April 25, 1944. W. L. FINLEY 2,347,546

LUBRICATING OIL COMPOSITION

Filed Dec. 7, 1940 3 Sheets-Sheet 1

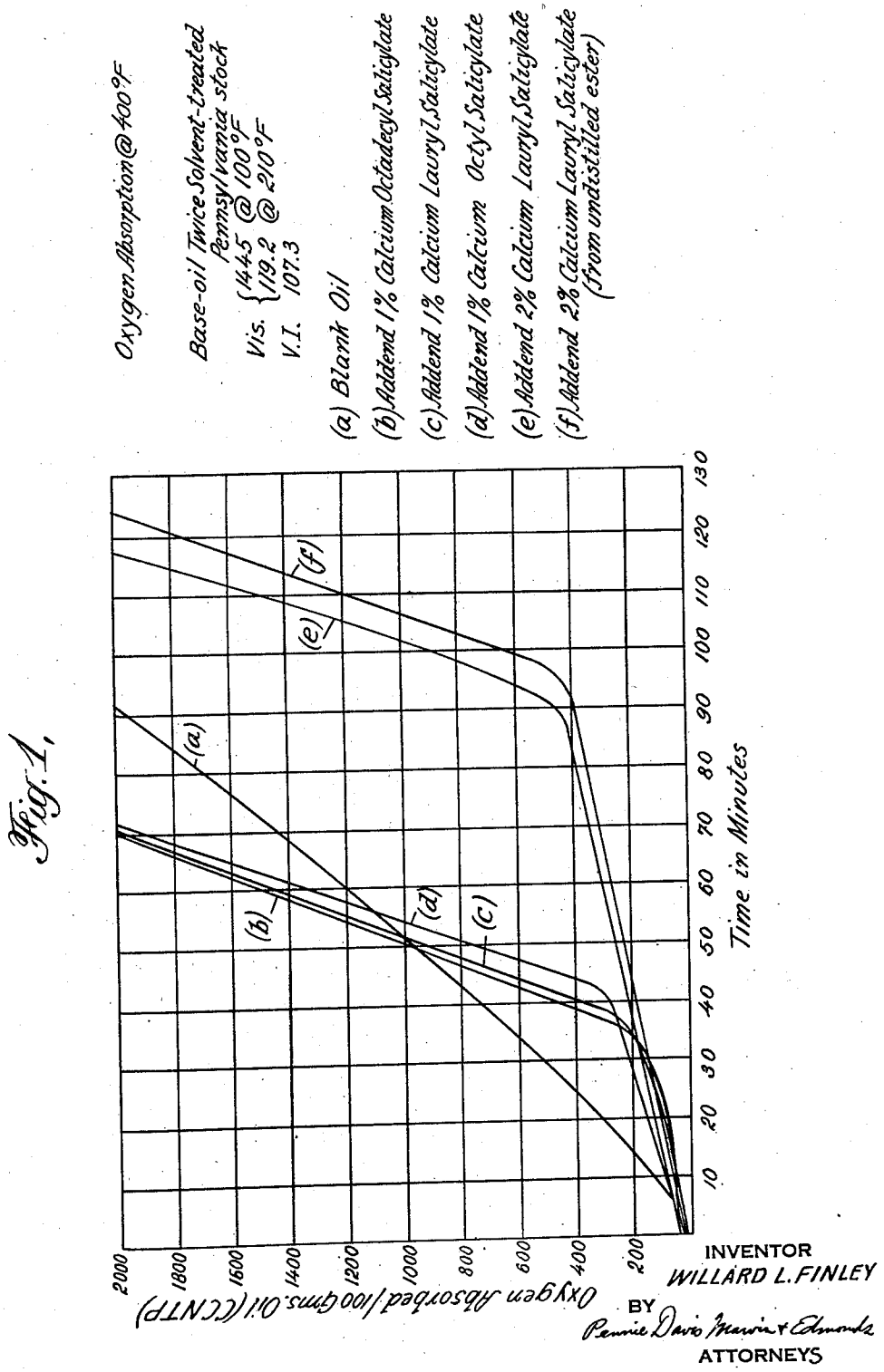


Fig. 1.

INVENTOR
WILLARD L. FINLEY
BY
Pennie Davis Marvin & Edmonds
ATTORNEYS

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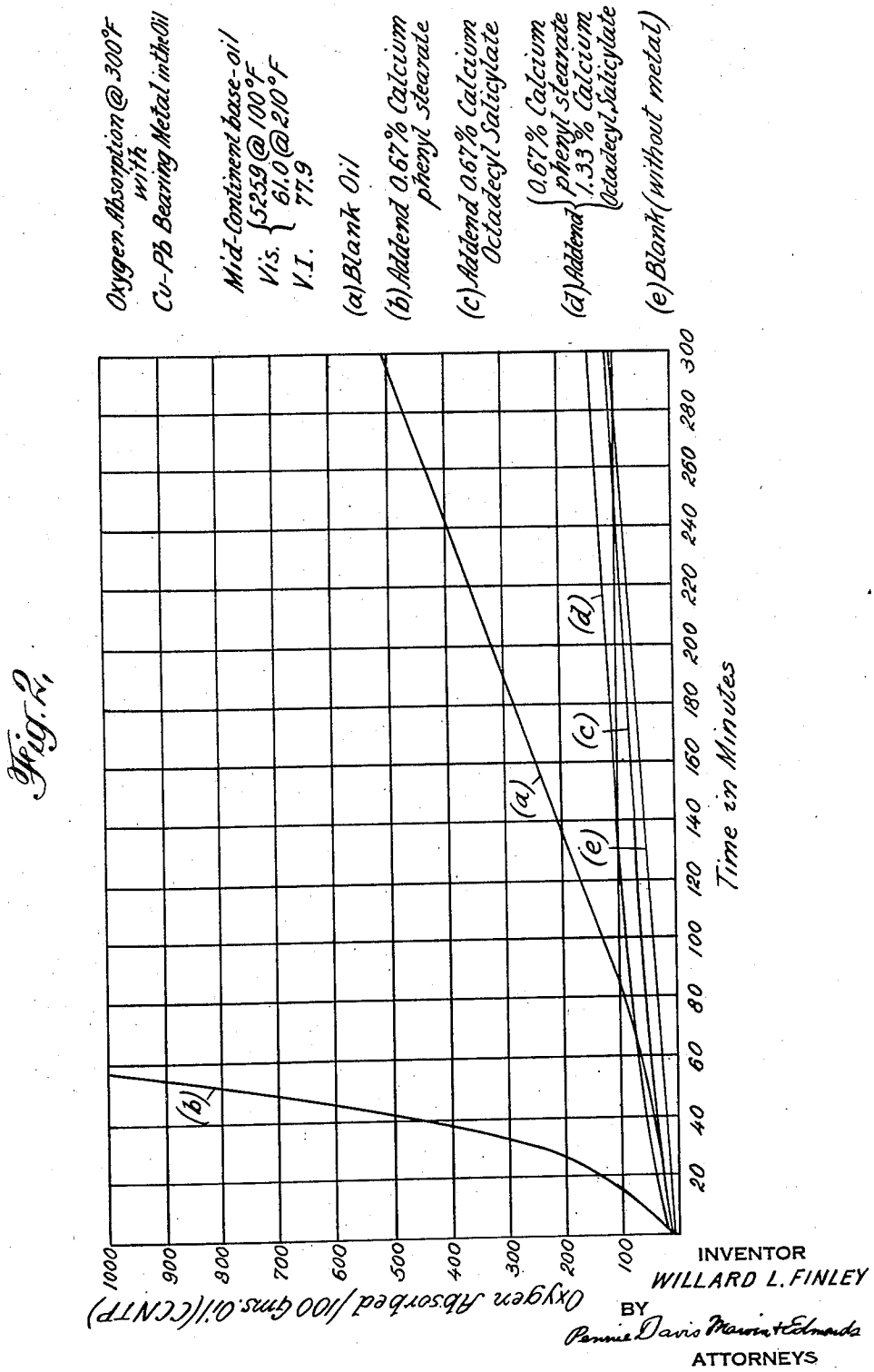


Fig. 2.

INVENTOR
WILLARD L. FINLEY
BY
Dennie Davis Marvin & Edmonds
ATTORNEYS

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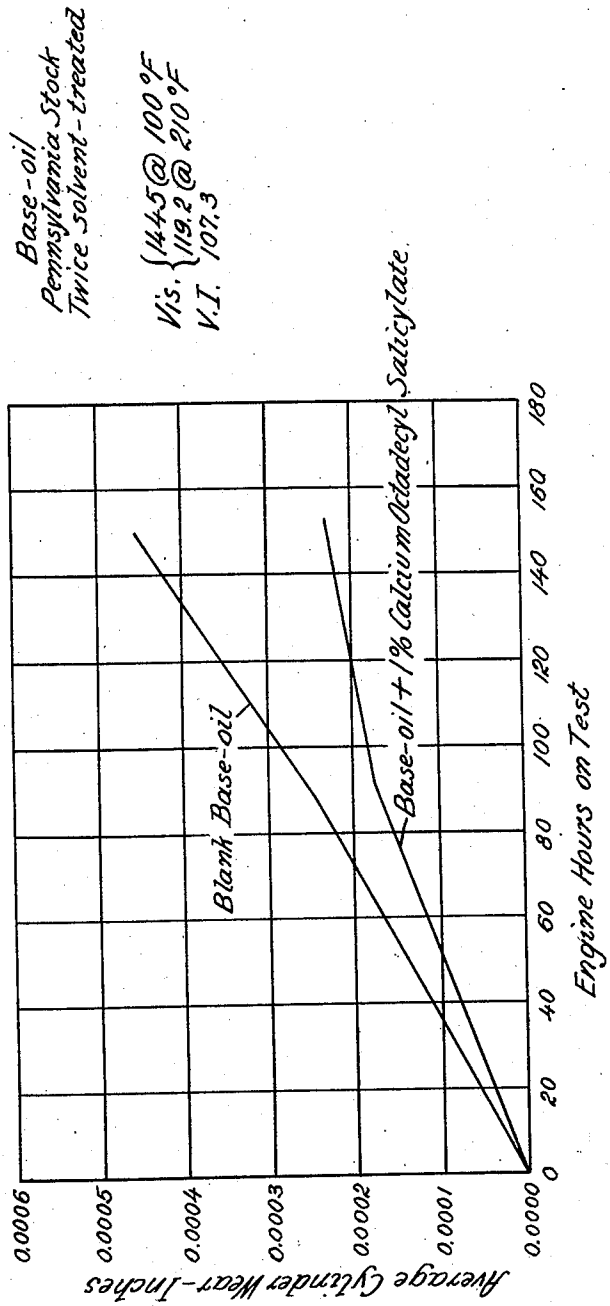


Fig. 3.

INVENTOR
WILLARD L. FINLEY
BY
Pennie Davis Marvin & Edmonds
ATTORNEYS

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UNITED STATES PATENT OFFICE

2,347,546

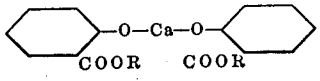
LUBRICATING OIL COMPOSITION

Willard L. Finley, Chicago, Ill., assignor to Sinclair Refining Company, New York, N. Y., a corporation of Maine

Application December 7, 1940, Serial No. 368,992

6 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 oil base and an addition agent comprising the calcium salt of an alkyl ester of salicylic acid, the addition agent being present in an amount insufficient materially to alter the normally liquid character of the petroleum lubricating oil itself, 0.5–5.0% on the oil for example. This addition agent may also be defined as an alkyl benzoate ortho calcium phenolate. These compounds have the following general structure:



where R is an alkyl chain of say 8 to 18 carbon atoms. They may be less accurately but more conveniently described as calcium alkyl salicylates. For convenience they will hereinafter be so described, it being understood that the term "calcium octyl salicylate" for example is intended to define the calcium salt of the octyl ester of salicylic acid.

The trend of development in internal combustion engines has imposed increasing burdens upon the oils used for their lubrication, particularly with respect to the 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 services, is determined in 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 oils of which they are compounded, a high solvent capacity for sludge of the character formed by oxidation of petroleum lubricating oils, 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 for 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 alkyl salicylates function not only to inhibit sludge formation and to modify the character of the "carbon" deposits, but they also function as strong anti-oxidants 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.

The calcium salts of the alkyl esters of salicylic acid may advantageously be prepared by first esterifying salicylic acid with the appropriate alcohol, using concentrated sulphuric acid as the catalyst, then replacing the hydrogen of the hydroxyl group by a metal such as sodium by reaction with sodium hydroxide, and finally reacting the resulting product with calcium chloride to form the calcium soap by double decomposition. The following example will serve to illustrate this method in the preparation of the calcium salt of the octyl ester of salicylic acid. 1380 grams (10 mols) of salicylic acid were placed in a 5-liter flask with 1820 grams (14 mols) of octyl alcohol. 10 ml. of concentrated sulphuric acid and 300 ml. of toluene were added. The flask was heated thereby distilling toluene and water up into a reflux condenser equipped with a trap the bottom of which was arranged to allow the condensed water to be drawn off and the toluene returned continuously to the flask. After four and one-half hours the theoretical yield of water (180 grams) was collected and the heating stopped. The product was then washed successively with water and with a sodium bicarbonate solution. It was thereafter washed four more times with water until all of the sodium salts were removed. The water and toluene were

then removed by distillation under vacuum—the distillation being stopped at 180° F. vapor temperature and at a pressure of 86 mm. The resultant crude ester product was then distilled under vacuum through a packed column from a still heated in an oil bath, three overhead fractions being obtained. These cuts, the boiling range and pressure at which they were obtained, their acid numbers and their saponification numbers are given in the following table:

Cut No.	Boiling range	Weight	Acid No.	Sap. No.
		Grams		
1	205–210° F. at 18 mm.	374	1.4	5.1
2	210–328° F. at 18 mm.	33	3.9	11.7
3	272–312° F. at 1 mm.	2,426	3.0	206.8
	Still bottoms and loss.	187		

Either the third cut from the above distillation, having a saponification number closely approaching the theoretical saponification number of the octyl ester of O-hydrobenzoic acid which is 224, or the crude undistilled ester product may be used in the preparation of the calcium salt useful in the composition of my invention. The calcium salt prepared from the undistilled ester is a somewhat more effective anti-oxidant than is the salt prepared from the ester of greater purity obtained from the distillation. In this instance the calcium salt was prepared from the distilled ester fraction obtained as above described by dissolving 2 mols of the ester in 1000 ml. of alcohol and 1000 ml. of benzol. A cold solution consisting of 2.3 mols of sodium hydroxide in 200 ml. of water was then stirred in. The resultant solution was then mixed immediately with 1.2 mols of calcium chloride in 250 ml. of water. An additional 1000 ml. of benzol was then added to dissolve the calcium octyl salicylate and sufficient water was stirred into the solution to cause separation of the alcohol water layer. This layer was drawn off and the benzol solution washed twice with warm water. The benzol solution was then filtered using a filter aid and the benzol was then distilled off under vacuum. The resulting calcium octyl salicylate had a calcium content of 7.85% as compared to a theoretical content of 7.43%.

Calcium octadecyl salicylate and calcium lauryl salicylate also were prepared by the procedure above described except that octadecyl alcohol and lauryl alcohol were used instead of the octyl alcohol in preparing the esters. The calcium contents of the octadecyl and of the lauryl salicylates thus prepared were found to be 5.08% and 6.10%, respectively, which closely approach the theoretical values of 4.89% and 6.15%.

The lubricating oil compositions of my invention may also be prepared with advantage by first incorporating the appropriate alkyl ester in a portion of the oil base and then adding lime to react directly with the ester. The following example will serve to illustrate the application of this method in the preparation of a lubricating composition containing approximately 5.0% calcium n-butyl salicylate:

To 921.5 grams of a South Texas pale oil having a Saybolt viscosity of about 500 seconds at 100° F. were added 48.3 grams of n-butyl salicylate, 18.5 grams of lime and 5 ml. of water. This mixture was digested with stirring for two hours during which the temperature was raised slowly to 280° F. The resulting product was then filtered to remove excess calcium. The calcium content of the finished blend was 0.611% compared to 0.51% theoretical. The excess of calcium appears to be due to the presence of a considerable proportion of basic calcium butyl salicylate. Where an excess of lime is present when neutralizing the ester, a portion of the ester appears to react to form the basic calcium alkyl salicylate. Basic calcium alkyl salicylate may be presented by the empirical formula:

$$ROOC.C_6H_4OCaOH$$

When preparing the lubricating oil compositions of my invention by neutralization of the ester in the oil as described, it is preferable to effect the neutralization in only a part of the oil eventually to be incorporated in the finished composition. That is, it is preferable first to prepare a concentrate containing 10 to 25% of the desired calcium alkyl salicylate which may then be admixed with additional oil in order to obtain the composition desired in the final product.

The calcium salt of the octadecyl salicylate is a solid at room temperature while the corresponding salts of the lauryl and octyl esters are viscous liquids. At ordinary room temperature all are very soluble in benzene and in petroleum lubricating oils, even in highly solvent-treated Pennsylvania lubricating oil stocks. However, at low temperatures the solubility of the salts prepared from the esters with the higher molecular weight organic radicals decreases appreciably particularly in lubricating oils prepared from Pennsylvania type stocks.

Incorporation of a calcium alkyl salicylate in a petroleum lubricating oil base causes a marked increase in the sludging time as indicated by the "Indiana oxidation test." The extent of the increase in sludging time varies with the amount of the addition agent and is different for different base-oils. For example the addition of 1.33% of calcium octadecyl salicylate to three base oils, derived respectively from a South Texas crude, a Mid-Continent crude and a Pennsylvania crude, caused increases in the Indiana sludging time as shown in the following table:

Base oil	Vis. at 100	Vis. at 210	V. I.	I. S. T. blank oil	I. S. T. with 1.33% calcium octadecyl salicylate
				Hours	*Hours*
South Texas	513.1	53.6	14.4	16	31
Mid-Continent	525.9	61.0	77.9	18	54
Pennsylvania	471.2	63.1	102.1	68	360

The effect of the proportion of the addition agent on the Indiana sludging time is shown by a comparison of the effects produced by adding 1.33% in one instance and 2.00% in another instance of calcium octadecyl salicylate to the same base-oil, the base-oil in this instance being the same Pennsylvania type lubricating oil as that used in the foregoing comparison. These effects are shown in the following table:

Base oil	Addition Agent	I. S. T.
Pennsylvania	1.33% calcium octadecyl salicylate	360
Do	2.00% calcium octadecyl salicylate	465

The length of the induction period, during which the rate of oxygen absorption is retarded, is influenced both by the amount of the addition agent and by the particular addition agent selected. In general the length of this induction period roughly parallels the calcium content of the addition agent. The amount of oxygen that may be absorbed before termination of the induction period is in many instances almost directly proportional to the calcium content of the addition agent. For example, a twice solvent-treated Pennsylvania base-oil containing 2% of calcium lauryl salicylate can absorb almost exactly twice as much oxygen before termination of the induction period as can a blend of the same base oil containing only 1% of the same addition agent. At 400° F. the lengths of the induction periods for the last-mentioned blends, as determined by the true oxidation test, were 90 minutes for the blend containing 2% of the addition agent and 37 minutes for the blend containing 1% of the addition agent. The addition of 1% of calcium octadecyl salicylate, of 1% of calcium lauryl salicylate and of 1% of calcium octyl salicylate respectively, to separate samples of the same base-oil, produced induction periods of 35 minutes, 37 minutes and 42 minutes in the order named. Calcium salts prepared from the undistilled esters have a higher calcium content than those prepared from the distilled esters, due to the presence of small amounts of esters of the lower molecular weight alcohols in the undistilled product. The observed greater anti-oxidant effect of the calcium salts prepared from the undistilled esters appears to be at least in part due to this circumstance.

The chart appearing as Fig. 1 of the drawings illustrates the relative effect of the octadecyl, the lauryl and the octyl salicylates respectively on the rate of oxygen absorption. The base-oil in each instance was a twice solvent-treated Pennsylvania lubricating oil stock having a gravity of 28.2° A. P. I., a viscosity of 1445 at 100° F. and of 119.2 at 210° F. and a viscosity index of 107.3. The oxygen absorption tests were carried out at 400° F. Three of these blends contained 1% of the addition agent. The others contained 2% of the addition agent. In Fig. 1 the rate of oxygen absorption for the blank oil is shown by curve *a* while the corresponding rates for blends including 1% of octadecyl, lauryl and octyl salicylates are shown by curves *b*, *c* and *d*, respectively. The corresponding rate for a blend containing 2% of the lauryl salicylate is shown by curve *e*, while that for a blend containing 2% of the calcium salt prepared from the undistilled lauryl ester is shown by curve *f*. This chart clearly illustrates the strongly anti-oxidant effect of the calcium alkyl salicylates prior to termination of the induction period of blends containing them. It also illustrates the effects of varying both the number of carbon atoms in the alkyl chain and the proportion of the addition agent. As a further illustration of the effect of the latter variation, I have found that the induction period for a blend consisting of 3.5% calcium octyl salicylate (prepared from the undistilled ester) in a Pennsylvania type base-oil, initially having a viscosity of 471.2 seconds at 100° F. and a viscosity index of 102.1, is approximately 215 minutes as indicated by the true oxygen absorption test conducted at 400° F.

In addition to reducing the rate of oxygen absorption during the induction period, the addition agents incorporated in the lubricating oil blends of my invention possess the capability of inhibiting the strongly pro-oxidant effect of other addition agents such as calcium phenyl stearate, as well as the capability of inhibiting the pro-oxidant effect exerted by the presence in the oil of copper-lead and cadmium-silver bearing metals. The chart appearing as Fig. 2 of the drawings illustrates the inhibiting effect of the calcium salt of the octadecyl ester of salicyclic acid both with respect to the pro-oxidant effect of a copper-lead bearing metal and the pro-oxidant effect of calcium phenyl stearate.

The base-oil used in the oxygen absorption tests involved in the chart comprising Fig. 2 was a medium heavy Mid-Continent lubricating oil stock having a gravity of 25° A. P. I., a viscosity of 525.9 at 100° F. and a viscosity index of 77.9. All of the oxygen absorption tests involved in this chart were conducted at a temperature of 300° F. A copper-lead bearing metal was present in the oil in all of the oxidation tests except that illustrated by curve *e*. Curve *e* shows the rate of oxygen absorption by the blank oil in the absence of the copper-lead bearing metal. Curve *a* shows the rate of oxygen absorption by the blank oil in the presence of the copper-lead bearing metal. Curve *b* shows the rate of oxygen absorption for a blend including 0.67% of calcium phenyl stearate as the addition agent. Curve *c* shows the rate of oxygen absorption for a blend containing 0.67% calcium octadecyl salicylate as the addition agent. Curve *d* shows the rate of oxygen absorption for a blend including as addition agents 0.67% of calcium phenyl stearate and 1.33% of calcium octadecyl salicylate. This chart strikingly illustrates the ability of the calcium salt of an alkyl ester of salicylic acid to inhibit the pro-oxidant effect of a copper-lead bearing metal as well as the strongly pro-oxidant effect of calcium phenyl stearate.

The capability of the addition agents employed in the lubricating oil compositions of my invention to inhibit the pro-oxidant effect of cadmium-silver bearings is shown by the results of the Underwood oxidation tests which are given in the table below. The base oil in this instance was a blend having a gravity of 28.7° A. P. I., a viscosity of 453 at 100° F. and a viscosity index of 95.4. The blend consisted of 70% of a Mid-Continent solvent refined neutral having a viscosity of approximately 250 at 100° F. and 30% of a lightly solvent refined Pennsylvania bright stock having a viscosity of 136.7 at 210° F. For the purpose of these tests .01% Fe_2O_3, as iron naphthenate, was added to the oil to accelerate the pro-oxidant action of the cadmium-silver bearings. Tests were run on the blank base-oil and on three blends of this base-oil including respectively 1.33% and 2.00% calcium octadecyl salicylate and 3.00% calcium lauryl salicylate. The viscosity at 130° F. and the carbon residue were recorded at the beginning of these tests and at 5 hours and 10 hours thereafter. At the termination of the 5 and 10 hour periods the neutralization number as determined by A. S. T. M. methods A and B, the bearing losses and the contents of material insoluble in naphtha and in chloroform were also re-

corded. The results are given in the following table:

		Blank oil	Base-oil plus 1.33% calcium octadecyl salicylate	Base-oil plus 2.00% calcium octadecyl salicylate	Base-oil plus 3.00% calcium lauryl salicylate
Original oil	Vis. at 130	206	207	216	217
	C. R.	0.35	0.56	0.72	0.97
	Neut. No.	0.05	(1)	(1)	(1)
5 hrs.	Vis. at 130	351	212	218	224
	C. R.	2.32	0.89	0.89	1.21
	Neut. No. A	4.50	0.38	0.35	0.28
	Neut. No. B	4.60	0.40	0.40	0.30
	Bearing loss (g)	0.937	0.001	0.001	0.001
	Naph. insol.	0.08	0.01	0.01	0.03
	$CHCl_3$ insol.	0.05	0.01	0.01	0.01
10 hrs.	Vis. at 130	771	567	237	232
	C. R.	4.27	2.71	1.20	1.25
	Neut. No. A	5.20	9.00	0.60	0.70
	Neut. No. B	5.60	9.25	0.70	0.40
	Bearing loss (g)	1.894	0.792	0.025	0.001
	Naph. insol.	0.47	0.01	0.01	0.03
	$CHCl_3$ insol.	0.21	0.01	0.01	0.01
	Copper baffle	(2)	(2)	(2)	(2)
	Result of test	(4)	(4)	(3)	(3)

[1] Alk.
[2] Slight tarnish.
[3] O. K.
[4] N. G.

Inspection of the data appearing in the above table clearly shows that in the case of the blends including 2% of calcium octadecyl salicylate and 3% of calcium lauryl salicylate, the pro-oxidant action of the iron naphthenate and cadmium-silver bearing metal had been inhibited as is indicated by the low bearing loss, the low carbon residue, the low neutralization numbers, and by the small amount of material insoluble in naphtha and in chloroform at the termination of the 10 hour test period. The data also shows that the addition of only 1.33% of the calcium octadecyl salicylate is insufficient to prolong the induction period of the blend to an extent enabling it to satisfactorily pass this test.

The addition agents embodied in the lubricating oil compositions of my invention do not materially increase the film strength of a base-oil in which they are incorporated. However, they are compatible with known film-strength agents such as chlorinated diphenyl, brominated diphenyl, sulphurized sperm oil, and the like. In lubricating oil blends including such film strength agents, the addition agents of my invention effectively inhibit the pro-oxidant effect that many of these known film-strength agents exert. In the general in such compositions the calcium alkyl salicylates reduce the rate of oxygen absorption and the tendency of the blend to become corrosive even though in some cases they are not capable of completely counteracting the tendency of certain film-strength agents to promote sludging. Thus the addition of 2% sulphurized sperm oil to a Pennsylvania type base-oil containing 1⅓% of calcium octadecyl salicylate reduces the I. S. T. to 20 hours, whereas the Indiana sludging time for the same blend without the sulphurized sperm oil was 365 hours as compared to 68 hours for the blank base-oil. However, notwithstanding the adverse effect of the sulphurized sperm oil on the sludging time, engine tests on these three lubricating oil compositions showed a ring rating of 100% free for the blend including only calcium octadecyl salicylate and for the blend including sulphurized sperm oil in addition to the salicylate, whereas for the blank oil the ring rating was only 98.7% free with correspondingly higher ring and ring groove deposits.

In service in a supercharged internal combustion engine a blend including only 1% of calcium octadecyl salicylate in addition to the base-oil showed a marked superiority over the blank base-oil as is illustrated by the following examples. The base-oil used in these supercharged engine tests was a twice solvent-treated Pennsylvania type base-oil. The physical characteristics of the blank base-oil and of the blend prepared therefrom are given in the following table:

	Blank	Blend including 1% calcium octadecyl salicylate
Gravity °A. P. I.	28.2	28.1
Flash	520	525
Fire	600	585
Viscosity at 100° F.	1445	1468
Viscosity at 210° F.	119.2	120.4
Viscosity index	107.3	107.3
Pour, °F.	+5	10
Carbon residue	0.614	0.66
Ash	0.00	0.114
Neutralization number	(1)	[2] 0.2
Saponification number	0.30	0.70
Indiana oxidation test:		
I. S. T., hrs.	420.0	520.0
Vis. rise 120° F./50 hrs.	8.8	9.6
Vis. rise 210° F./100 hrs.	27.4	24.6

[1] Neutral.
[2] Basic.

Engine tests of 150 hours were conducted both on the blank oil and on the blend above described, the intake manifold boost pressure in each test being maintained at 1.6" vacuum for the first five hours, 3.5 lb. gauge pressure for the second five hours, 5.7 lbs. for the third five hours, and 8 lbs. for the remainder of the test. Measurements of the cylinder wear and inspections of the piston and ring conditions were made at the end of 89 hours as well as at the end of the 150 hour test period. These inspections showed that both the ring wear and cylinder wear were lower and that there was less scoring of the rings and cylinder walls for the blend than for the blank oil. Likewise the oil sump was considerably more free from sludge in the test on the blend than in the test on the blank oil. Both the condition of the piston skirt and of the ring belt were cleaner for the test on the blend than for the test on the blank oil. For the test on the blend all rings were 100% free both at the 89 hour inspection and at the end of the test, whereas for the test on the blank oil the ring rating was 93.1% free at 89 hours, and only 92.1% free at the end of the test.

The average cylinder wear for the last-described test on the blank oil and for the corresponding test on the blend are shown in the chart appearing as Fig. 3 of the drawings. The values for the average cylinder wear in inches for the test on the blank oil being .00025 at 89 hours and .00046 at the end of the test and for the blend .000175 at 89 hours and .000231 at the end of the test. As is clearly shown by Fig. 3 the rate of cylinder wear in the test on the blank oil increased toward the end of the test, whereas for the blend the rate of cylinder wear, initially less than that for the blank oil, further decreased as the test was continued. The total ring wear loss, expressed in grams, was 1.71 for the test on the blank oil and 0.45 for the test on the blend. The total ring and ring groove de-

posits for all pistons, expressed in grams, was 19.606 for the test on the blank oil and only 7.968 for the blend.

I claim:

1. A liquid lubricating oil composition comprising a petroleum lubricating oil and the calcium salt of an alkyl ester of salicylic acid.

2. A liquid lubricating oil composition comprising a petroleum lubricating oil and 0.5–5.0% of the calcium salt of an alkyl ester of salicylic acid having from 8 to 18 carbon atoms in the alkyl chain.

3. A liquid lubricating oil composition comprising a petroleum lubricating oil and the calcium salt of the octyl ester of salicylic acid.

4. A liquid lubricating oil composition comprising a petroleum lubricating oil and the calcium salt of the lauryl ester of salicylic acid.

5. A liquid lubricating oil composition comprising a petroleum lubricating oil and the calcium salt of the octadecyl ester of salicylic acid.

6. A liquid lubricating oil composition comprising a Pennsylvania type petroleum lubricating oil and a minor proportion of the calcium salt of an alkyl ester of salicylic acid.

WILLARD L. FINLEY.