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WATER RESISTING GREASE

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This invention relates to the preparation of water-resistant lubricating greases.

Lubricating greases are, generally speaking, semi-solid solutions or dispersions of soaps of alkali, alkaline earth or heavy metals in mineral oil. A great number of modifying materials are being added to greases to impart certain desired service characteristics such as preferential wetting, rustproofing, load carrying ability, water resistance, high temperature stability, structure stability, etc. At the present instance, we are chiefly concerned with the means of rendering greases water resistant. The importance of this feature is clear from the fact that grease-lubricated machine parts are encountered in port installations, on deck of navy and marine vessels, in steel rolling mills, in water pumps of all kinds, in mining machinery, in oil-well drilling equipment, all of which depend, in their operation, on the ability of the grease charge to resist the action of water, salt or fresh, in the form of spray or waves (sea), pressure water stream (steel rolling mills and oil well drilling), moisture seepage and condensation (underground) etc. Under the action of water, a grease containing water soluble soap, may swell and thin out into a liquid which leaks out from the bearing. Other greases may be lost from the lubricated surfaces mechanically because of impact of the water stream and poor cohesion of the grease particles. In either case, lubricant starvation, with all its consequences will result as only exceptional installations are equipped with constant-feed central greasing systems; common practice is to charge the bearing with as much grease as it holds and repack it at rare intervals.

The problem of rendering greases waterproof is a more general one than it may seem at first thought. It is true that some greases, e. g., lime base and lithium base are inherently water resistant; so, it may appear that they do not need any improvement in this respect. Unfortunately, the commonly used rustproofing additives for greases, such as mineral oil sulfonates, ruin the water-resisting characteristics and degrade the formerly satisfactory product to a grease which absorbs water; hence, waterproofing is needed not only for soda-base and similar greases which are emulsifiable in water by virtue of their major components, but also for originally water-resistant greases the waterproofness of which has been affected by modifying materials, e. g., rustproofers and E. P. additives.

Among the prior art waterproofing agents known to the inventors, the major are calcium stearate, zinc hydroxystearate, and zinc naphthenate.

It has been discovered that resinates of zinc, cadmium, magnesium and calcium added to a grease in amounts from 0.5% to 3.0% impart

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water-resisting properties to the products to a remarkable degree.

The materials designated herein as metal resinates are the salts of divalent metals of group II of the periodic table and naturally occurring rosin acids, such as abietic, pimaric, sapinic, sylvic, and various mixtures thereof, derived from the various grades of gum rosin or of wood rosin. These acids may be used as they occur naturally or may be polymerized or hydrogenated.

Numerous examples demonstrating the efficiency of resinates as waterproofers are given in the following tables. As a basis of judgment, we have selected the best available tests for water resistance, namely that of the naval ordnance, known as the water absorption test, and the army-navy water resistance test, which is commonly called the wash test.

The former has been designed to determine the amount of water which can be worked into a sample of grease to saturation, and to observe the change in consistency of the grease caused by the absorbed water. Greases absorbing not more than 50% water and showing an increase of worked penetration not more than about 40 points have been considered waterproof. In view of the very small amount of sample used in this test (the original charge is 20 grams) actual determinations of penetration cannot be made in accordance with the A. S. T. M. procedure. While an arbitrary micro-penetration test could be developed for such applications, it has been common practice to go by visual inspection of the hydrated sample rejecting the liquefied and greatly softened products and approving those which have softened only slightly.

The "wash test" has been developed to determine the percent loss of grease from a ball bearing rotated at 600 R. P. M. and subjected to the washing action of a stream of water. A loss of grease not more than 50% by weight has been considered satisfactory.

More detailed descriptions of these tests follow.

Water absorption test (from Specification OS-1350-C dated June 22, 1945, and covering "Grease especially developed for low temperature and antirust properties, to be used in lubrication of ordnance equipment"):

This test is made in the navy water absorption apparatus which consists of a cup 2¾" dia. x 1½" high and a ¾" dia. upright electric stirrer actuated by a 1200 R. P. M. motor. A 20 gram sample of grease is placed in the cup and one milliliter (5%) additions of water are worked into the grease for 2 minutes. If there is no evidence of free water at the expiration of the 2 minute period, an additional one ml. of water is added and the grease is again worked for 2 minutes. This operation is repeated until free

water is evident. The final reading is made when the water cannot be worked in the grease after a total of 5 minutes.

Water resistance test (from Specification AN-G-5a dated Oct. 4, 1944, and covering "Grease, high temperature, lubricating"):

A No. 204 ballbearing shall be packed with 4 grams of grease and clamped in a tight fitting housing which allows the inner race to turn freely, mounted on a horizontal shaft, and rotated at 600 R. P. M. A fine stream of distilled water, circulating at the rate of 5 milliliters per second, shall be directed against the end plate of the housing from a one mm. capillary connected to a pump taking suction from the reservoir of water under the bearing so that it impinges on the end plate one-quarter of an inch above the outer opening of the bearing housing. Operation shall be continued for one hour when the bearing shall be removed, dried at 82° C. and reweighed to determine the grease loss. This grease loss divided by the weight of the grease used in packing the bearing shall be reported as the percent grease loss.

TABLE I

Waterproofing of soda-base greases

Example	1	2	3	4	5
Composition					
12-hydroxy stearic acid per cent	12.60	12.60	12.60	7.00	12.00
Stearic Acid do	2.40	2.40	2.40	7.00	none
Sodium hydroxide do	2.20	2.20	2.20	2.00	1.80
Mineral Oil 150″ @ 100° F. SUV per cent	81.80	81.05	81.55	82.00	85.70
Oxidation Inhibitor do	1.00	1.00	1.00	none	none
Zinc resinate do	none	0.75	none	2.00	0.50
Cadmium resinate do	none	none	0.25	none	none
Properties of Grease					
Worked Penetration	270	280	285	280	240
Loss in water wash test per cent	80	20	50	25	25

A comparison of Examples 2, 4 and 5 with Example 1 shows the efficiency of the zinc resinate, while the comparison of Example 3 with Example 1 demonstrates the efficiency of the cadmium resinate.

TABLE II

Waterproofing of lithium-base greases

Example	6	7	8	9	10	11	12	13	14	15
Composition										
Lithium Stearate per cent	12.0	12.0	12.0	12.0	12.0	10.0	10.0	10.0	15.0	15.0.
Mineral Oil Sulfonate [1] do	1.0	1.0	1.0	1.0	1.0	1.5	1.5	1.5	1.5	1.5.
Oxidation Inhibitor do						1.0	1.0	1.0		
Zinc Resinate do					1.0		0.5			
Zinc 12-Hydroxystearate do		1.0								
Zinc Naphthenate do			1.0	3.0						
Cadmium Resinate do								0.5	0.4	
Magnesium Resinate do										0.4.
Mineral Oil, 105″ SUV @ 100° F. per cent	87.0	86.0	86.0	84.0	86.0					
Mineral Oil, 280″ SUV @ 100° F. per cent						87.5	87.0	87.0		
Mineral Oil, 150″ SUV @ 100° F. per cent									83.1	83.1.
Properties of Grease										
Worked Penetration	250	245	245	260	240	283	290	280	225	235.
Water Absorption per cent	100+	25	50	25	25	100+	40	70	40	55.
Consistency of Hydrated Grease	very fluid.	slightly softer than original.	a little softer than original.	somewhat softer than original.	slightly softer than original.	fluid.	softened only slightly.	softened but retained grease structure.	slightly softer.	a little softer.

[1] Commercial product containing 3–5% H_2O, 40% oil and 55% sodium sulfonates.

The efficiency of zinc resinate is shown by Examples 10 and 12 in comparison with Examples 6 and 11, respectively. The improvement in Example 13 over Example 11 is due to the cadmium resinate, while Example 15 illustrates the waterproofing effect of magnesium resinate. Examples 7, 8 and 9 refer to waterproofing additives of prior art.

TABLE III

Waterproofing of mixed Na-Li base greases

Example	16	17	18	19	20	21	22	23
Composition								
Li Stearate percent	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0.
Na Stearate do	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0.
Hydrogenated fish oil fatty acids per cent				0.5	0.5	0.5	0.50	0.50.
Oxidation Inhibitor [1] do				1.0	1.0	1.0	1.00	1.00.
Mineral Oil 150″ SUV @ 100° F per cent	84.0	83.6	83.6	81.0	82.0	81.5	80.75	80.75.
Mineral Oil Sulfonate [2] do				1.5			1.50	1.50.
Cd resinate do		0.4					0.25	
Mg resinate do			0.4					0.25.
Zn resinate do						0.5		
Al Stearate do					0.5	0.5		
Properties of Grease								
Worked Penetration	265	220	220	267	260	280	255	270.
Water Absorption percent	90	30	50	100+	100+	25	80	90.
Consistency of Hydrated grease	very fluid	slightly softer than original.	a little softer than original.	very fluid	fluid	only slight softening.	very soft	nearly fluid.

[1] Oxidation inhibitor, an amine.

[2] Commercial product, same as in Table II.

Examples 17 and 18 show the waterproofing action of Cd and Mg resinates on a grease (Example 16) possessing some water resistance. Example 20 shows that Grease of Example 19 is not improved by the addition of Al stearate, but the same grease is improved by further addition of Zn resinate (Example 21). Small additions of Cd and Mg resinates (Examples 22 and 23) also show improvement over the blank, Example 19.

TABLE IV

Waterproofing of aluminum base greases

Example	24	25	26
Composition			
Al stearate, per cent	12.0	12.0	12.0.
Mineral Oil Sulfonate [1] do		1.0	1.0.
Mineral Oil 105" SUV @ 100° F. per cent	88.0	87.0	86.0.
Mg resinate do			1.0.
Properties of Greases			
Worked Penetration	250	253	245.
Water Absorption, per cent	45	100+	40.
Consistency of hydrated grease	slightly softened.	fluid	slightly softened.

[1] Commercial product, same as in Table II.

The above examples show that the water resisting characteristics of an aluminum grease have been ruined by the addition of the rust-proofer (mineral oil sulfonates) and restored to the original value by further addition of Mg resinate.

TABLE V

Waterproofing of lime-base greases

Example	27	28	29	30
Composition				
Ca-tallow soap, percent	15.0	15.0	15.0	15.0.
Water do	2.0	2.0	2.0	2.0.
Mineral Oil, 105" SUV @ 100° F. do	83.0	82.0	81.0	81.0.
Mineral oil sulfonate [1] do		1.0	1.0	1.0.
Zn resinate do			1.0	
Ca resinate do				1.0.
Properties of Grease				
Worked Penetration	250	255	257	252.
Water Absorption, percent	10	100+	90	55.
Consistency of hydrated grease	nearly same as original.	very fluid.	softened but retained grease structure.	somewhat softened.

[1] Commercial product, same as in Table II.

The above series of experimental greases demonstrates the adverse effect of mineral oil sulfonates on the water resistance of a lime base grease (Example 28 vs. Example 27) and the partial restoration of the water resistance by the addition of Zn and Ca resinates (Examples 29 and 30).

In general, these improvements may be gotten by using the resinates of divalent metals of the second group of the periodic table in amounts comprising from about 0.2% to about 6.0% by weight of the finished grease. Preference is had for the resinates of zinc, cadmium, calcium and magnesium in amounts ranging from about 0.5% to about 3.0% by weight of the finished grease. As to the resinates themselves, the metal content thereof should not deviate more than about 50% above or below the stoichiometric ratio.

The incorporation of the metal resinates gives rise to no problem, since they may be added either to the oil component of the grease prior to the cooking stage, or they may be added at any intermediate stage of manufacture or to the finished grease.

We claim:

1. A grease composition of increased water resistivity comprising a major proportion of a mineral lubricating oil, from about 10% to about 30% of metal soaps of fatty acids, sufficient to impart the desired grease body, and in addition thereto a small amount from about 0.2% to about 6.0% by weight of a resinate of a divalent metal selected from the group consisting of zinc, cadmium, calcium and magnesium.

2. A grease composition of increased water resistivity comprising a major proportion of a mineral lubricating oil, from about 10% to about 30% of metal soaps of fatty acids, sufficient to impart the desired grease body, and in addition thereto a small amount from about 0.5% to about 3.0% by weight of a resinate of a divalent metal, selected from the group consisting of zinc, cadmium, calcium and magnesium.

3. A grease composition of increased water resistivity comprising a major proportion of a mineral lubricating oil, from about 10% to about 30% of metal soaps of fatty acids, sufficient to impart the desired grease body, and in addition thereto a small amount, from about 0.2% to about 6.0% by weight of zinc resinate.

4. A grease composition of increased water resistivity comprising a major proportion of a mineral lubricating oil, from about 10% to about 30% of metal soaps of fatty acids, sufficient to impart the desired grease body, and in addition thereto a small amount, from about 0.5% to about 3.0% by weight of zinc resinate.

5. A grease composition of increased water resistivity comprising a major proportion of a mineral lubricating oil, from about 10% to about 30% of metal soaps of fatty acids, sufficient to impart the desired grease body, and in addition thereto a small amount, from about 0.5% to about 3.0% by weight of cadmium resinate.

6. A grease composition of increased water resistivity comprising a major proportion of a mineral lubricating oil, from about 10% to about 30% of metal soaps of fatty acids, sufficient to impart the desired grease body, and in addition thereto a small amount, from about 0.5% to about 3.0% by weight af magnesium resinate.

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(References on following page)

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,780,315	Schmidt	Nov. 4, 1930
2,111,907	Zimmer et al.	Mar. 22, 1938
2,394,790	Liehe	Feb. 12, 1946
2,398,075	Brunstrum et al.	Apr. 9, 1946
2,399,063	Schantz	Apr. 23, 1946
2,409,950	Meyer	Oct. 22, 1946
2,417,264	Morway et al.	Mar. 11, 1947

FOREIGN PATENTS

Number	Country	Date
14,383	Great Britain	1892