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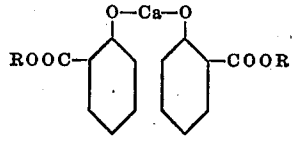
CHEMICAL MANUFACTURE

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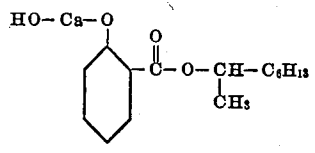
2 Claims. (Cl. 252—53)

My invention relates to improvements in compounded petroleum lubricating oils. The improved lubricating oil compositions of my invention consist essentially of a petroleum base oil and an addition agent comprising the calcium salt of the 1 methyl heptyl ester of salicylic acid, the addition agent being present in an amount insufficient materially to alter the normal liquid character of the petroleum lubricating oil itself, 0.5% to 5.0% on the oil, for example. This addition agent may also be defined as the calcium salt of the capryl ester of salicylic acid and it may be graphically represented as follows:



where R represents the alkyl radical of capryl alcohol, a secondary alcohol. This compound is, for convenience, herein referred to as calcium capryl salicylate.

The calcium salt having the structural formula given above is the normal calcium salt of the ester. The invention also includes lubricating oil compounds in which the calcium salt addition agent comprises, in addition to the normal calcium salt, a limited amount of the basic calcium salt wherein only one of the hydrogen atoms of the hydroxy radical of calcium hydroxide has been replaced by the ester. The basic calcium salt may be graphically represented as follows:



The trend of development of internal combustion engines has imposed increasing burdens upon the oils used for their lubrication, particularly with respect to operating temperatures and pressures. Extreme requirements in both of these respects are represented by the Diesel type of engine and supercharged aircraft engines.

The useful operating life of a lubricating oil in such severe service is determined in a large measure by its thermal stability and by its physical capacity to continue functioning as a lubricant at the high temperatures and pressures encountered. One measure of thermal stability is resistance to oxidation. Oxidation promotes either the formation of sludge or the formation of acids corrosive to bearing metals or both. However, in another aspect, the effect of thermal stability is determined not only by the extent of oxidation or decomposition but also by the character of the products of such decomposition or oxidation and by the extent and location within the engine of deposits of such products.

The improved lubricating oil compositions of my invention have in addition to the lubricating properties of the petroleum oil of which they are compounded, a high solvent capacity for sludge of the character formed by oxidation of petroleum lubricating oil, and perhaps of even greater importance, the property of rendering deposits of sludge and "carbon" within the engine soft and friable rather than hard and coherent and of disintegrating and removing such deposits as an incident of the normal operation of the engine. In engines of this type the high temperature to which lubricating oil is subjected, particularly at the top of the stroke, frequently causes deposition of sludge and carbonization in the groove before and behind one or more of the piston rings. Consequent sticking of the rings rapidly deprives the piston and cylinder wall of proper lubrication inducing excessive wear and frequently scoring of the cylinder wall. The formation of such "carbon" deposits hard enough and coherent enough to involve sticking of the rings is materially retarded, if not avoided, by the use of the improved lubricating oil compositions of my invention.

In the lubricating oil compositions of my invention, the calcium capryl salicylate functions not only to inhibit sludge formation and to modify the character of the "carbon" deposits but it also functions as a strong anti-oxidant effective to inhibit, at least over a prolonged induction period, the rate of oxygen absorption at elevated temperatures, thus rendering such lubricating oil compositions non-corrosive, or less corrosive, to alloy bearing metals.

While this addition agent does not materially increase the film strength of a base oil in which it is incorporated, it is compatible with well known film strength agents such as diamyl diphenol sulfide, chlorinated diphenyl, brominated diphenyl, sulfurized sperm oil, and the like. In lubricating oil blends, including such film strength agents, the calcium capryl salicylate effectively inhibits the pro-oxidation effect that many of these known film strength agents exert.

In my co-pending applications Serial No. 368,992, filed December 7, 1940, and Serial No. 407,002, filed August 15, 1941, I have disclosed

lubricating compositions including as addition agents calcium salts of various alkyl esters of salicylic acid. The lubricating oil compositions therein described have been found to give excellent results in the respects above noted. However, I have discovered that calcium capryl salicylate is a particularly effective addition agent in lubricating oil compositions, having under severe operating conditions a prolonged effective life as an anti-oxidant and corrosion inhibitor, and that lubricating oil compositions comprising calcium capryl salicylate have several outstanding advantages including superior thermal stability.

The superior thermal stability of the lubricating oil containing calcium capryl salicylate is illustrated by the results of thermal stability tests in which 1% of the calcium salts of various alkyl esters of salicylic acid were incorporated in an S. A. E. 30 Pennsylvania type petroleum lubricating oil. Each sample was placed in a glass tube in an atmosphere of nitrogen. The tubes thus charged were placed in a high temperature oil bath and observed periodically to determine the time in hours at which the first visible precipitate was formed by decomposition of the calcium salicylate. The following table shows the results of these tests on compositions comprising, respectively, the calcium salts of normal octyl salicylate, of iso-octyl salicylate and capryl salicylate, under different temperature conditions, the lubricating oil base in each instance being identical:

	At 341° F.	At 400° F.
	Hours	*Hours*
Calcium n-octyl salicylate	8	1
Calcium iso-octyl salicylate	24	2
Calcium capryl salicylate	72	4.5

The effectiveness of calcium capryl salicylate as a corrosion inhibitor in lubricating oil compositions and its superiority in this respect are illustrated by the results of corrosion tests wherein for comparison identical tests were made, in one instance, using the blank petroleum lubricating oil (sample A); in another, the identical lubricating oil containing 1.33% of calcium iso-octyl salicylate (sample B); and, in the third instance, 1.33% of the calcium capryl salicylate (sample C). The base oil used in each instance was an S. A. E. 30 Pennsylvania-type lubricating oil having a gravity of 28.1 A. P. I., a Saybolt viscosity of 527.4 at 100° F. and 66.3 at 210° F., and a viscosity index of 102. The corrosion loss of a cadmium-silver bearing during identical 5 hour tests and 10 hour tests of each sample is given in the following table:

	Sample A	Sample B	Sample C
5 hour test	.813	.001	.001
10 hour test	1.542	.611	.001

From the results of these tests it appears that, with respect to bearing corrosion losses, both sample B and sample C were decidedly superior to the blank coil, sample A, and that, though the calcium iso-octyl salicylate and the calcium capryl salicylate were equally effective in reducing corrosion losses during the 5 hour test period, the effectiveness of the calcium capryl salicylate in this respect remained unimpaired over a considerably longer period than the calcium iso-octyl salicylate.

The thermal stability of the lubricating oil composition of the present invention is further evidenced by the results of Indiana sludging tests. For example, by the addition of 4% of calcium capryl salicylate to a base oil from a South Texas petroleum lubricating oil stock, having a gravity of 20.2 A. P. I., a Saybolt viscosity of 506.8 at 100° F., and of 53.2 at 210° F., and a viscosity index of 11.3, the Indiana sludging time was increased from 13 for the base oil to 60 for the lubricating oil composition containing the calcium capryl salicylate. Similarly, by the addition of 4% calcium capryl salicylate to a base oil from an S. A. E. 30 Pennsylvania-type petroleum lubricating oil stock having a gravity of 28.3 A. P. I., a Saybolt viscosity of 563 at 100° F. and 67.8 at 210° F., and a viscosity index of 100.3, the Indiana sludging time was increased from 200 for the base oil to 328 for the lubricating oil composition containing the calcium capryl salicylate.

As previously stated, the calcium capryl salicylate addition agent used in compounding the lubricating oil composition of the present invention is compatible with well-known film-strengthening addition agents. This fact is illustrated by the results of oxygen absorption and sludging tests in which there was used as the base oil a blended lubricating oil stock consisting of 28% West Texas neutral having a Saybolt viscosity of 45 at 210° F., 6% of a Pennsylvania-type 150 neutral, 36% of a Pennsylvania-type neutral having a Saybolt viscosity of 60 at 210° F., and 30% of a Pennsylvania-type solvent-refined bright stock. This blend had a gravity of 26.8 A. P. I., a Saybolt viscosity of 519 at 100° F., and 64.4 at 210° F., a viscosity index of 96.4 and an Indiana sludging time of 67.

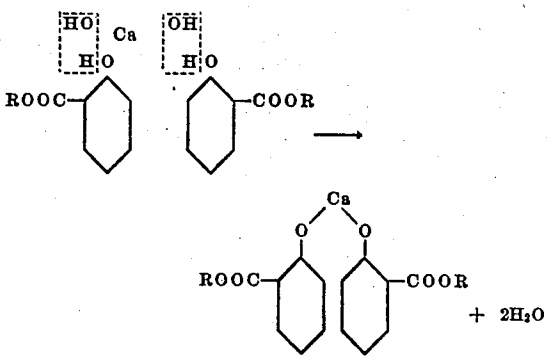
By the addition of 4% of calcium capryl salicylate and 0.25% diamyl diphenol sulfide, the latter being a film-strengthening agent, the Indiana sludging time was increased to 267. For comparison, the Indiana sludging test was also run on the identical lubricating oil compositions except that 4% calcium iso-octyl salicylate was substituted for the calcium capryl salicylate. The Indiana sludging time of this comparative sample containing 4% calcium iso-octyl salicylate was 175.

Oxygen absorption tests at 400° F., on two lubricating oil compositions prepared from the same blended base oil gave an induction period of 235 minutes for the lubricating oil composition resulting from the addition of 4% calcium capryl salicylate and 0.25% diamyl diphenol sulfide to the base oil blend and an induction period of 213 minutes for the lubricating oil composition in which calcium iso-octyl salicylate was substituted for the calcium capryl salicylate. The average oxygen absorption rate for each over its induction period was approximately 7 cubic centimeters per 100 grams of oil per minute.

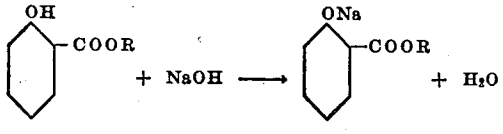
The calcium capryl salicylate used in the compounding of a lubricating oil composition of the present invention may be prepared by reacting the capryl salicylic acid ester directly with hydrated lime, suspended in a volatile inert solvent such as benzene, at an elevated temperature, as described in my co-pending application Serial No. 409,841, filed September 6, 1941. For example, 1 gram mole of hydrated lime (74 grams) is suspended in 827 grams of benzene by rapid stirring. The suspension is heated to 160° F. and 2 gram moles (500 grams) of capryl salicylate and 12.5 grams of water added. Vigorous stirring is continued for approximately 2 hours to maintain the lime in suspension until the reaction is completed.

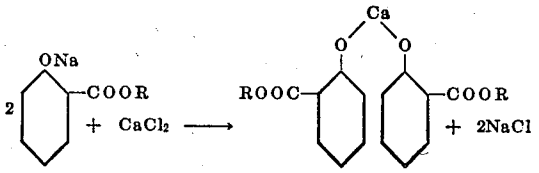
The mixture is thereafter filtered and heated to remove the remaining water and benzene. The last traces of benzene are advantageously removed by the application of a high vacuum leaving the finished product as a viscous liquid residue.

The reaction by which the neutral calcium salt of the ester is formed may be graphically represented as follows:



As an alternative method, the calcium salt may be prepared by double decomposition or methasis, as also described in my co-pending application, just noted, by first reacting the capryl salicylate ester with sodium hydroxide to form the sodium salt of the ester and reacting the sodium salt with calcium chloride to form the calcium capryl salicylate, as indicated by the following graphical representation of the reaction:





where R represents the capryl radical.

The calcium capryl salicylate may be prepared by the double-decomposition method as follows: 2 gram moles (500 grams) of the capryl salicylate is dissolved in 1000 milliliters of alcohol and 1000 milliliters of benzol. A cold solution of 2.3 gram moles (92 grams) of sodium hydroxide in 200 milliliters of water is then stirred into the mixture. This solution is then mixed immediately with 1.2 gram moles (133 grams) of calcium chloride in 250 milliliters of water. An additional 1000 milliliters of benzol is then added to dissolve the calcium salt and sufficient water is stirred into the solution to cause separation of the alcohol-water layer. The alcohol-water layer is then drawn off and the benzol solution containing the calcium capryl salicylate is washed twice with warm water and thereafter filtered, using a conventional filter aid. The benzene is then distilled off under vacuum.

The calcium capryl salicylate may also be prepared by reacting capryl salicylate directly with hydrated lime in a lubricating oil medium. For example, 74 pounds (1 pound mole) of calcium hydroxide is suspended in 827 pounds of a Pennsylvania-type petroleum lubricating oil having an S. A. E. viscosity rating of 30 and the mixture heated to 180° F. To this suspension there is added about 250 pounds (1 pound mole) of capryl salicylate and finally 12.5 pounds of water. During these additions the mixture is stirred vigorously. The mixture is then kept at 160–190° F. and stirred vigorously for about 2 hours to complete the reaction of the ester with the lime. The mixture is then dehydrated by heating to about 280° F. A filter aid may then be added and the mixture passed through a blotter press while maintaining a temperature of 200–220° F.

By the above method, a clear concentrated solution of the calcium capryl salicylate in lubricating oil may be prepared which may be diluted by the addition of further lubricating oil to prepare the finished lubricating oil composition of the present invention with or without the incorporation of other addition agents.

The capryl salicyclate used in the preparation of the calcium salt may be prepared by reacting salicylic acid with capryl alcohol using concentrated sulfuric acid as a catalyst, as described in my co-pending application Serial No. 409,846, filed September 6, 1941. However, I prefer to prepare the capryl salicylate by reacting capryl alcohol with methyl salicyclate using metallic sodium as a catalyst. In this method of preparation a temperature of 285–375° F. should be maintained to promote the alcohol exchange and to distill off the methanol as formed. Upon completion of the reaction, the residual reaction products are neutralized and fractionally distilled to recover the capryl salicylate and unreacted reactants. In excess of 90% of the methyl salicylate may be converted into capryl salicylate of high purity by this method of preparation. However, this method of preparation is not my invention but is the joint invention of Robert H. Gardner and Franklin M. Watkins and is described in detail in application Serial No. 421,372, filed December 2, 1941.

In the preparation of the calcium salts of the alkyl esters of salicylic acid described in my co-pending application Serial No. 409,841, filed September 6, 1941, by direct reaction of the lime with the ester, the formation of the basic calcium salt is generally promoted by the presence of excess lime. These basic calcium salts contain a greater proportion of calcium than the corresponding neutral salt. In general, it has been observed that the length of the induction period during which the rate of oxygen absorption is retarded roughly parallels the calcium content of these calcium salt addition agents. The amount of oxygen which may be absorbed before termination of the induction period is, in many instances, almost directly proportional to the calcium content of the addition agent.

From the standpoint of prolonging the induction period, it is therefore generally advantageous to promote the formation of the basic salt. However, this advantage is usually offset to a considerable extent by the lower thermal stability of the basic salts. Numerous tests have shown that the basic calcium ethyl-hexyl salicylate is less thermally stable than the neutral calcium ethyl-hexyl salicylate. Similarly, the lesser thermal stability of the basic calcium capryl salicylate as compared to the neutral salt is made evident by the tendency of a lubricating composition containing an excessively large proportion of the former to exhibit a considerable viscosity rise in service, particularly during the initial period of service.

In the preparation of calcium capryl salicylate the salt has consistently been found to contain a greater excess of calcium over the theoretical

proportion for the neutral salt than is the case in the preparation of calcium ethyl-hexyl salicylate, even though the ethyl-hexyl ester has the same molecular weight as the capryl ester. This indicates that the calcium capryl salicylate has a greater tendency to form the basic salt. However, in spite of this greater tendency to form the basic salt, the lubricating oil compositions of the present invention have greater thermal stability than that of a similar lubricating composition in which calcium iso-octyl salicylate is substituted for the calcium capryl salicylate, providing comparable care has been exercised in the preparation of both addition agents to prevent formation of excessive proportions of the basic salt.

I claim:

1. A liquid lubricating oil composition comprising a petroleum lubricating oil and the calcium salt of the capryl ester of salicylic acid, the latter being present in an amount insufficient materially to alter the normal liquid character of the lubricating oil constituent.

2. A liquid lubricating oil composition comprising a petroleum lubricating oil and about 0.5–5.0% based on the oil, of the calcium salt of the capryl ester of salicylic acid.

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