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SULFONATE GREASE

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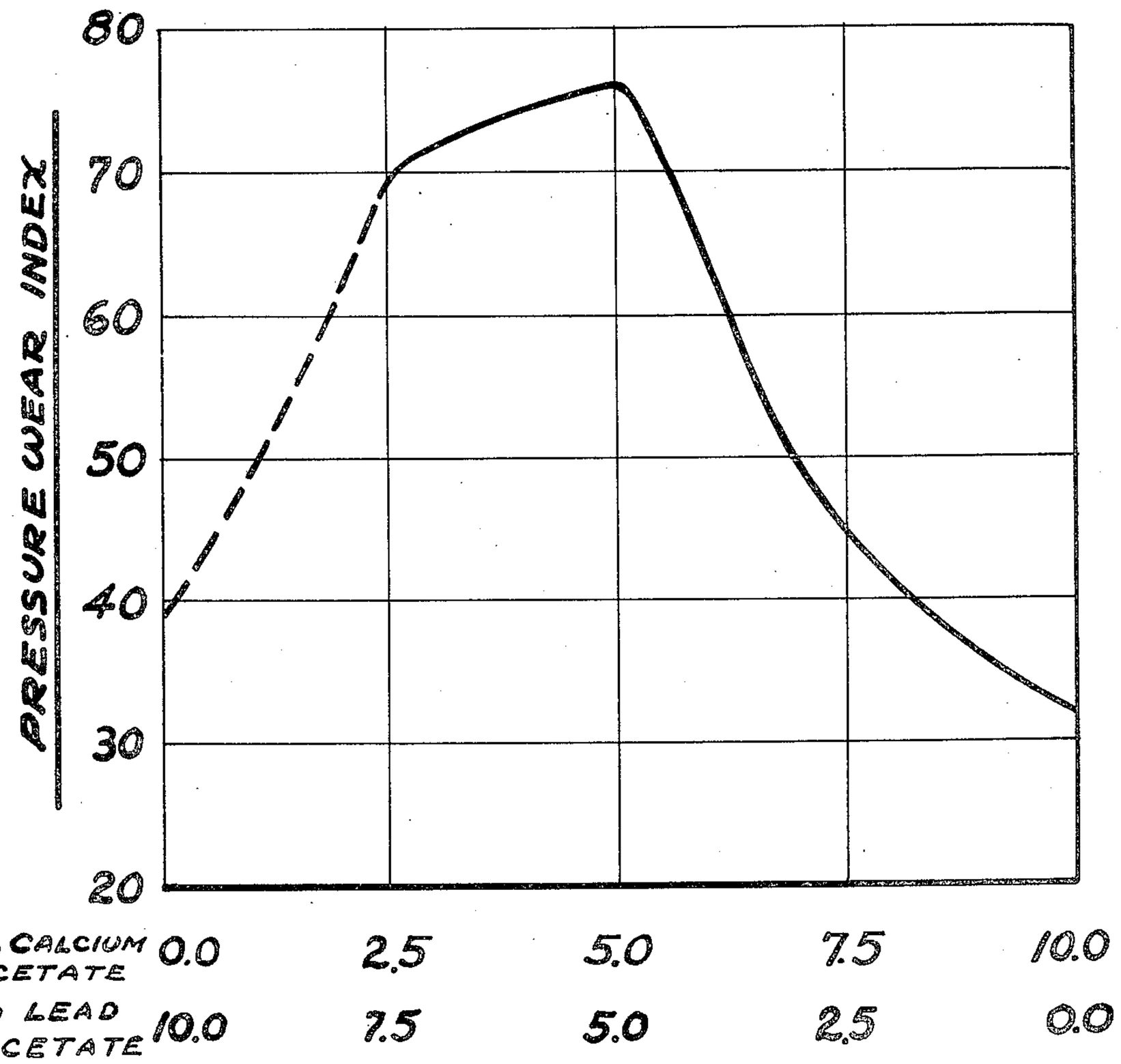

PRESSURE WEAR INDEX CURVE
FOR
CALCIUM ACETATE—LEAD ACETATE
GREASES

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SULFONATE GREASE

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This invention relates to improved sulfonate greases and more particularly to a sulfonate grease containing a mixture of the calcium and lead salts of a low molecular weight aliphatic carboxylic acid.

In the patent issued to Zimmer and Duncan, No. 2,444,970, later reissued as 23,084, it is disclosed that a superior grease composition providing lubrication both at high and low temperatures and having good structural stability may be obtained by combining with a mineral lubricating oil a so called Werner complex formed by the conversion of an oil-soluble sulfonate into an oil-soluble complex, using a water soluble salt. In this patent it is taught that a sulfonate grease combined with a metallic salt of an aliphatic carboxylic acid may be made by reacting a polyvalent metal sulfonate, such as calcium sulfonate, with a salt containing a monovalent metal, such as sodium, potassium or lithium. There is also disclosed that polyvalent metal sulfonates may be reacted with the nitrates or acetates of similar or dissimilar polyvalent metals, such as magnesium, calcium, barium, lead, tin, etc. There is also a disclosure of the fact that excess chloride ions present in the sulfonate solution used in the manufacture of a petroleum sulfonate based grease may be removed or inactivated by incorporating sufficient lead acetate with the potassium acetate used to combine all the chloride ions as insoluble lead chloride. To precipitate the maximum amount of chloride ion present in the sulfonate about 2.3% by weight of lead acetate would be needed.

It has recently been found that the presence of the calcium salt of low molecular weight acids in combination with metallic sulfonates imparts considerable extreme pressure properties to the product. This increase in the extreme pressure properties of the grease at high load pressures is apparently due to the activation of the sulfur which is present in the sulfonate. The formation of a metallic sulfide film, due to the presence of the activated sulfur, is evidenced by the black film which appears on the wear area of the testing equipment and produces an outstanding improvement in the load carrying abilities of the grease. Greases prepared from high molecular weight sulfonates and low molecular weight acid salts show extreme pressure properties superior even to those of greases which contain extreme pressure additives. It has now been found that these extreme pressure properties may be considerably enhanced by the substitution of a part of the calcium salt by a lead salt.

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In brief this invention comprises a lubricating grease composition containing a petroleum sulfonate salt in admixture with a calcium salt and a lead salt of a low molecular weight aliphatic carboxylic acid.

The oil-soluble metallic sulfonates operable in this invention may be any of the alkaline earth metallic sulfonates such as calcium, barium, or strontium sulfonate and may be prepared by any of the methods known in the art. It is preferred that the molecular weights of the sulfonic acids be in the range of from about 300 to about 600, the preferred range being a molecular weight of from 350 to 500. The amount of the sulfonate present in the finished grease may range from between about 0.5% by weight for soft greases up to about 50% by weight in the extremely hard greases. However, a range of from 5 to 20% by weight is preferred. The low molecular weight carboxylic acid which may be reacted with the calcium or lead to form the calcium or lead salt may be acetic acid, oxalic acid, proprionic acid, or lactic acid. Of these acetic acid is the one preferred. The sum total of the mixture of the calcium and lead salts of the low molecular weight acid is 10% by weight of which total 2.5% to 7.5% by weight should be the lead salt.

A series of four greases showing satisfactory structures were obtained by combining with a petroleum sulfonate salt various percentages of lead and calcium acetate, as a thickening media. Satisfactory greases were obtained using three parts of lead acetate to one part of calcium acetate, using one part of lead acetate to one part of calcium acetate, and when using three parts of calcium acetate to one part of lead acetate. However, when using lead acetate without admixing calcium acetate, a resinous precipitate which separated from the oil was formed.

The greases formed by combining lead acetate and calcium acetate were better in appearance, being almost transparent, than with the greases prepared using calcium acetate alone. The mixture of calcium and lead acetate greases possess better B. E. C. test properties. The B. E. C. test consists of rotating a semi-shielded bearing on a vertical shaft for 20 minutes at 3500 R. P. M. The results being expressed as the percent of the original 3 gram charge lost from the bearing.

The method of manufacture of these greases and the general test and inspection results are as follows:

FORMULATION

20% of a 50% concentrate of the strontium salt of a 450 molecular weight petroleum sulfonic acid was dissolved in an acid treated coastal distillate, having a 55 SUS viscosity @ 210° F., at a temperature of about 150° F. A 20% aqueous solution of calcium acetate in sufficient quantity to introduce the desired amount of calcium acetate was added and the batch partially dehydrated at 200° F. The lead acetate was then added as a 30% solution. After the addition of the lead acetate solution the batch was then dehydrated at 240° F. and placed in an oven at 300° F. for 2–3 hours to finish the dehydration.

TABLE I

Sulfonate greases

Composition, Per Cent by Weight			Appearance	B. E. C. Test at 200° F. Per Cent Loss
Strontium Sulfonate 450 Mol. Wt.	$CaAc_2$	$PbAc_2$		
10	--------	10	Resinous ppt. separated from oil	----------
10	2.5	7.5	Almost transparent	7
10	5	5	----do	3
10	7.5	2.5	Semi-opaque	17
10	10	--------	Opaque	20

As was stated above it has recently been found that the presence of the calcium salt of low molecular weight acids in combination with the metal salts of petroleum sulfonic acids in lubricating grease compositions imparts considerable extreme pressure properties to the product. This very desirable result is believed to be due to the activation of the sulfur of the sulfonate to form a metallic sulfide film which acts as a boundary lubricant on the bearing surfaces under conditions of high load. In accordance with the present invention the substitution of a lead salt for a portion of the calcium salt considerably enhances these extreme pressure properties.

With the increase in industrial bearings having extremely small clearances and bearing increasingly heavier loads, it has become necessary to develop lubricants which are capable of withstanding these more stringent work conditions. The development of these lubricants has necessitated a method of measuring in the laboratory their behavior under extreme conditions of high pressure and high rubbing speeds. Metal to metal contact between heavily loaded gears running at high speeds often results in the welding together of microscopic areas of the contacting surface. The tearing apart of such welded points roughens the gear surface and leads to more generation of heat, further welding and tearing of the surface, and possible seizure.

The damage done to a metal surface by continued rubbing after scoring or seizure has started may be either large or small depending on the ability of the lubricant to aid in quickly repolishing a damaged area. The tendency of a lubricant to minimize wear resulting from seizure is a property distinct from the ability to prevent seizure and provides a further index for evaluating extreme pressure lubricants.

In order to mechanically test in the laboratory the behavior of lubricants under extreme conditions of pressure and rubbing speeds, there has been developed a testing machine known as the "Four-ball tester." A controlled load is placed upon one rotating ball which is supported by three stationary balls of like characteristics. The lubricant being tested surrounds the contact surface. Upon application of the load for a specific period of time under condition of load and high rubbing speeds, a wear spot appears on each of the three supporting balls. These wear spots are measured under a microscope and their diameters are functions of the extreme pressure qualities of the lubricant used.

As the pressure applied is increased on the contact surface, a point is reached at which scoring of the wear spot begins. This point is called the point of incipient seizure. Up to this point of incipient seizure, the wear spot diameter is a linear function of the load applied. As the pressure or load is increased, a point is reached at which immediate seizure occurs followed by a breaking away of the seizure. Between the points of incipient seizure and immediate seizure the extreme pressure properties of the lubricant are brought into play, that is, a good lubricant will restrict the area of seizure to the minimum and aid in repolishing the damaged area.

Using data obtained with the Four-ball tester, the Bureau of Ships have set up a pressure wear index calculation based on the data on the points of incipient and immediate seizure which is a numerical measurement of the extreme pressure properties of lubricants. In its Interim Specification 17L8 (INT) the Bureau has set forth conditions for the determination of pressure wear index. By dividing the increase in load between the point of incipient seizure and the point of immediate seizure by the difference in the squares of the wear spot diameters at the same two points a value is obtained which is directly proportional to the increase in pressure supported per unit area of the wear spot. This value is designated as the pressure wear index.

In Table II below the pressure wear indices of the greases made according to this invention and the data from which these indices were calculated are given.

TABLE II

Extreme pressure properties in 4-ball test

10% Sr. Sulfonate Grease Plus: (per cent by wt.)		Load at Incip. Seiz., Kg.	Wear Spot Diam. at Inc. Seiz., mm.	Load at Imm. Seiz., Kg.	Wear Spot Diam. at Imm. Seiz., mm.	Pres. Wear Index
$Ca(AC)_2$	$PB(AC)_2$					
0.0	10.0	------	------	------	------	------
2.5	7.5	30.0	0.38	90.0	1.02	70
5.0	5.0	35.0	0.34	110.0	1.04	76
7.5	2.5	30.0	0.38	84.0	1.16	45
10.0	0.0	30.0	0.38	110.0	1.61	32
Std. E. P. Grease (Lithium Grease plus 7.5% sulfurized sperm oils)		18.0	0.38	65.0	1.40	25
Ord. Soap Grease		35.0	0.35	45.0	1.60	4

It will be noted from an examination of this table that the pressure wear indices of the greases made according to this invention vary from 45 to 76. These values compare very favorably with the pressure wear indices of a standard extreme pressure grease which range from 15 to 25.

The single figure is a graphic illustration of the extreme pressure properties of the grease of this invention. In the figure, the pressure wear index is plotted against the grease composition. As will be seen from an examination of the figure the optimum composition is one containing equal percentages of calcium acetate and lead acetate. However, the grease containing some 2½% to

10% calcium acetate and from 7½% to 0% lead acetate have also excellent extreme pressure properties.

It will be understood that the conventional additive materials such as V. I. improvers, oxidation resisting agents, corrosion inhibitors, tackiness agents and the like, may be incorporated into the grease compositions of this invention. The invention is not limited to solid greases but is also applicable to fluid compositions which demand extreme pressure properties such as gear oils, cutting oils, drawing compounds and the like.

What is claimed is:

1. A lubricating grease composition consisting essentially of a mineral lubricating oil thickened to a grease consistency with from 5 to 20% of a strontium petroleum sulfonate formed from a sulfonic acid having a molecular weight of between 300 to 600, and about 10% by weight of a mixture of the lead and calcium salts of an acid selected from the group consisting of low molecular weight aliphatic carboxylic acids having not more than 6 carbon atoms said mixture containing from about 2.5% to 7.5% by weight of the calcium salts and from about 7.5% to 2.5% by weight of the lead salt.

2. A lubricating grease composition consisting essentially of a mineral lubricating oil thickened to a grease consistency with from 5 to 20% by weight of a strontium petroleum sulfonate formed from a sulfonic acid having a combining weight of 450 and about 10% by weight of a mixture of equal amounts of lead acetate and calcium acetate.

3. A lubricating grease composition comprising a mineral lubricating oil, from 10 to 30% by weight of an alkaline earth metal petroleum sulfonate prepared from a sulfonic acid having a combining weight of between 300 and 600 and about 10% by weight of a mixture of the lead and calcium salts of an acid selected from the group consisting of low molecular weight aliphatic carboxylic acids having not more than 6 carbon atoms said mixture containing from about 2.5% to 7.5% by weight of the calcium salts and from about 7.5% to 2.5% by weight of the lead salt.

4. A lubricating grease composition consisting essentially of a mineral lubricating oil thickened to a grease consistency with from about 5% to 20% by weight of an oil-soluble metal sulfonate, and about 10% by weight of a mixture of the lead and calcium salts of an acid selected from the class consisting of low molecular weight aliphatic carboxylic acids having not more than 6 carbon atoms, said mixture containing from 2.5 to 7.5% by weight of the calcium salt and from 7.5 to 2.5% by weight of the lead salt.

5. A lubricating grease composition comprising a mineral lubricating oil, 10% of an alkaline earth metal sulfonate, and 10% of a mixture of the lead and calcium salts of an acid selected from the group consisting of a low molecular weight aliphatic carboxylic acid having not more than 6 carbon atoms, said mixture containing from 2.5 to 7.5% by weight of the calcium salt and from 7.5 to 2.5% by weight of the lead salt.

6. A lubricating grease composition comprising 80% of a mineral lubricating oil, 10% of an alkaline earth salt of a sulfonic acid having a molecular weight of 450, 5% of calcium acetate, and 5% of lead acetate.

7. A lubricating grease composition comprising a mineral lubricating oil thickened to a grease consistency with 20% by weight of a mixture of 10% by weight of an alkaline earth metal sulfonate, prepared from a sulfonic acid with a molecular weight of from 300 to 600, with 5% by weight of a calcium acetate, and 5% by weight of lead acetate.

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REFERENCES CITED

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

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Number	Name	Date
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