans isomer form in an amount represented by a dip of at least one-fifth in the standard infra-red graph.

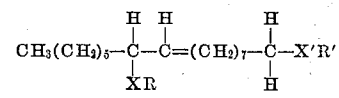
3. A lubricant consisting of di-phenylamyl thio-ether of ricinoleyl alcohol.

4. The method of preparing a lubricant, which comprises subjecting ricinoleyl alcohol to an ether-forming reaction and thereby coupling the ricinoleyl radical through an element selected from the group consisting of oxygen and sulfur to another radical selected from the group consisting of hydrocarbon radicals of 1 to 18 carbon atoms, terminating the reaction before completion, and recovering a product containing ricinoleyl alcohol and with at least five percent of at least one ether of ricinoleyl alcohol selected from the group consisting of the oxy and thio ethers thereof.

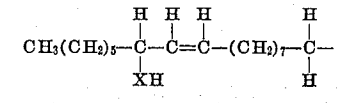
5. A lubricant made as in claim 4.

6. A lubricant consisting of ricinoleyl alcohol and an ether, said ether constituting at least 5 percent by weight

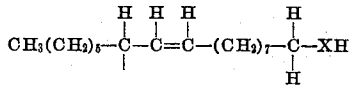
of the mixture of alcohol and ether, said ether being selected from the compounds of the general formula:



wherein at least one of the R and R′ radicals is selected from a member of the class consisting of straight and branched saturated aliphatic hydrocarbon chains of 1 to 18 carbons, the phenyl radical, the

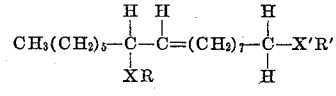


radical, the

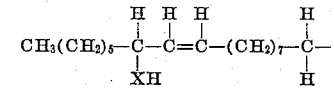


radical, and aralkyl hydrocarbon radicals of 7 to 18 carbon atoms and the second of the R and R′ radicals from a member of the class consisting of hydrogen, the radicals of straight and branched saturated aliphatic hydrocarbon chains of 1 to 18 carbon atoms, the phenyl radical, and aralkyl hydrocarbon radicals of 7 to 18 carbon atoms, and wherein X and X′ of the above formulas is a member of the class consisting of oxygen and sulfur.

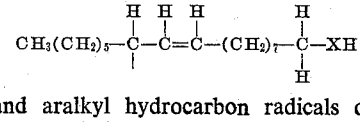
7. A lubricant consisting of an ether compound of the general formula:



wherein at least one of the R and R′ radicals is selected from a member of the class consisting of straight and branched saturated aliphatic hydrocarbon chains of 1 to 18 carbons, the phenyl radical, the



radical, the



radical, and aralkyl hydrocarbon radicals of 7 to 18 carbon atoms and the second of the R and R′ radicals from a member of the class consisting of hydrogen, the radicals of straight and branched saturated aliphatic hydrocarbon chains of 1 to 18 carbon atoms, the phenyl radical, and aralkyl hydrocarbon radicals of 7 to 18 carbon atoms, and wherein X and X′ of the above formulas is a member of the class consisting of oxygen and sulfur.

8. A lubricant consisting of a di-ether of the general formula set out in claim 7.

9. A lubricant consisting of a mono-ether of the general formula set out in claim 7.

10. A lubricant consisting of a mixed ether of the general formula set out in claim 7, in which the R and R′ radicals are different.

11. A lubricant consisting of a mixture of different ethers each of which has the general formula set out in claim 7.

12. A lubricant consisting of an ether of the general formula set out in claim 7, in which one of the radicals R and R′ is an aralkyl hydrocarbon radical of 7 to 18 carbon atoms.

13. A lubricant consisting of an ether of the general formula set out in claim 7, in which one of the radicals R and R′ is a hydrocarbon radical of 1 to 18 carbon atoms.

14. A lubricant consisting of a mixture of 20 to 50 parts by weight of an ether, and 80 to 50 parts by weight of diphenylheneicosanone, totalling 100 parts by weight, said ether being of the general formula set out in claim 7.

15. A lubricant consisting of an ether with 0.1 to 1.5 percent by weight of an antioxidant, said ether being of the general formula set out in claim 7.

16. A lubricant consisting of an ether of the general formula set out in claim 7, in which the trans-isomer form is present in an amount represented by a dip of at least one-fifth in the standard infra-red graph.

17. A lubricant consisting of an ether of the general formula set out in claim 7, in which X and X' are oxygen atoms.

18. A lubricant consisting of an ether of the general formula set out in claim 7, in which X and X' are sulfur atoms.

19. The method of lubrication between two relatively movable bearing surfaces, which comprises applying to

at least one of said surfaces an ether having the general formula set out in claim 7, and maintaining a film of said ether between said surfaces during relative movements thereof.

20. The method as in claim 19, in which one of said radicals R and R' is an aralkyl hydrocarbon radical of 7 to 18 carbon atoms including an aryl hydrocarbon terminal group.

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