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LUBRICATING OIL COMPOSITIONS AND IMPROVEMENT AGENTS THEREFOR

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This invention relates to lubricating oil compositions and improvement agents therefor, and more particularly, to improved detergent lubricating oil compositions having antioxidant properties which are capable of suspending gums, resins, carbon and varnish-like materials which are formed on the pistons and rings of internal combustion engines.

Petroleum lubricating oils, and some compounded oils, are prone to deteriorate under the conditions existing in internal combustion engines, with development of resinous products, ultimately resulting in sludging, ring sticking, and varnishing, which lower the efficiency of the motor. There is also a tendency to form so-called separable sludge, which settles in the crankcase with undesirable effects.

It is well known to incorporate various metal soaps (metallo-fatty acid compounds) as well as other additives in oils to improve the oils in these and other respects. There are difficulties in incorporating these normal soaps and in keeping them dispersed in oils in stable condition; and moreover, it often happens that a very small amount of soap produces a considerable change in the viscosity of an oil. For example, a lime soap prepared in the ordinary wet way can be dissolved in oil, but even small amounts tend to thicken the oil. The moisture present in the soap assists in the production of a colloidal soap dispersion or gel, but at the same time it results in an excessive viscosity. Such a lime soap is difficult to dehydrate and the dry soap is a hard material which is very difficult to work into mineral oils. Furthermore, in some instances, the ordinary soaps accelerate oil oxidation, thus necessitating the addition of a separate antioxidant compound to the composition.

It is an object of this invention to provide a new improvement agent for mineral lubricating oils, which will improve the detergent qualities of the oils in reducing ring sticking, carbon deposition and the formation of separable sludge without excessively increasing the viscosity of the oils, and which, at the same time, will act as an antioxidant and oiliness agent.

It is a further object of this invention to provide new detergent lubricating oil compositions having improved antioxidant and oiliness properties.

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These and other objects are achieved by the present invention wherein we provide an anhydrous, non-hygroscopic improvement agent comprising the lime saponification products of a sperm oil. Such an agent, prepared in accordance with the methods of our invention, is soluble in a wide variety of mineral lubricating oils and is effective, even in small amounts, in imparting to mineral lubricating oils improved detergent, antioxidant and oiliness properties. We consider mineral lubricating oils containing such an agent as part of our invention.

More particularly, our new improvement agent is an anhydrous, non-hygroscopic mixture of sperm oil alcohols and the calcium salts of sperm oil fatty acids, and is derived from a sperm oil by saponification thereof with lime. While we do not desire to be limited to any theory of the action of the individual components of our new improvement agent, it is our present belief that the free sperm oil acohols act to prevent the calcium salts of the sperm oil fatty acids from solidifying, thereby maintaining the agent as a whole in a fluid condition readily soluble in mineral oils. In fact, as is set forth hereinafter, it is possible to prepare stable concentrates of the agent in mineral oils which contain as much as 50 per cent by weight of the agent.

As indicated in U. S. Patent No. 2,179,066 to Smith, sperm oil is composed principally of the higher molecular weight unsaturated aliphatic monohydric alcohol esters of the higher molecular weight unsaturated fatty acids. The unsaturated character of sperm oil and its other characteristics are fully set forth in the patent. The reaction product secured by the saponification of sperm oil with lime in accordance with our invention does not have the normal characteristics of a calcium soap of an ordinary fatty acid, such as calcium oleate or calcium stearate. The reaction product is a thick liquid, and as previously stated, dissolves readily in a mineral oil without appreciably affecting the viscosity of the oil. Furthermore, the effects of the use of this material in a mineral oil are different from those secured from the addition of a corresponding amount of an ordinary calcium soap, particularly in regard to viscosity, solubility, antioxidant and oiliness effects.

Sperm oil often contains some glycerides, and since the preparation of our new improvement agent involves a saponification, any glycerides present will yield free glycerol. If the glycerol were allowed to remain in the agent, serious corrosion difficulties would be encountered in the use of lubricating oil compositions containing the agent. This is due to the facts that (1) glycerol is hygroscopic and absorbs moisture, and (2) under service conditions, glycerol itself breaks down into compounds which are corrosive. Accordingly, it is an important feature of our invention that our new improvement agent be both anhydrous and non-hygroscopic. To this end, any glycerol and/or water formed or present in the saponification product are removed. The formation of glycerol during the saponification may be entirely avoided by using as a starting material a purified sperm oil which contains no glycerides.

The saponification of a sperm oil in accordance with our invention is conveniently accomplished by reacting the sperm oil with lime at an elevated temperature. Either quicklime or slaked lime, that is calcium oxide or calcium hydroxide may be employed. If quicklime is used, some water, say 18 parts of water per 56 parts of quicklime is added in order to accelerate the saponification reaction. In any event, the lime is preferably employed in slight excess of the amount theoretically required to react with all of the fatty acids liberated in the saponification of the sperm oil, an excess of about 5 per cent being suitable. Generally, the amount of lime used ranges from 7.5 per cent to 11 per cent by weight of the sperm oil. Any unreacted excess of lime is removed by filtering. Accordingly, the saponification product obtained is a mixture of sperm oil alcohols and the calcium salts of sperm oil fatty acids, the fatty acids in the form of their calcium salts and the sperm oil alcohols existing in the same relative proportions as the corresponding alcohols and acids exist in the unsaponified sperm oil.

The temperatures employed for the saponification may range from 440° F. to 550° F. Temperatures much above 550° F. should be avoided because at such temperatures pyrolysis of the sperm oil fatty acids may take place. Glycerol, which may be encountered in small amounts, boils at a higher temperature, viz., 554° F., but at the temperatures of the saponification, glycerol and water are distilled off completely as an azeotropic mixture with some of the sperm oil alcohols. About 10 hours heating usually suffices for the complete saponification of the sperm oil and the complete removal of glycerol and water. If desired, the removal of the glycerol may be expedited by steam distilling the reaction mixture in the later stages of reaction or after the saponification is complete. After all the glycerol has been distilled off, the condensate from the distillations separate into two layers, a lower layer containing glycerol and water and an upper layer of substantially pure sperm oil alcohols. The sperm oil alcohols are separated, dried and returned to the reaction mass remaining in the reaction vessel.

In an especially good embodiment of the invention, the sperm oil is diluted with a mineral oil prior to saponification. Conducting the saponification in the presence of mineral oil reduces the consistency of the reaction products, and the resulting concentrate of agent in mineral oil may be blended with mineral lubricating oil in the intended ultimate proportion with very little equipment, little effort, and without heating the oil in which the concentrate is to be blended. In conducting the saponification in the presence of a mineral oil, it is convenient to use approximately equal proportions by weight of the sperm oil and mineral oil, but higher proportions of mineral oil, as high as 3 parts of mineral oil to 1 part of sperm oil or higher, may advantageously be employed. It is desirable to employ for this purpose a mineral oil of substantially similar quality as the mineral lubricating oil to which the concentrate of agent is to be added, but it is preferred to employ a naphthenic oil because of the greater solubility of the agent in this type of oil than in a paraffinic oil.

In general, our new improvement agent is present in the final lubricating oil composition in an amount sufficient to confer improved detergent, antioxidant and oiliness properties on the composition. While larger amounts may be used without harmful effects, it is ordinarily sufficient to employ a small amount of the improvement agent, from 0.1 to 5.0 per cent by weight on the mineral lubricating oil.

The following examples are further illustrative of our invention. Unless otherwise stated, all parts are by weight.

Example 1.—One hundred parts of 45° natural winter sperm oil were treated with 10 parts hydrated lime in a suitable still and maintained at a temperature of 500° F. while agitating the mixture. Steam was introduced in the later stages of the reaction to distill over all the sperm oil alcohols and contaminating glycerol. The condensate from the still consisted of a lower layer containing the glycerol and water and an upper layer of substantially pure sperm oil alcohols (which are insoluble in water). The sperm oil alcohols were separated, dried and then mixed with the calcium fatty acid salts remaining in the still to yield a liquid mass. The liquid was filtered to remove any excess lime. The resulting filtrate was an excellent improvement agent for mineral lubricating oils.

As stated, there are advantages in conducting the saponification of sperm oil, and dehydration and deglycerinization of the products, in the presence of mineral oil as a diluent. The mineral oil reduces the consistency of the products of the above-described saponification and increases the fluidity of the material so as to facilitate handling and mixing with the lubricating oil with which the material is to be blended to form the final lubricating oil composition. A convenient mixture for the treatment is about equal parts of sperm oil and mineral oil. The following examples show the use of mineral oil in the preparation of our new improvement agent.

Example 2.—A blend was prepared of 50 parts of 45° natural winter sperm oil and 50 parts of 55 SUV/100° F. naphthene-type mineral lubricating oil. This blend was agitated mechanically and heated to a temperature of 450° F., 5 parts of lime added, and the mixture maintained at about this temperature until the reaction was complete. The concentrate of agent in the mineral oil was cooled to about 300° F. and filtered to remove any excess of insoluble matter or unreacted lime. The product was a clear liquid, readily miscible with lubricating oils.

Example 3.—In another example, the same procedure was used except that 100 SUV/100° F. oil of the same type base was substituted for the 55 viscosity oil and a slightly higher reaction temperature, 480° F. was employed.

The following table of typical properties refers to the products of Examples 2 and 3 as well as to the starting materials.

Description	45° N. W. Sperm Oil	55 Vis. Naphthene Oil (Oil A)	Lime-Saponified Sperm Oil Concentrate in Oil A	100 Vis. Naphthene (Oil B)	Lime-Saponified Sperm Oil Concentrate in Oil B
Gravity: °API	28.9	28.1	23.6	24.2	20.2
Sp. Gr., 60°/60° F	0.8822	0.8866	0.9123	0.9088	0.9328
Viscosity, SUV:					
100° F	99	55	707	104	14,839
210° F			750	39	20,239
Flash, OC: °F	515	275	295	325	
Fire, OC: ° F	580	300	320	370	
Pour: ° F	+40			below −50	
Color, NPA	1.5		4.75	2.0	lt. brown
Copper Strip Test				pass	
Neutralization No	0.68		0.57	0.06	0.52
Carbon Residue: Percent			4.2		
Acidity, Organic Oleic Acid Equiv	0.34				
Saponification No	133				

The above concentrates can be blended with other naphthenic type lubricating oils in any desired proportions. The solubility of the sperm oil saponification products in a paraffin type oil is somewhat lower, but enough may be dissolved to confer the improved properties of our invention.

As stated, the invention is applicable to a glyceride-free sperm oil. Following is a comparative tabulation of certain properties of a commercially available glyceride-free sperm oil and ordinary sperm oil.

	Glyceride-free Sperm Oil	Sperm Oil
Gravity: °API	30.9	29.7–28.6
Sp. Gra.: 60°/60° F	0.8713	0.878–0.884
Viscosity, SUV: 100° F	86.5	95–100
Flash, OC: °F	475	490
Color, NPA, not darker than	1.0	3.0
Neutralization No., max	0.3	2.0
Saponification No	117.3	120–140
Iodine No., Mod. Hanus	75.5	75–90

Such purified sperm oil preparations are worked up in a manner quite similar to the treatment of sperm oil.

Example 4.—A glyceride-free sperm oil preparation as described above was treated as in Example 3, yielding a blend of equal parts of the lime saponification products and naphthenic mineral lubricating oil. A comparison of this concentrate with the base oil is as follows:

	Napthenic Type Mineral Lubricating Oil	Lime Saponified Glyceride-free Sperm Oil Concentrate
Gravity: ° API	24.2	23.6
Viscosity, SUV:		
100° F	104	276
210° F	39	106
Pour: ° F	below −50	−20
Color, NPA	2.0	3.75
Neutralization No	0.06	0.48

An improved Diesel engine oil may be prepared

by adding to a Diesel lubricating oil base, for example, 4 per cent of the above described concentrate. A comparison of this improved oil with the base oil is given below:

	Improved Oil	Base Oil
Gravity: ° API	26.2	26.5
Sp. Gr.: 60°/60° F	0.8973	0.8956
Viscosity, SUV:		
100° F	1,850	1,819
210° F	126	122
Viscosity Index	97	93
Flash, OC: ° F	485	525
Fire, OC: ° F	570	595
Pour: ° F	+5	+5
Color, NPA	6.0	5.5
Carbon Residue: Percent	0.64	0.46
Neutralization No	0.05	0.03
Copper Strip Test 212° F	passes	passes
Motor Service Test [1] Piston Rating	1	4
Almen Test: Lb	8	6
Timken Test, Special: Lb	16	14

[1] See U. S. Patent No. 2,179,067, page 6.

Even with this relatively large addition of our new improvement agent to the base oil, the effect on viscosity is negligible, as is apparent from the table.

Our new improvement agent and its concentrates in mineral oil, when used in small proportions, have sufficiently good color ordinarily so as not to degrade the color of the oil with which they may be mixed, but when they are to be blended with an especially light colored oil, it is desirable to improve the color of the agent. This decolorization may be accomplished in known manner by treatment with a small quantity of decolorizing material such as fuller's earth, decolorizing clay, activated alumina, activated carbons or activated silicates.

As shown in the preceding disclosure, lubricating oil compositions containing our new improvement agent possess excellent detergent properties. Thus, any gums, resins, carbon and varnish-like materials which tend to form on the pistons and rings of internal combustion engines are suspended and not deposited. Furthermore no separable sludge is formed. In addition to conferring detergent properties, our new improvement agent provides enhanced oiliness characteristics to mineral lubricating oils, and is a good antioxidant in itself. The agent is simply and cheaply prepared, and its excellent solubility in mineral oils not only enables the convenient preparation of its blends with mineral lubricating

oils, but insures that the agent will not separate out from the oils either in storage or use. Notwithstanding the fact that our new agent contains the calcium salts of sperm oil fatty acids, the effect of our agent on the viscosity of lubricating oil compositions is negligible.

What we claim is:

1. An improved liquid lubricating oil composition comprising a mineral lubricating oil and an anhydrous, non-hygroscopic mixture of sperm oil alcohols and the calcium salts of sperm oil fatty acids, the fatty acids in the form of their calcium salts and the sperm oil alcohols existing in substantially the same relative proportions as the corresponding alcohols and acids exist in the unsaponified sperm oil, and being present in an amount sufficient to confer improved detergent, antioxidant and oiliness properties to the composition.

2. An improved liquid lubricating oil composition comprising a mineral lubricating oil and from 0.1% to 5% by weight based on the mineral oil of an anhydrous, non-hygroscopic mixture of sperm oil alcohols and the calcium salts of sperm oil fatty acids, the fatty acids in the form of their calcium salts and the sperm oil alcohols existing in substantially the same relative proportions as the corresponding alcohols and acids exist in the unsaponified sperm oil, said composition having improved detergent, antioxidant and oiliness properties.

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