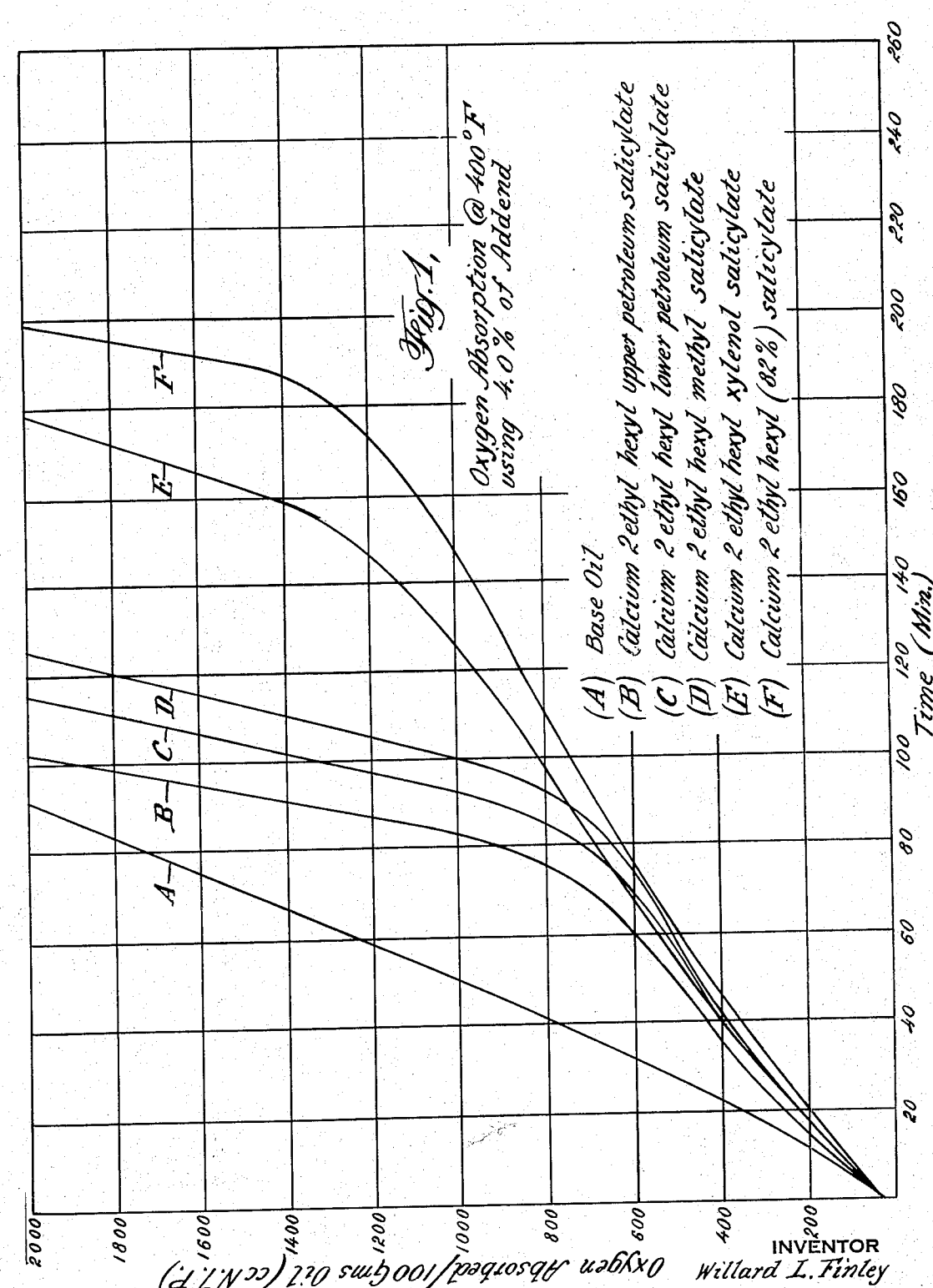
Aug. 15, 1944. W. L. FINLEY 2,356,043

LUBRICATING OIL COMPOSITION

Filed Oct. 28, 1941 2 Sheets-Sheet 1



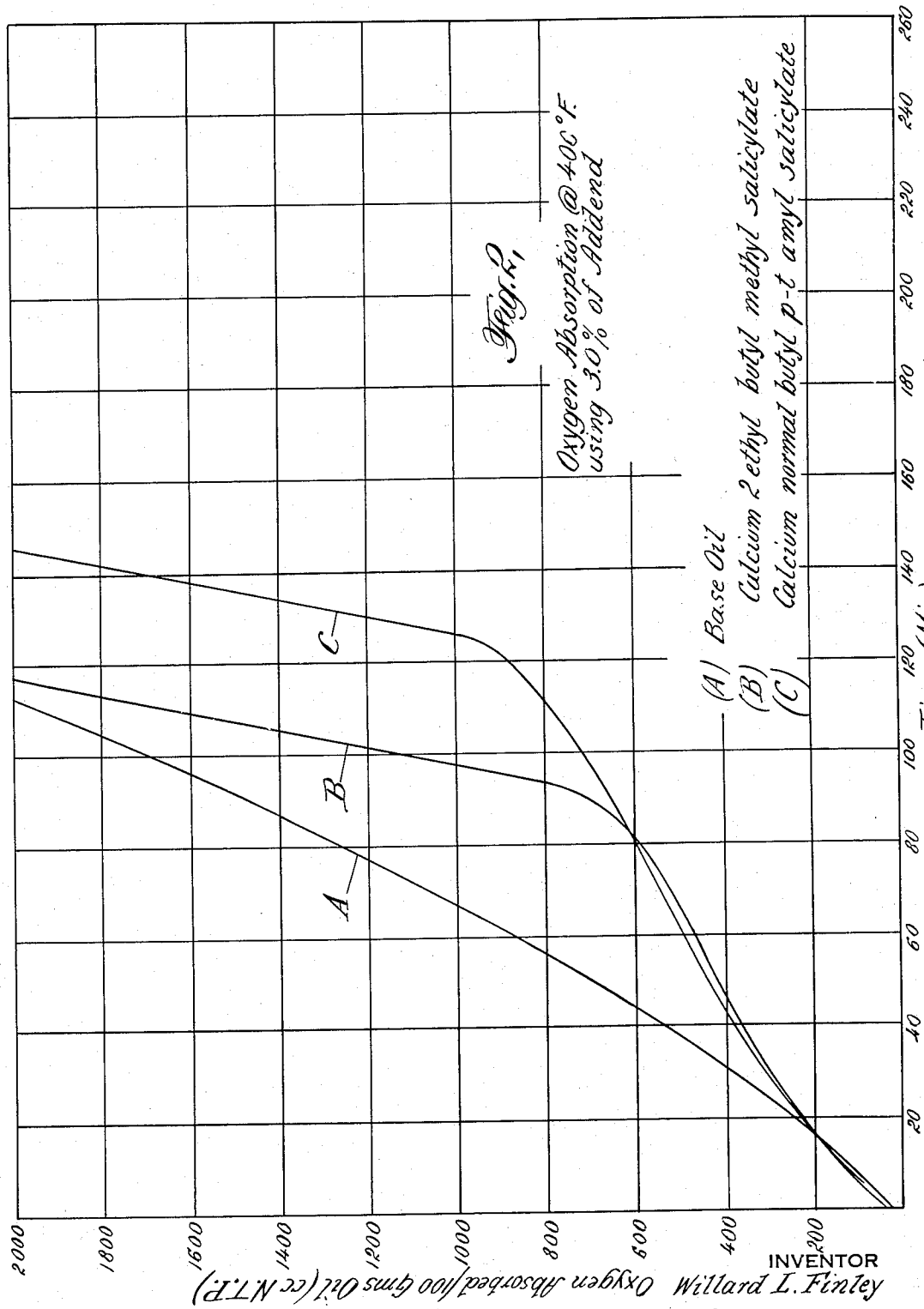
INVENTOR
Willard L. Finley

BY
Pennie, Davis, Marvin & Edmonds
ATTORNEYS

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LUBRICATING OIL COMPOSITION

Filed Oct. 28, 1941 2 Sheets-Sheet 2



INVENTOR
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BY
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Patented Aug. 15, 1944 2,356,043

UNITED STATES PATENT OFFICE

2,356,043

LUBRICATING OIL COMPOSITION

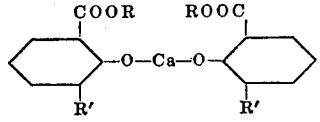
Willard L. Finley, Edgewood Arsenal, Md., assignor to Sinclair Refining Company, New York, N. Y., a corporation of Maine

Application October 28, 1941, Serial No. 416,831

8 Claims. (Cl. 252—57)

This invention relates to an improved lubricating oil containing calcium salts of an alkyl ester of an alkylated salicyclic acid.

The new compositions of matter are herein designated "calcium salts of an alkyl ester of alkylated salicyclic acid" and may be graphically represented by the following structural formula:



where R represents an alkyl radical of, say, 4 to 18 carbon atoms, and R' represents an alkyl radical of 1 to 9 carbon atoms.

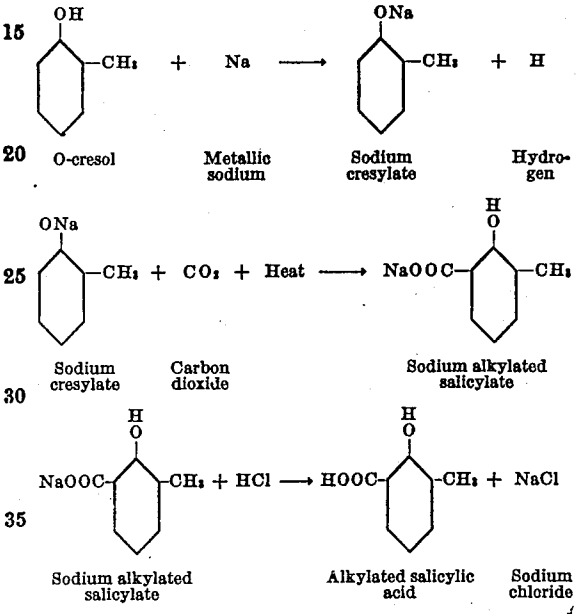
In the above structural formula R' is shown in the meta position with respect to the carboxyl group. However, it will be understood that the R' radical may occupy other positions on the benzene ring. It will also be understood that there may be more than one of the R' radicals.

The use of calcium salts of alkyl esters of salicylic acid as addends in lubricating oil compounds has been described and claimed in my applications Serial No. 368,992, filed December 7, 1940, and Serial No. 407,002, filed August 15, 1941. Also, various calcium salts suitable as addends in lubricating oil compounds have been described and claimed in my application Serial No. 409,841, filed September 6, 1941. These calcium salts of the alkyl esters of salicyclic acid described in the aforementioned applications are relatively expensive.

I have discovered a new class of organic calcium salts which may be represented by the foregoing structural formula and have found that they are highly effective as addition agents inhibiting oxidation when incorporated in lubricating oils in relatively small proportions. These materials have the further advantage that they may be prepared from relatively inexpensive crude materials containing alkylated phenols, cresols, xylenols and the like, such, for instance, as crude coal tar acids and petroleum cresylic acids.

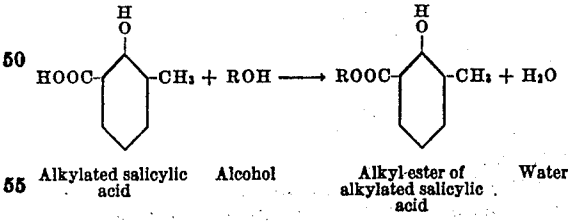
These crude materials may be converted to alkylated salicylic acids which in turn may be esterified and the calcium salts of the present invention produced therefrom by the method presently to be described. For example, a crude raw material containing alkylated phenols is dried and treated with metallic sodium at a temperature of about 300° F. to form the corresponding sodium phenates in which the hydrogen atom of the hydroxy group is replaced by sodium. The resulting mixture is then allowed to cool to about 280° F. and dry carbon dioxide gas is bubbled therethrough at atmospheric pressure, while the mixture is constantly stirred, and sodium alkylated salicylate is formed as a precipitate. This precipitate of crude sodium alkylated salicylate is then separated from the mixture and, after washing, is treated in aqueous solution with a strong acid such as hydrochloric acid whereby a crude alkylated salicylic acid is formed.

The chemical reaction by which the crude alkylated salicylic acid is formed from the crude materials as noted above may be illustrated by the following graphical representation of a reaction in which cresylic acid is used as the starting material:



In place of the hydrochloric acid, other strong acids such as sulfuric acid may be used.

The crude alkylated salicylic acid is then caused to react with an alcohol to form the corresponding alkyl ester; for instance using a sulfuric acid catalyst as hereinafter described in greater details. This reaction may be represented graphically as follows:

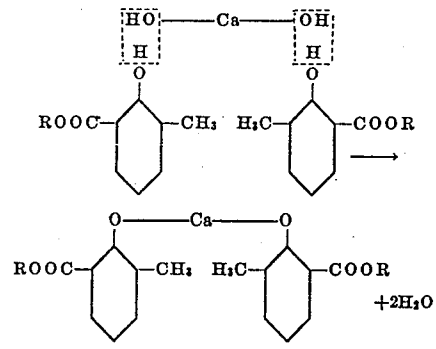


where R represents the alkyl radical of the alcohol.

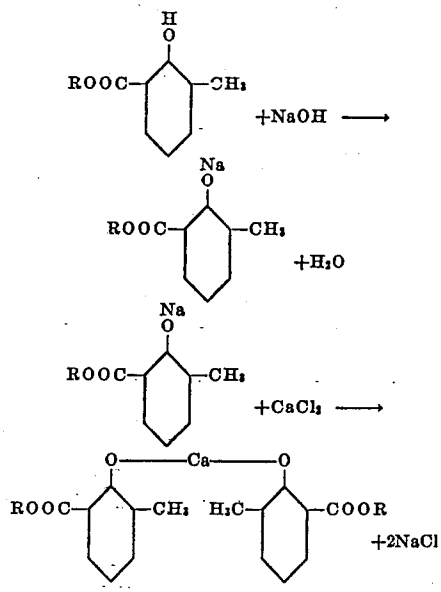
The calcium salt of the alkyl ester of the alkylated salicylic acid is then formed by reacting the

ester directly with lime or by double decomposition.

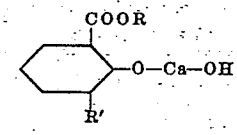
The reaction of the calcium salt directly with lime may be represented as follows:



The reactions involved in the formation of the calcium salt by double decomposition may be represented as follows:



I have observed that the calcium alkylated salicylates of my invention as prepared by either of the foregoing methods usually contain somewhat more than the theoretical percentage of calcium for the neutral salt. While I cannot state with certainty the reason for the presence of this excess calcium, it is my present belief that it is due to the formation of a small amount of the basic calcium alkylated salicylate during the foregoing reaction. This basic calcium alkylated salicylate may be graphically represented as follows:



where, as above, R represents the alkyl radical of the particular alcohol used to form the ester and wherein only one of the hydroxy radicals of the calcium chloride has been replaced by the ester.

In no instance has the excess calcium in the product been in excess of 50% and, in most instances, it has been found to vary between 5% and 20%.

In some instances, the presence of such an excess of combined calcium in the product has been found desirable; for example, in the compounding of lubricating oils, I have found the calcium alkylated salicylate of the present invention which contains a considerable excess of combined calcium, to be superior in some respects to those which contain more nearly the theoretical amount for the neutral salt.

The amount of combined calcium present in the product in excess of the theoretical amount for the neutral salt, and which I believe to be due to the presence of the basic calcium alkylated salicylate, may be increased by using an amount of lime in considerable excess over that indicated by the foregoing representation of the reaction; for example, a 100% excess of lime may be used to advantage.

A specific illustration of the process using as the raw material a crude cresylic acid of petroleum origin consisting primarily of a mixture of alkylated phenols having a total of from 2 to 3 carbon atoms in the alkyl radicals, about 80% of the crude material having a boiling range from 421° F to 445° F., is as follows:

Approximately 10 moles of the crude cresylic acid is thoroughly dried by distilling with about 200 cc. of toluene in a flask provided with a reflux condenser and water trap. After the mixture is thoroughly dehydrated the toluene is also removed by distillation and 1.67 moles of metallic sodium is added, a temperature of about 300° F. being maintained, whereby the corresponding sodium cresylate is rapidly formed with the evolution of hydrogen. The resulting solution consists of sodium cresylate and solvent cresylic acid in molar ratios of approximately 1:5.

The solution is then allowed to cool to about 280° F. and carbon dioxide gas dried over sulfuric acid and Dehydrite is bubbled into the solution at atmospheric pressure while the mixture is being constantly stirred. The bubbling of the carbon dioxide through the solution is continued for a total of about 15 hours during which time the temperature is gradually reduced to about 215° F.

Within two hours of the beginning of the carbon dioxide introduction, a precipitate of the sodium alkylated salicylate begins to come down. This precipitate is so heavy that it will stop the ordinary air-driven laboratory stirrer within three or four hours after the introduction of the carbon dioxide gas has begun. A special stirrer of rigid construction, driven for instance by an electric motor, is therefore recommended.

The reaction mass is a soft grey solid, more nearly liquid at and around the stirrer than in the upper portion of the reaction vessel. This mass is taken up in about 4 liters of water. Upon standing the solvent cresylic acid layer separates out and is removed from the aqueous solution. Carbon dioxide gas is then bubbled through the aqueous solution to convert any unreacted sodium cresylate to cresylic acid and sodium bicarbonate. The aqueous solution which contains the sodium alkylated salicylate is then extracted three times with benzol to remove unreacted cresylic acid and the benzene washes are extracted with water to recover therefrom any sodium alkylated salicylate they contain.

The wash water is then combined with said aqueous solutions and the combined solution containing the alkylated salicylate is acidified strongly with an inorganic acid, advantageously hydrochloric acid, to convert the sodium alkylated salicylate to the alkylated salicylic acid.

By the process just described, a 73% yield of crude alkylated salicylic acid has been obtained having an acid number of 322 against a theoretical acid number of 339 and an ash content of 0.05%.

Yields from about 70 to 83% of the theoretical yield of alkylated salicylic acid have been obtained by the foregoing method from various crude materials such as previously mentioned.

The esters of the alkylated salicylic acid, for instance, the iso-octyl ester, may be prepared by causing the alkylated salicylic acid to react with an alcohol; for instance, iso-octyl alcohol, by the following method:

The reaction vessel may consist of a 12 gallon flask fitted with a thermometer well and a vapor line leading to a reflux condenser and heated by means of an oil bath. The flask may be charged with approximately equal molar proportions of the alkylated salicylic acid and the alcohol and a relatively small amount of concentrated sulfuric acid. However, I have found it desirable to use an excess of the alcohol; for instance 1.05 moles to about 1.2 moles of alcohol per mole of the acid. The sulfuric acid used is advantageously 95.5% H_2SO_4 and this acid may be used in amounts approximating 0.5% by weight on the alcohol and alkylated salicylic acid charged to the flask.

The mixture in the flask is gradually heated to a temperature of approximately 300° F., by the application of heat to the oil bath, and maintained at about that temperature until substantially the theoretical amounts of water produced by the reaction has been distilled off. Thereafter, the material remaining in the flask is washed with water at a temperature of about 130 to 150° F., to remove the sulfuric acid therefrom, and then with a large excess of sodium carbonate as a 20% aqueous solution to remove any unreacted alkylated salicylic acid. The partially purified ester is then further purified by repeated washing with water and is thereafter distilled. Yields of the distilled ester varying from 79% to 94% of the theoretical yield have been obtained by this method.

The calcium salt of these esters may be prepared as previously stated either by direct reaction with lime or by double decomposition. These salts may be prepared by double decomposition as follows: Approximately 2 gram moles of the ester is dissolved in a mixture of 1000 milliliters of alcohol and 1000 milliliters of benzol. A cold solution of about 2.3 gram moles of sodium hydroxide in 200 milliliters of water is then stirred into the mixture. This solution is then mixed immediately with about 1.2 gram moles 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 salt of the ester is washed twice with warm water and thereafter filtered, using a conventional filter-aid. The benzene is then distilled off under vacuum.

As previously indicated by the foregoing representation of the reaction, 1 mole of sodium hydroxide is required to react with each mole of the ester to form the sodium salt and 2 moles of the resulting sodium salt are required to react with each mole of the calcium chloride to form the neutral calcium salt of the ester. However, in carrying out the reaction, it is usually desirable to use an excess of sodium hydroxide and of the calcium chloride such as indicated above to promote full utilization of the ester and the sodium salt thereof. The proportions of sodium hydroxide and calcium chloride used may be varied somewhat. However, I have found proportions approximating those illustrated to give generally satisfactory results. By this process I have obtained yields of the calcium salt ranging from 43 to 100% of the theoretical yield.

Where the calcium salt is prepared by the direct reaction of the ester with lime, the following procedure may be employed:

1 gram mole of hydrated lime is suspended in 827 grams of benzene by rapid stirring. This suspension is heated to about 160° F. and 2 gram moles of the ester and about 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 then 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.

By the method above described, I have prepared numerous calcium salts of alkyl esters of alkylated salicylic acid, highly desirable as addends in the compounding of lubricating oil. from relatively inexpensive crude materials, of which the following will serve as illustrations:

(1) From a crude material of coal tar origin of the following approximate composition: 18.7% ortho ethyl phenol, 34.5% cresols, 46.2% ortho xylenols, and traces of higher phenols, 80% of which boiled between 400 and 408° F., I have prepared a crude "xylenol" salicylic acid having an acid number of 349 as against a theoretical acid number of 348, and an ash content of 0.26%. By reacting this acid with normal butyl alcohol, as described above, the normal butyl ester was prepared having a boiling range of 213–224° F. at a pressure of 1.0 millimeters of mercury, an acid number of 1 and a saponification number of 247 as against the theoretical saponification number of 259. By the double decomposition method herein described, the calcium salt of this ester was prepared and was found to contain 9.36% calcium as against a theoretical calcium content of 8.47% for the neutral calcium salt. This product is, for convenience, hereinafter referred to as "calcium normal butyl xylenol salicylate" though it will be appreciated that the designation is not wholly accurate. It is a brittle, pale yellow solid having purplish fluorescence.

(1a) By reacting this crude "xylenol" salicylic acid with 2 ethyl hexyl alcohol, as described above, the 2 ethyl hexyl ester was prepared having a boiling range of 283–287° F., at a pressure of 0.7–0.8 millimeter of mercury, an acid number of 1 and a saponification number of 204.8 as against a theoretical saponification number of 205.5. By the double-decomposition method herein described, the calcium salt of this ester was prepared and was found to contain 7.5% calcium as against a theoretical calcium content of 6.85% for the neutral calcium salt. This product is, for convenience, hereinafter referred to as "calcium 2 ethyl hexyl xylenol salicylate" though it will be appreciated that the designation is not wholly accurate. It is a soft, golden jelly-like mass with blue-violet fluorescence and is soluble in lubricating oil stocks to an extent in excess of 4%.

(2) From a crude material of coal tar origin consisting principally of ortho cresol, 80% of which had a boiling range of 370–375° F., a crude alkylated salicylic acid was prepared having an acid number of 364 as against a theoretical acid number of 369 and an ash content of 0.06%.

Upon reacting this acid with 2 ethyl butyl alcohol, by the method previously described, the 2 ethyl butyl ester was prepared having a boiling range of 240–244° F., at a pressure of 0.6–0.9 millimeter of mercury, an acid number of 1.5 and a saponification number of 234 as against the theoretical saponification number of 237.7. By the double-decomposition process previously described, the calcium salt of this ester was prepared and was found to contain 6.07% calcium as against the theoretical calcium content of 7.84 for the neutral calcium salt. For convenience, this product is hereinafter referred to as "calcium 2 ethyl butyl methyl salicylate" though it will be appreciated that the designation is not wholly accurate. It is a grey-pink, soft wax-like solid and is soluble in petroleum lubricating oil stock to an extent approximating 3%.

(2a) By reacting the acid prepared as described in the preceding paragraph with 2 ethyl hexyl alcohol, the 2 ethyl hexyl ester was prepared. The residual fraction of this ester, obtained by separating therefrom such material as would distill off at an overhead temperature of 275° F. under a pressure of 6 millimeters of mercury, had an acid number of 4.1 and a saponification number of 200.6 as against a theoretical saponification number of 212.6. The calcium salt produced therefrom by the double-decomposition method was found to contain 5.56% calcium as against a theoretical calcium content of 7.07% for the neutral calcium salt. For convenience, this calcium salt is hereinafter referred to as "calcium 2 ethyl hexyl methyl salicylate" though it will be appreciated that this designation is not wholly accurate. It is a soft, dark-brown solid.

(3) From a lower boiling range petroleum cresylic acid consisting primarily of a mixture of ethyl, propyl, dimethyl and trimethyl phenols, 80% of which had a boiling range of 421 to 445° F., a crude alkylated salicylic acid was prepared having an acid number of 322, as against the theoretical acid number of 339, and an ash content of 0.05%. The 2 ethyl hexyl ester of this acid was prepared by reaction with 2 ethyl hexyl alcohol by the method described and the resulting ester was found to have a boiling range of 297–310° F. at a pressure of 1.2 millimeters of mercury, an acid number of 0.8 and a saponification number of 194 as against the theoretical saponification number of 202. The calcium salt prepared therefrom by the double-decomposition method was found to contain 5.31% calcium as against the theoretical calcium content of 6.67% for the neutral calcium salt. For convenience, this product is hereinafter referred to as "calcium 2 ethyl hexyl lower petroleum salicylate." It is a semi-liquid, sticky, yellow-white mass.

(4) From an upper boiling range petroleum cresylic acid consisting primarily of a mixture of alkylated phenols with alkyl groups totalling at least 4 carbon atoms, the crude alkylated salicylic acid was prepared having an acid number of 225 as against a theoretical acid number of 256 and an ash content of 0.07%. By esterification with 2 ethyl hexyl alcohol, the 2 ethyl hexyl ester was prepared and was found to have a boiling range of 300 to 350° F., at a pressure of 1 millimeter of mercury, an acid number of 1 and a saponification number of 174 as against a theoretical saponification number of 170. The calcium salt prepared therefrom by the double-decomposition method was found to contain 5.44% calcium as against a theoretical calcium content of 5.69% for the neutral calcium salt. For convenience, this product is hereinafter referred to as "calcium 2 ethyl hexyl upper petroleum salicylate." It is a semi-liquid mass, purple by reflected light, green by transmitted light, and soluble in petroleum lubricating oil stock to an extent in excess of 4%.

(5) From a crude phenol of coal tar origin consisting of approximately 82% phenol and 18% ortho cresol, 80% of which boiled off between 350 and 354° F., crude salicylic acid was prepared having an acid number of 389 as against the theoretical acid number of 399 and an ash content of 0.25%. The ester prepared therefrom by reaction with 2 ethyl hexyl alcohol by the method described was found to have a boiling range of 260–275° F. at a pressure of 1.3 to 1.6 millimeters of mercury, an acid number of 0.9 and an actual saponification number of 209.6 as against the theoretical saponification number of 222.6. The calcium salt prepared therefrom by the double-decomposition method was found to have a calcium content of 8.02% as against the theoretical calcium content for the neutral salt of 7.38%. For convenience, this product is hereinafter referred to as "calcium 2 ethyl hexyl (82%) salicylate." It is a soft, golden jelly with purple fluorescence and is soluble in petroleum lubricating oil stock to an extent in excess of 4%.

(6) From para-tertiary amyl phenol of approximately 99% purity and having a boiling range of 482–500° F., the corresponding alkylated salicylic acid was prepared having an acid number of 251 as against the theoretical acid number of 270, and an ash content of 0.12%. By reaction with normal butyl alcohol the normal butyl ester was prepared therefrom and was found to have a boiling range of 238 to 242° F., at a pressure of 0.6 millimeter of mercury, an acid number of 0.8 and a saponification number of 188.2 as against a theoretical saponification number of 212.5. The calcium salt prepared therefrom by the double-decomposition method was found to contain 7.76% calcium as against a theoretical calcium content of 7.07% for the neutral salt. For convenience, this product is hereinafter referred to as "calcium normal butyl p-t amyl salicylate." It is a pale yellow, brittle solid and is soluble in petroleum lubricating oil stock to an extent in excess of 4%.

In each of the foregoing examples the alkyl ester of the carboxyl group has between 4 to 8 carbon atoms, alkyl esters having a number of carbon atoms within this range being particularly effective for use in accordance with the invention.

The lubricating oil compositions of my invention may be prepared by compounding the previously prepared calcium salt addend with a petroleum lubricating oil base in an amount insufficient materially to alter the normally liquid character of the lubricating oil itself, from 0.5 to 5% on the oil, for example. However, my improved lubricating oil compositions may also be prepared with advantage by first adding to a portion of the base oil the appropriate alkyl ester of an alkylated salicylic acid and then adding lime to the oil mixture to react directly with the ester therein.

For example, the ester may be added to a base oil in an amount sufficient to produce a concentrate containing 10–25% of the calcium salt, and lime then added to the mixture in an amount somewhat in excess of that required to react with the ester together with a small amount of water.

This mixture is then digested with stirring for about two hours during which period the temperature is raised slowly to about 280° F. The resulting product is then filtered to remove excess lime and is thereafter admixed with additional base oil in order to obtain the composition desired in the final product; for example, from 0.5 to 5% of the calcium salt addend.

In the improved lubricating oil compositions of my invention these calcium salt addends have been found to 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 length of the induction period during which the rate of oxygen absorption is retarded is influenced both by the amount of the addition agent incorporated with the oil 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 effect of these addends on the rate of oxidation absorption of the compounded lubricating oil and on the length of the induction period is illustrated by the following tabulated results of oxidation absorption tests made by the True oxidation test method. These tests were conducted at a temperature of 400° F. The tests, the results of which are recorded in Table I, were made using 4% of the indicated addend in a base oil from a Pennsylvania stock having a gravity of 28.3 A. P. I., a viscosity of 514.8 at 100° F., and a viscosity index of 103. The tests, the results of which are recorded in Table II, were made using 3% of the indicated addend in a similar base oil from a Pennsylvania stock having a gravity of 28.1 A. P. I., a viscosity of 522 at 100° F., and a viscosity index of 102. The amounts of oxygen absorbed recorded in these tables are in terms of cubic centimeters of oxygen (at normal temperature and pressure) per 100 grams of the oil or oil compound, the oxygen absorption characteristics of the base oils being included for comparison. The addends used, are those, the preparation of which has been previously described herein.

Table I

	Induction period	Mean rate of oxygen absorption during induction period
	Minutes	*Cc./minute*
Base oil		22
Calcium 2 ethyl hexyl (82%) salicylate	186	6.8
Calcium 2 ethyl hexyl xylenol salicylate	155	7.9
Calcium 2 ethyl hexyl methyl salicylate	93	7.9
Calcium 2 ethyl hexyl lower petroleum salicylate	86	8.6
Calcium 2 ethyl hexyl upper petroleum salicylate	79	9.6

Table II

	Induction period	Mean rate of oxygen absorption during induction period
	Minutes	*Cc./minute*
Base oil		17.5
Calcium normal butyl p-t amyl salicylate	124	7.0
Calcium 2 ethyl butyl methyl salicylate	90	7.2

The mean rates of oxygen absorption recorded above for the base oils are the mean ratio for a period during which 2000 c. c. of oxygen was absorbed per 100 grams of the base oil.

The effect of these addends upon the oxygen absorption characteristics of lubricating oil compounds is further illustrated by the charts appearing as Figures I and II of the drawings on which the results of the tests referred to in the foregoing Tables I and II, respectively, have been plotted.

The improved lubricating oil compositions of my invention have also been found to have a high solvent capacity for sludge of the character formed by oxidation of petroleum lubricating oils and to have 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 the Diesel type, for instance, the high temperature to which the lubricating oil is subjected, particularly at the top of the stroke, frequently causes a deposition of sludge and carbonization in the grooves 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, causing excessive wear and frequently scoring 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 use of the improved lubricating oil compositions of my invention.

The incorporation of these calcium salts of the alkyl ester of alkylated salicylic acid in a petroleum lubricating oil base has been found to cause 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 type of base oil, the particular addend and amount thereof used. For instance, the base oil from Pennsylvania crude used in the tests reported in Table I had a sludging time as indicated by the Indiana oxidation test of 200. The incorporation of 4% of the calcium normal butyl para-tertiary amyl salicylate in this base oil increased the sludging time to 275 and the incorporation in said base oil of 4% of the calcium 2 ethyl hexyl (82%) salicylate increased the I. S. T. value to 506. Further, in a base oil from a South Texas crude having a gravity of 20.2 A. P. I., a viscosity of 506.8 at 100° F., 53.2 at 210° F., a viscosity index of 11.3 and an I. S. T. of 16, the I. S. T. value was increased to 34.5 by the incorporation of 4% of the calcium normal butyl para tertiary amyl salicylate, was increased to 50 by the incorporation in the base oil of 4% calcium 2 ethyl hexyl xylenol salicylate and was increased to 55 by incorporating in this base oil 4% of calcium 2 ethyl hexyl (82%) salicylate.

I claim:

1. A liquid lubricating oil composition comprising a petroleum lubricating oil and the calcium salt of an alkyl ester of alkylated salicylic acid, the alkyl radical in the carboxyl group having from 4 to 18 carbon atoms.

2. A liquid lubricating oil composition comprising a petroleum lubricating oil and about 0.5 to 5.0% of the calcium salt of an alkyl ester of alkylated salicylic acid the alkyl radical in the carboxyl group having from 4 to 18 carbon atoms and the nuclear alkyl radical having from 1 to 9 carbon atoms.

3. A liquid lubricating oil composition comprising a petroleum lubricating oil and the cal-

cium salt of an alkyl ester of alkylated salicylic acid, the alkyl ester of the carboxyl group having from 4 to 8 carbon atoms.

4. A liquid lubricating oil composition comprising a petroleum lubricating oil and a minor proportion of the calcium salt of a crude alkyl ester of alkylated salicylic acid the alkyl radical in the carboxyl group having from 4 to 18 carbon atoms and there being attached to the ring nucleus an alkyl radical of from 1 to 9 carbon atoms.

5. A liquid lubricating oil composition composition comprising a petroleum lubricating oil and the calcium salt of an alkyl ester of alkylated salicyclic acid, the alkyl radical in the carboxyl group having from 4 to 18 carbon atoms and the nuclear alkyl radical having from 1 to 9 carbon atoms.

6. A liquid lubricating oil composition comprising a petroleum lubricating oil and the calcium salt of an alkyl ester of alkylated salicylic acid, the alkyl radical in the carboxyl group having from 4 to 18 carbon atoms and there being attached to the ring nucleus a plurality of alkyl radicals of from 1 to 9 carbon atoms each.

7. A lubricating oil composition comprising a petroleum lubricating oil and a calcium salt of an iso-octyl ester of an alkylated salicylic acid having attached to the ring nucleus a plurality of alkyl radicals of from 1 to 9 carbon atoms each.

8. A liquid lubricating oil composition comprising a petroleum lubricating oil and a calcium salt of an octyl ester of alkylated salicylic acid having attached to the ring nucleus at least one alkyl radical containing from 1 to 9 carbon atoms.

WILLARD L. FINLEY.

CERTIFICATE OF CORRECTION.

Patent No. 2,356,043. August 15, 1944.

WILLARD L. FINLEY.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, lines 3, 6 and 33, for "salicyclic" read --salicylic--; and second column, line 45-46, for "details" read --detail--; page 2, first column, line 38, for that portion of the formula reading "ROOC" read --$_2$ ROOC--; page 3, second column, line 22, after "oil" strike out the period and insert instead a comma; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of November, A. D. 1944.

(Seal)

Leslie Frazer
Acting Commissioner of Patents.