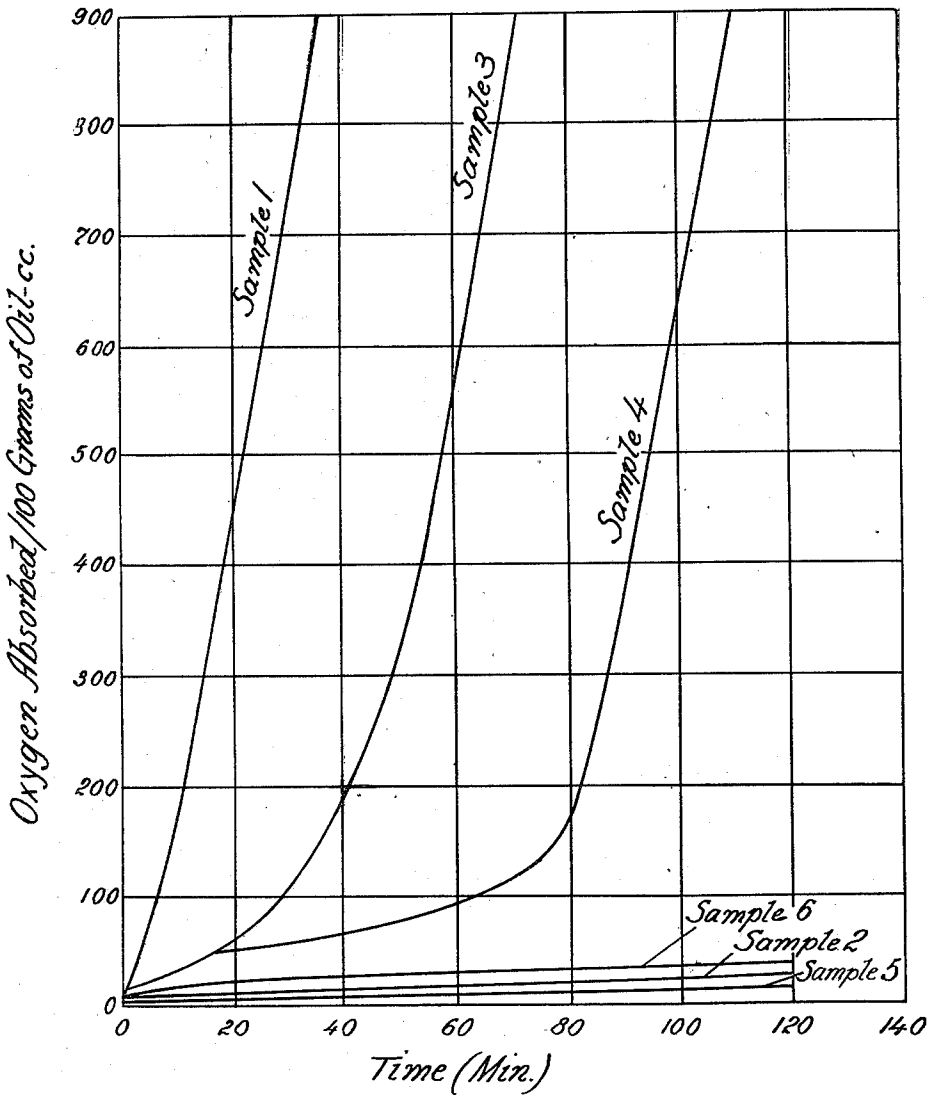
June 6, 1944. L. E. BEARE 2,350,489

LUBRICATING OIL COMPOSITION

Filed April 5, 1941 7 Sheets-Sheet 1

Fig. I,




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June 6, 1944. L. E. BEARE 2,350,489

LUBRICATING OIL COMPOSITION

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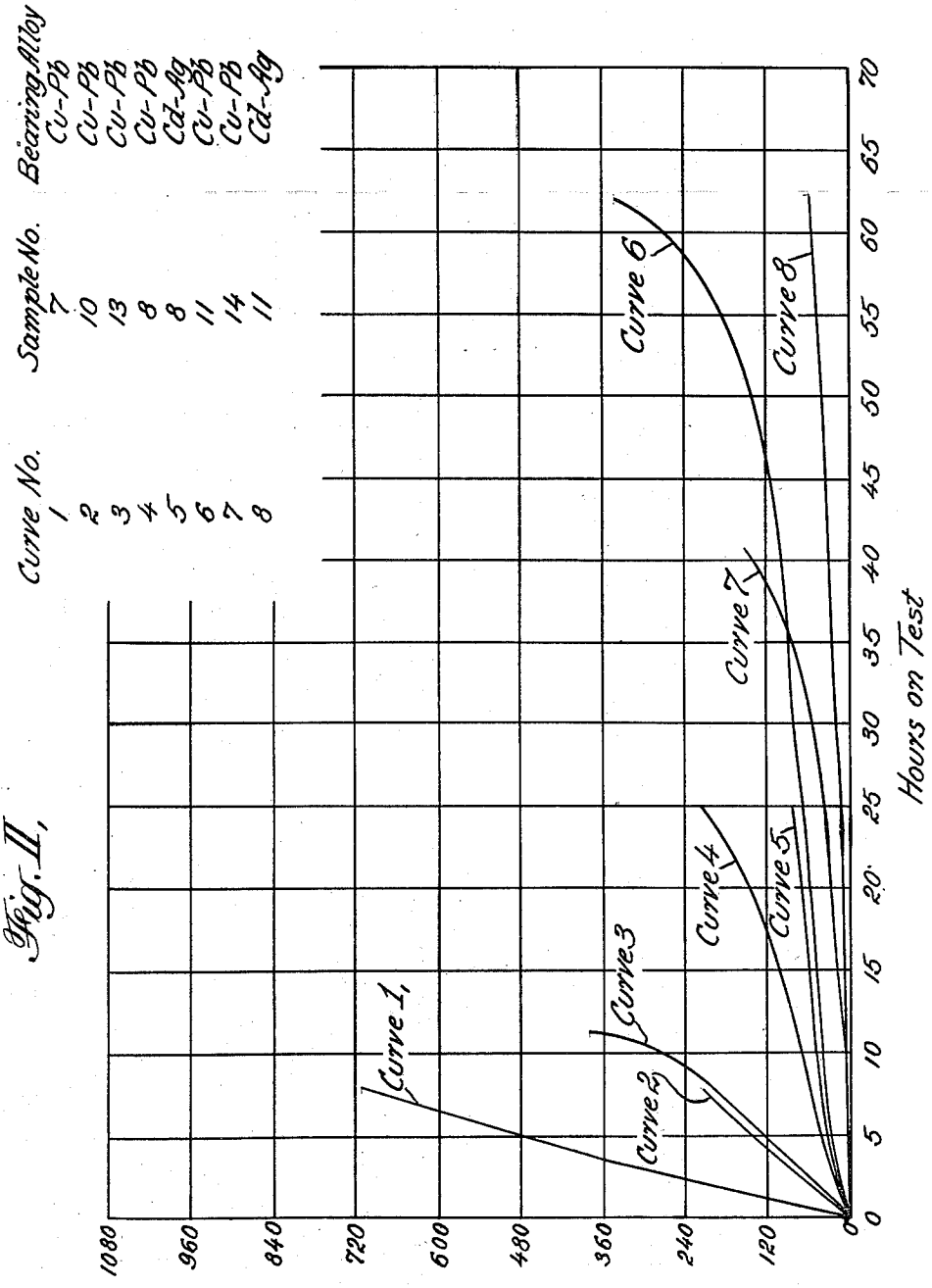



Fig. II,

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LUBRICATING OIL COMPOSITION

Filed April 5, 1941 7 Sheets-Sheet 3

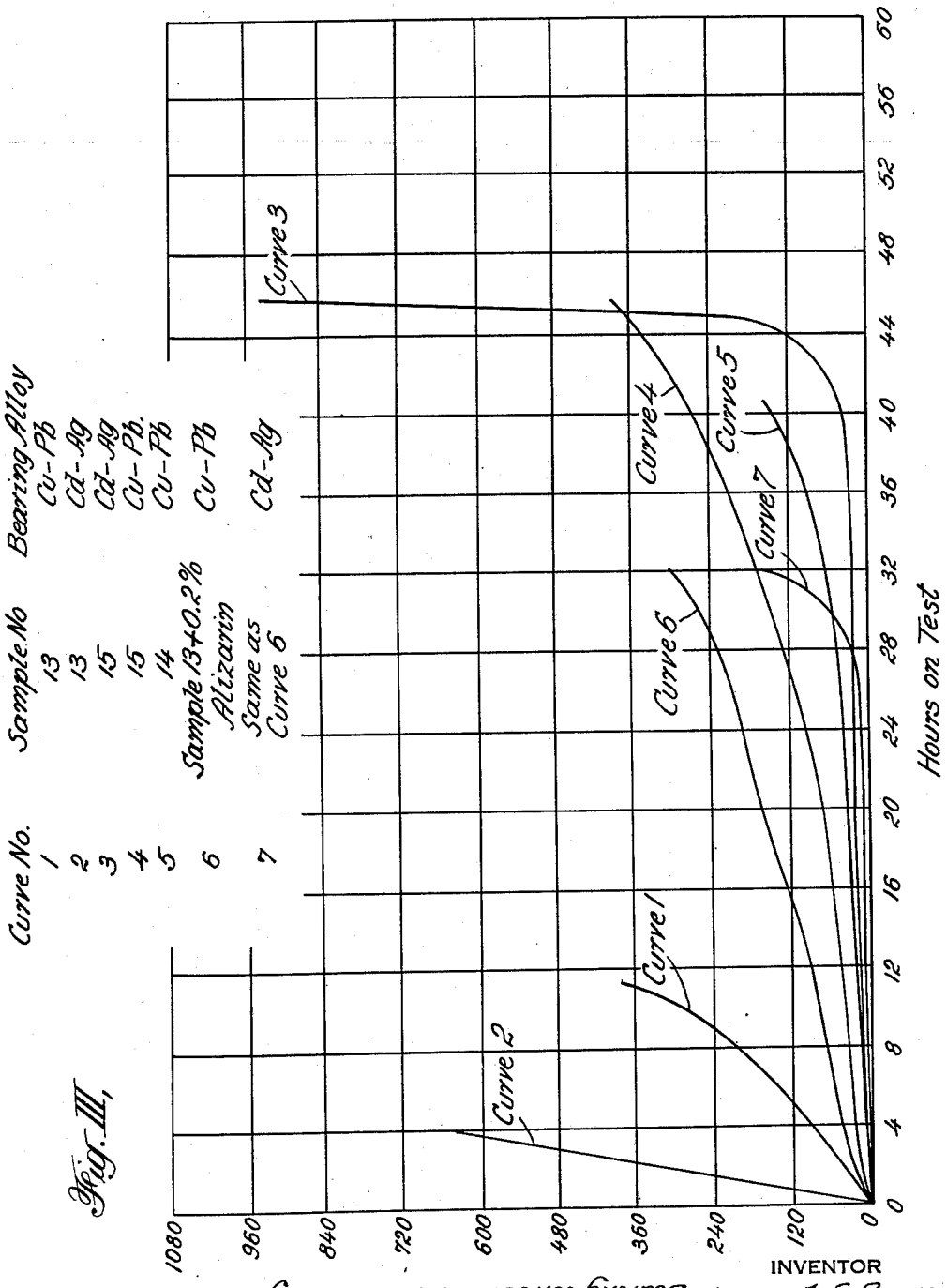



Fig. III.

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June 6, 1944. L. E. BEARE 2,350,489

LUBRICATING OIL COMPOSITION

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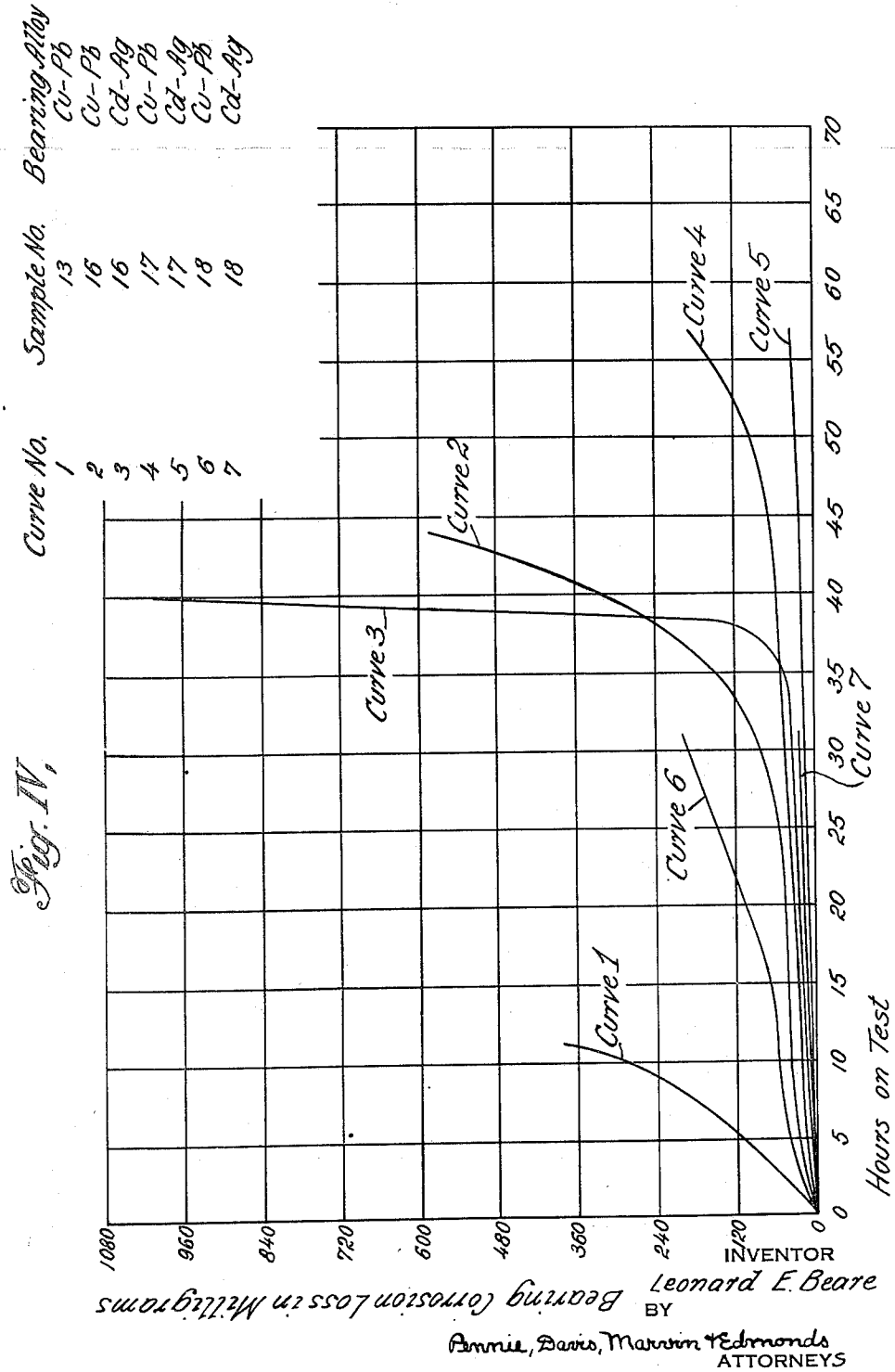



Fig. IV.

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June 6, 1944. L. E. BEARE 2,350,489

LUBRICATING OIL COMPOSITION

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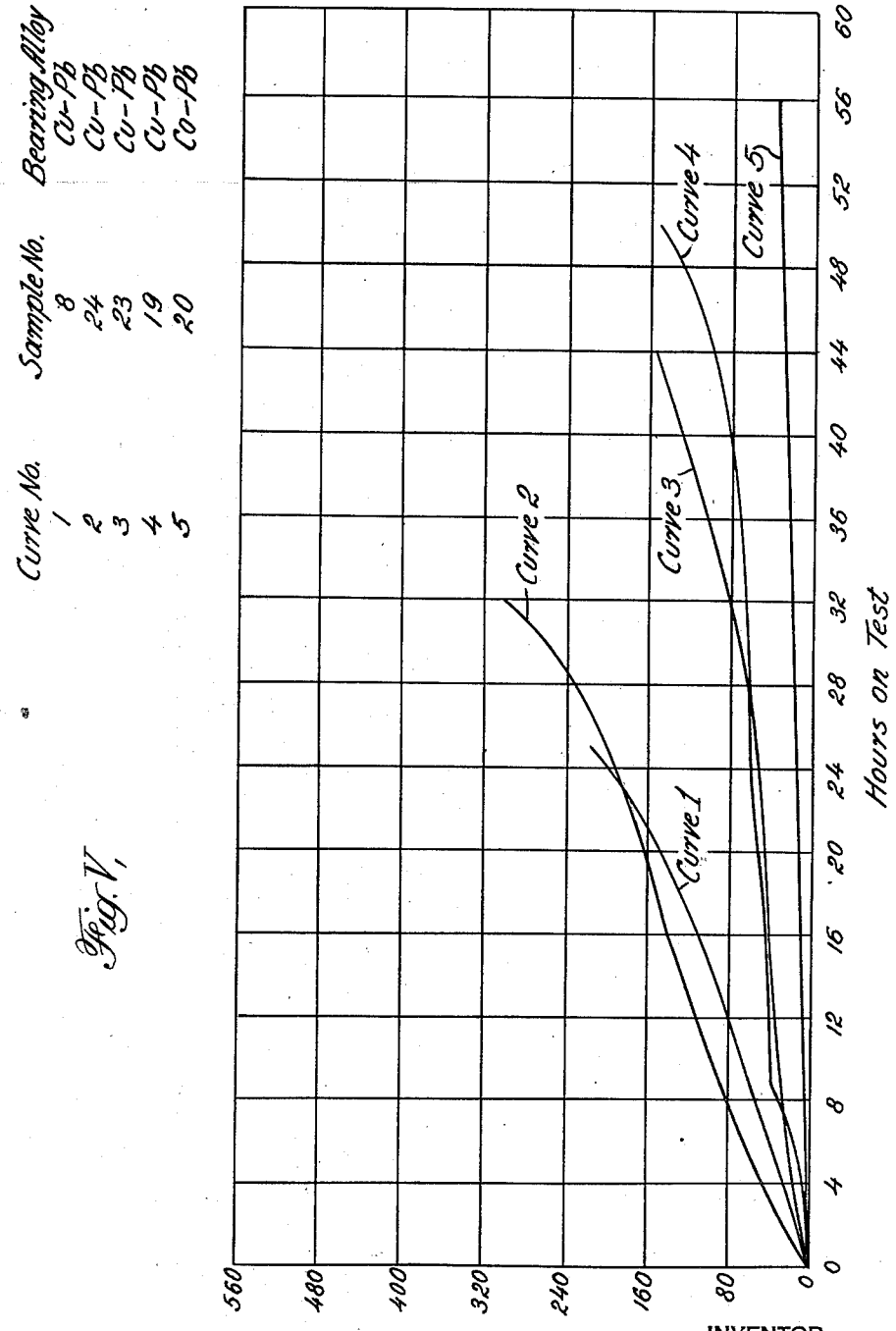



Fig. V.

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LUBRICATING OIL COMPOSITION

Filed April 5, 1941 7 Sheets-Sheet 6

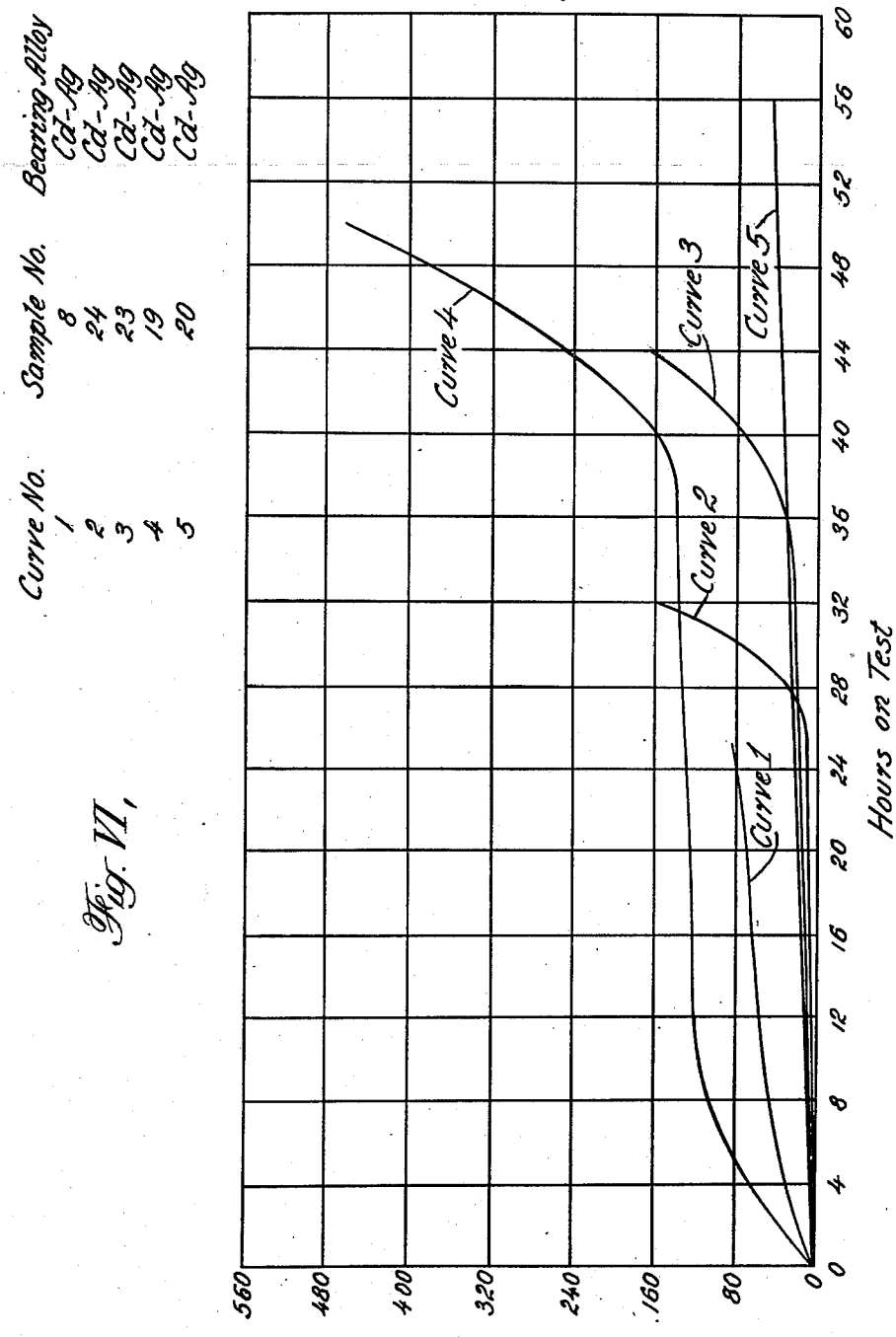



Fig. VI,

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June 6, 1944. L. E. BEARE 2,350,489

LUBRICATING OIL COMPOSITION

Filed April 5, 1941 7 Sheets-Sheet 7

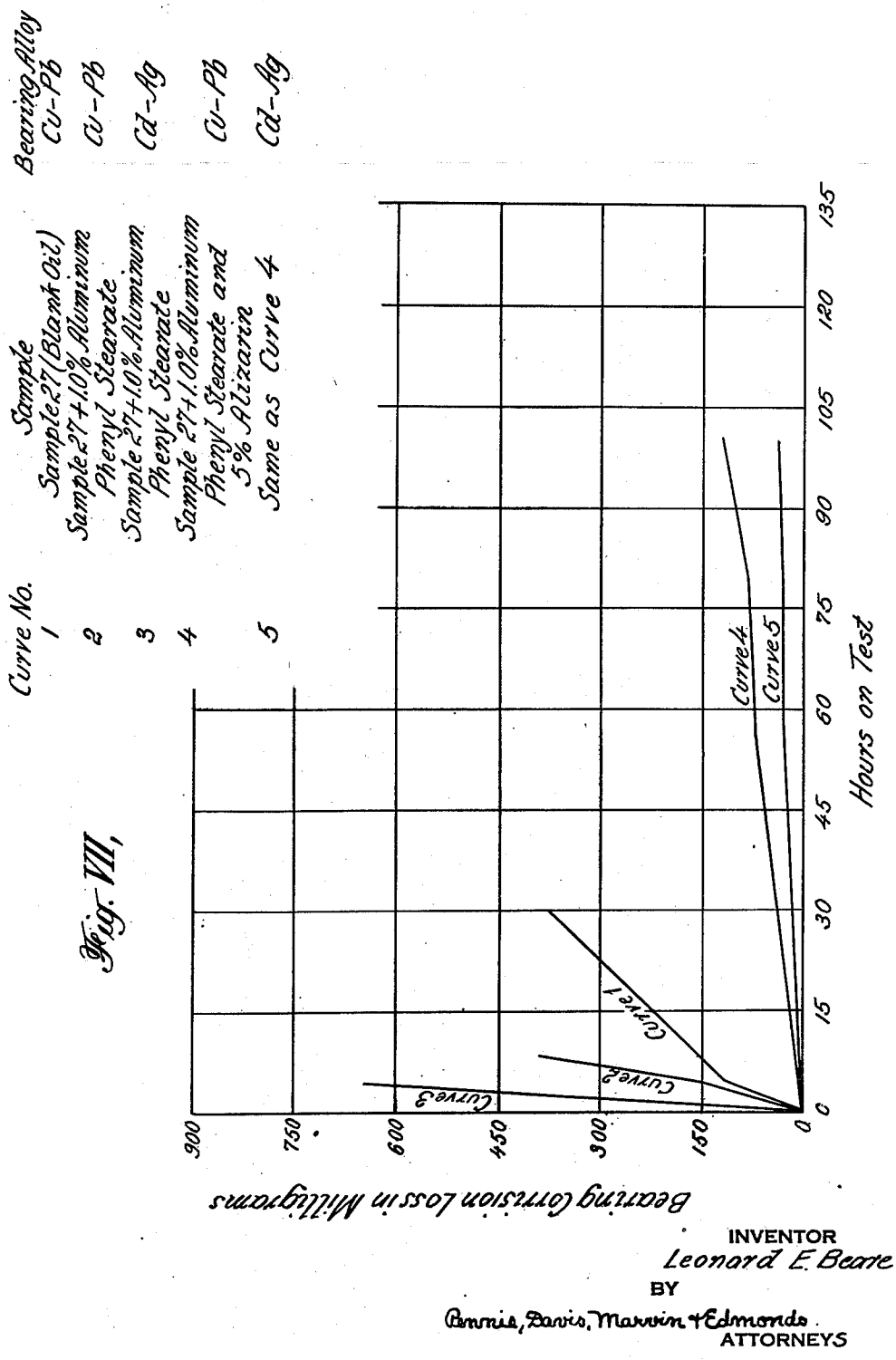



Fig. VII,

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Patented June 6, 1944 2,350,489

# UNITED STATES PATENT OFFICE

2,350,489

## LUBRICATING OIL COMPOSITION

Leonard E. Beare, Lansing, Ill., assignor to Sinclair Refining Company, New York, N. Y., a corporation of Maine

Application April 5, 1941, Serial No. 387,014

12 Claims. (Cl. 252—37)

This invention relates to improvements in lubricating oil compositions. It relates more particularly to compounded petroleum lubricating oils containing one or more addition agents which impart corrosiveness to the compounded oils but wherein the corrosiveness of the compounded oil is substantially inhibited by the addition thereto of relatively small proportions of alizarin or of the fatty acid sters of alizarin or mixtures thereof.

The trend of development in modern machinery, notably in Diesel and other internal combustion engines, has imposed increasing burdens on the oil used for their lubrication, particularly with respect to operating temperatures and pressures. The useful operating life of a lubricating oil in such service 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 of the measures of thermal stability is resistance to oxidation and a consequent tendency to form sludge but in another aspect the effect of thermal instability is determined not only by the extent of oxidation or decomposition but also by the character of the products of such decomposition and oxidation and by the extent and location within the engine or the like of the deposits of such products.

In the Diesel type of engine, for example, the high temperature to which the lubricating oil is subjected, particularly at the top of the stroke, frequently causes deposition of sludge and carbon in the groove before and behind one or more of the piston rings. Consequent sticking of the rings rapidly deprives the engine and cylinder wall of proper lubrication, inducing excessive wear and frequently scoring of the cylinder wall. For satisfactory lubrication, it is essential that this condition be avoided.

Another essential characteristic of lubricating oil to be used under severe conditions is the ability to maintain a satisfactory lubricating film between the bearing surfaces at the high temperatures and pressures encountered. This property of the lubricant is usually characterized as film strength.

The operating conditions in certain types of machinery are so severe that the natural characteristics of petroleum lubricating oils have been found inadequate for the satisfactory lubrication of these machines over extended periods. In such instances it has been necessary to supplement or alter the natural characteristics of the lubricating oil by the addition of one or more agents, commonly referred to as addition agents.

Various metal soaps, notably soaps of aromatic stearic acids such as phenyl stearic acid or mixtures comprising such soaps. have been found to be particularly effective addition agents.

For instance, the remarkable advantages derived from the addition of relatively small amounts of certain metal phenyl stearates or mixtures of such phenyl stearates with phenyl stearic acid or stearic acid or metal stearates to petroleum lubricating oils have been related in United States Letters Patent No. 2,081,075, 2,095,538 and 2,180,697 to Arnold C. Vobach.

Lubricating oils compounded with such material, as described in said patents have a high solvent capacity for sludge of a character formed by oxidation or decomposition of petroleum lubricating oils and render deposits of sludge and carbon within the engine soft and friable rather than hard and coherent and appear to disintegrate and remove such deposits as are formed so that the formation on the piston of carbon deposits hard enough and coherent enough to involve sticking of the rings is materially retarded, if not avoided.

However, lubricating oil compositions containing such addition agents have been found to be decidedly corrosive toward some of the alloy bearings, notably copper-lead and cadmium-silver alloy bearings, commonly used in internal combustion engines.

I have discovered that the corrosive action of such lubricating oil compositions is substantially inhibited by the addition thereto of relatively small proportions of alizarin or the fatty acid esters of alizarin; for example, alizarin stearates, such as alizarin monostearate and alizarin distearate.

Not only are the bearings or the like protected from destructive corrosion, in accordance with my invention, but other desirable characteristics of the lubricating oil compound are materially improved, as will appear from the following detailed description thereof.

As previously noted, certain metal phenyl stearates and mixtures thereof have proven to be very effective addition agents in lubricating oils. The advantages derived from the use of and the method of preparing calcium phenyl stearate or mixtures of calcium phenyl stearate and unsaponified phenyl stearic acid or calcium stearate or both and the method of compounding these addition agents in lubricating oils are fully described in the previously referred to Patent No. 2,081,075.

Also, in the above-referred-to Patent No. 2,095,538, there are described the advantages derived from the use of and the method of preparing and compounding with lubricating oils, calcium phenyl stearate or mixtures of calcium phenyl stearate and calcium stearate modified by the inclusion of the equivalent of 7–20% stearic or palmitic acid or mixtures thereof.

A further advantageous type of calcium phenyl stearate addition agent is one containing an amount of calcium greater than that corresponding to the neutral soap. It may be prepared, for

example, by neutralizing phenyl stearic acid with such an excess of lime as results in the production of a soap mixture consisting of one part of basic calcium phenyl stearate to four parts of neutral calcium phenyl stearate. This mixture of neutral and basic soap is herein designated "basic calcium phenyl stearate."

The calcium phenyl stearate addition agent wherein the phenyl stearic acid or mixture of phenyl stearic acid and fatty acid are completely neutralized, no excess of lime over that corresponding to the neutral soap being present, is herein designated "neutral calcium phenyl stearate." That in which the phenyl stearic acid or mixture of phenyl stearic acid and fatty acid are not completely neutralized but contain an equivalent of 7–20% excess phenyl stearic acid or palmitic or stearic acid are herein designated "acid calcium phenyl stearate."

References herein to phenyl stearic acid or to calcium phenyl stearate are to be interpreted as meaning the material or materials so designated in the above-referred-to patents to Vobach.

Each of these calcium phenyl stearate addition agents, i. e. acid, neutral and basic, has been found to be very effective with respect to carbon deposition, as above noted. However, lubricating oil compounded with either has a decided corrosive action toward the alloy bearings heretofore mentioned.

Also, other metal phenyl stearates have been found to be effective addition agents, notably aluminum phenyl stearate. Its use and advantages, together with the method of preparation, are described in the previously mentioned Patent No. 2,180,697 and reference herein to aluminum phenyl stearate is intended to mean the material so designated in that patent. Lubricating oil compounded with aluminum phenyl stearate likewise has a tendency to attack alloy bearings of the type referred to above.

In accordance with my present invention, the corrosive action of such lubricating oil compounds is substantially retarded or even eliminated without destroying the desirable characteristics imparted to the compound by the corrosion-inducing addition agents. This is accomplished by incorporating in the lubricating oil composition relatively small proportions of one or more of the previously named corrosion-inhibiting compounds.

Alizarin is relatively insoluble in a mineral oil at normal temperatures, its solubility under such conditions ranging from about .02% in highly paraffinic oil to about .05% in naphthenic oils. Alizarin stearates are more soluble and for this reason their use is in some cases preferable to alizarin. However, other conditions may influence the choice of one over the other as the characteristics of the resulting lubricating oil compounds differ in some respects.

The alizarin under some conditions appears to be more effective than the alizarin stearates in inhibiting corrosion but in the presence of calcium phenyl stearates there is a tendency for the alizarin to precipitate out of the oil, probably as calcium alizarate. Alizarin stearates are more stable under such conditions.

Also, alizarin stearates appear to have the added function of an anti-oxidant in calcium phenyl stearate lubricating oil compounds. However, they do not appear to have this function in uncompounded oils, though alizarin does. Further, though alizarin definitely inhibits corrosion in aluminum phenyl stearate compounds, it does not appear to function as an anti-oxidant in such compound.

The invention will be further described by specific illustration of applications of the principles thereof and of the beneficial results so obtained.

The effect of the addition of alizarin stearate to acid and basic calcium phenyl stearate-lubricating oil compounds is illustrated by the following Tables I and II in which are recorded the results of tests of acid and basic calcium phenyl stearate compounds, respectively, both with and without the addition of alizarin stearate. The mineral oil constituent of each such compound tested was a South Texas pale oil (from a Gulf Coast crude) having a viscosity of about 500 seconds at 100° F. Saybolt Universal and boiling 10% up to 700° F. and 90% up to 900° F. approximately.

As to each sample referred to in Table I, 1.33% of acid calcium phenyl stearate was compounded with the mineral oil and as to each of those referred to in Table II, 1.33% of basic calcium phenyl stearate was compounded with the mineral oil. Alizarin monostearate was included in these compounds in the proportions indicated.

*Table I*

| | Sample No. | |
|---|---|---|
| | 1 | 2 |
| Alizarin monostearate.....per cent.. | None | 0.75 |
| Total oxygen absorbed per 100 grams of compounded oil.....cc.. | 3,502 | 27 |
| Bearing metal loss, copper-lead.....milligrams.. | 23.8 | 3.9 |

*Table II*

| | Sample No. | | | |
|---|---|---|---|---|
| | 3 | 4 | 5 | 6 |
| Alizarin monostearate..per cent.. | None | 0.10 | 0.20 | 0.75 |
| Total oxygen absorbed per 100 grams of compounded oil...cc.. | 2,560 | 1,350 | 12 | 37 |
| Bearing metal loss, copper-lead milligrams.. | 26.5 | 15.6 | 6.0 | 2.9 |

The amount of oxygen absorption recorded in the above tables is at normal temperature and pressure and was determined by the true oxidation test—the bearing metal, in this case copper-lead alloy, being present in the oil during the test. The test was in each case conducted at a temperature of 300° F. and the duration of the test was 120 minutes. The bearing metal losses shown in the above tables were determined from the weight of the pieces of bearing metal present in the true oxidation test before and after the test.

The alizarin monostearate used in compounding these samples was prepared by refluxing 5 parts of dry powdered alizarin in 50 parts of toluene and adding 6 parts of stearyl chloride drop by drop over a period of ten hours. The extremely slow addition of the latter was an extra precaution against the possible formation of alizarin distearate, but is not believed to be essential.

The alizarin went completely into solution soon after all of the stearyl chloride had been added. This was assumed to indicate the substantial completion of the reaction as only a small fraction of alizarin is soluble in the toluene. The mixture was refluxed for an additional ten hours as a precaution against any lumps remaining un-

dissolved and the toluene then distilled off to the point at which foaming occurred. The product was then air-dried at 150–200° F. until free from any odor of toluene. The yield was 10.4 parts of alizarin stearate which is substantially the theoretical yield.

The alizarin stearate product was a brown, brittle waxy solid, melting at about 150–160° F. Its analysis showed a trace of chlorine (0.08%) and a small amount of sulfur (0.12%).

The effect of the presence of varying proportions of alizarin monostearate on the rate of oxygen absorption by the calcium phenyl stearate compounded oils, Samples 1 to 6, inclusive, under the above-described conditions, is graphically illustrated by Figure I of the drawings in which the amount of oxygen absorbed in cubic centimeters, measured at normal temperature and pressure conditions, per hundred grams of the compounded oil, is plotted against time expressed in minutes. From this chart it will be observed that the addition of 0.1% of alizarin monostearate to the basic calcium phenyl stearate compounded oil considerably prolonged the period within which oxygen absorption was relatively inactive. In other words, it substantially inhibited oxidation for a considerable period of time. For example, within the first hour of the test, less than 100 cubic centimeters of oxygen were absorbed. The addition of larger proportions of alizarin stearate still further increased the period of relative inactivity, 0.2% being even more effective than 0.75%. Such period of relative inactivity of the compounded lubricating oil, with respect to oxidation or corrosion, is herein referred to as the induction period.

The effect of the addition of alizarin monostearate to calcium phenyl stearate compounded oils is further illustrated by Table III wherein there is tabulated data concerning tests in which varying proportions of the alizarin stearate were added to acid calcium phenyl stearate compounded oils of the type and composition previously described.

*Table III*

| | Sample No. | | |
|---|---|---|---|
| | 7 | 8 | 9 |
| Calcium phenyl stearate, per cent | 1.33 | 1.33 | 1.33 |
| Alizarin monostearate, do | None | 0.75 | 0.5 |
| Indiana sludging time, hours | 27 | 25 | 26 |
| 1% A. S. T. M.—naphtha insoluble, do | 43 | 40 | 42 |
| Viscosity at 210° F.—end of 50 hours | 79 | 70 | 73 |
| Viscosity rise at 210° F. in 50 hours | 22.1 | 14.3 | [1] 17 |
| 100 milligram induction period: | | | |
| Copper-lead alloy, hours | 1 | 14.5 | ..... |
| Cadmium-silver alloy, do | .5 | 25 | ..... |

[1] Approximate.

The Indiana sludging time noted in Table III and elsewhere herein is expressed in terms of the time required to form 10 milligrams of sludge per 10 grams of material tested in a glass container at 341° F. by the Indiana oxidation test described in the Society of Automotive Engineers Journal 34, page 173 (1934). The 1% A. S. T. M. naphtha insoluble figure is the time required to produce, under the same conditions, 1% of material which is insoluble in A. S. T. M. naphtha. The viscosity figures are in seconds Saybolt Universal and were taken after a period of treatment by the said Indiana oxidation test.

The 100 milligram induction period is the time required for a loss of 100 milligrams in weight of the particular alloy bearing in contact with the compounded lubricating oil maintained at 250° F. as determined by the Chrysler bearing corrosive test machine.

Similar data, but with respect to neutral calcium phenyl stearate compounded oils containing different proportions of neutral calcium phenyl stearate and alizarin monostearate, is presented in Table IV:

*Table IV*

| | Sample No. | | |
|---|---|---|---|
| | 10 | 11 | 12 |
| Calcium phenyl stearate, per cent | 1.33 | 1.33 | 0.67 |
| Alizarin monostearate, do | None | 0.75 | 0.5 |
| Indiana sluding time, hours | 30 | 24 | 15 |
| 1% A. S. T. M.—naphtha insoluble, do | 44 | 65 | 40 |
| Viscosity at 210° F.—end of 50 hours | 74 | 65 | 72 |
| Viscosity rise at 210° F. in 50 hours | 13.7 | 11.6 | ..... |
| 100 milligram induction period: | | | |
| Copper-lead alloy, hours | 3.5 | 42.0 | 35.5 |
| Cadmium-silver alloy, do | .5 | 62.0 | 39.5 |

Data corresponding to that presented in the foregoing tables, but with respect to basic calcium phenyl stearate compounded oil comprising the indicated proportions of basic calcium phenyl stearate and alizarin monostearate in the previously described South Texas pale oil, is presented in Table V, following:

*Table V*

| | Sample No. | | | | | |
|---|---|---|---|---|---|---|
| | 13 | 14 | 15 | 16 | 17 | 18 |
| Calcium phenyl stearate, per cent | 1.33 | 1.33 | 1.33 | 0.67 | 1.0 | 2.0 |
| Alizarin monostearate, per cent | None | 0.75 | 0.5 | 0.5 | 0.68 | 0.68 |
| Indiana sludging time, hours | 36.5 | 30.0 | 32.5 | 9.0 | 25.0 | 40.0 |
| 1% A. S. T. M. naphtha insoluble, hours | 49.0 | 47.0 | 45.0 | 39.0 | 60.0 | 60.0 |
| Viscosity at 210° F.—end of 50 hours | 73.8 | 66.0 | 71.0 | 68.0 | 65.0 | 65.0 |
| Viscosity rise at 210° F. in 50 hours | 17.6 | 13.2 | 17.7 | 15.0 | 11.0 | 11.0 |
| 100 milligram induction period: | | | | | | |
| Copper-lead alloy, hours | 4.0 | 36.5 | 24.5 | 31.5 | 51.0 | 20.0 |
| Cadmium-silver alloy, hours | 0.5 | ..... | 41.5 | 36.5 | 57.0 | 31.0 |

Thus, it appears that by the inclusion of various proportions of alizarin stearate in calcium phenyl stearate lubricating oil compositions, comprising either acid, neutral or basic calcium phenyl stearate, the induction period, i. e. the time required for the initial loss of 100 milligrams of bearing metal by corrosion, is markedly increased without in most instances greatly affecting detrimentally the sludging characteristics of the compounded oil.

In each instance the Indiana sludging time was somewhat reduced and in some cases the 1% naphtha insoluble time was slightly reduced while in others, notably Samples 11, 17 and 18, the latter was materially increased. However, in every instance, except Sample 15, there was a decided reduction in viscosity rise during the 50 hour test period.

Corrosion is also inhibited by the addition of alizarin to the calcium phenyl stearate compounded oils. Where 0.2% alizarin was compounded with a basic calcium phenyl stearate compounded oil, such as described above, comprising 1.33% basic calcium phenyl stearate, the 100 milligram induction period with copper-lead

bearings was increased to 11 hours and, with cadmium-silver, was increased to 30½ hours. Alizarin, as previously noted, is only slightly soluble in uncompounded naphthenic base oil. However, it is soluble to the extent of about .2% in these compounded oils containing 1.33% calcium phenyl stearate, though it is relatively less stable therein than is alizarin stearate and has a tendency to form a precipitate at temperatures in the range from 250° to 350° F.

The advantages with respect to inhibition of bearing corrosion derived from the incorporation of relatively small proportions of alizarin stearate in calcium phenyl stearate lubricating oil compounds is graphically illustrated by Figs. II to IV, inclusive, of the drawings whereon bearing corrosion loss in milligrams, as determined by the Chrysler bearing corrosion test machine, is plotted against time in hours. These tests were conducted at 2540 R. P. M., 250° F. oil feed temperature and 2700 pounds load.

On Fig. II is shown the rate of bearing corrosion losses of copper-lead and cadmium-silver alloy bearings when using acid, basic and neutral calcium phenyl stearate compounded oils, respectively, and the decided decrease in corrosion rate in each where alizarin stearate is incorporated in the compounded oil. It will be observed that the induction period was in each instance materially prolonged by the addition of alizarin monostearate to the lubricating oil composition.

The corrosion-inhibition obtained by the incorporation of various proportions of alizarin stearate or alizarin in basic calcium phenyl stearate compounded oils containing 1.33% basic calcium phenyl stearate is shown on Fig. III of the drawings. The effect of varying the proportions of calcium phenyl stearate and alizarin monostearate in the basic calcium phenyl stearate compound is similarly shown on Fig. IV of the drawings.

It was observed that at relative concentrations greater than 0.75% alizarin monostearate to 1.33% calcium phenyl stearate a dark red precipitate started to form at temperatures above 450° F. but that below this ratio no precipitate was formed.

In order more carefully to appraise the products of my invention under operating conditions, certain of the samples referred to above were subjected to test on a one-cylinder Caterpillar Diesel engine. This test comprised a six hour break-in period followed by 100 hours of operation at 850 R. P. M. and 75 pounds per square inch brake mean effective pressure at a power output of 16.7 brake horsepower. When subjected to this test Sample 13 above, which contained no alizarin stearate, showed a copper-lead alloy bearing corrosion loss of 2860 milligrams while the identical compound to which 0.75% alizarin monostearate was added showed no perceptible bearing corrosion loss. Samples 14 and 16 above, when subjected to this test under more severe conditions (the hot box test), showed, respectively, 190 and 50 milligrams bearing corrosion loss. Comparable piston conditions with respect to carbon deposition at the end of the test were obtained in each case.

It is sometimes desirable to include in the lubricating oil compound of my invention relatively small proportions of a solubilizer such as lauryl alcohol. The lauryl alcohol has a stabilizing influence on mineral oil compounds comprising calcium phenyl stearate and alizarin or alizarin stearates. The proportion of lauryl alcohol so employed is generally in the range of approximately 0.5 to 1.0% by weight.

I have discovered that alizarin distearate is generally more stable in lubricating oil compounds containing calcium soaps than is alizarin or the monostearate of alizarin. The distearate appears to equal the monostearate in corrosion-inhibiting power but has the advantage over the monostearate that there is a higher critical ratio of the distearate to calcium phenyl stearate permissible before precipitation occurs on heating. Similarly, alizarin alone, in concentrations up to 0.2% in a lubricating oil compounded with basic calcium phenyl stearate, does not cause a precipitate to form on heating. However, on heating a calcium phenyl stearate compounded oil containing both alizarin and alizarin distearate, a slight precipitate may occur.

Illustrations of specific proportions of calcium phenyl stearate, lauryl alcohol and alizarin or alizarin stearates which have been found to give particularly advantageous results when compounded with the previously described lubricating oil appear in the following Table VI in which Sample No. 21, which contains no alizarin or alizarin stearate, is included for comparison:

*Table VI*

| | Sample No. | | | | | |
|---|---|---|---|---|---|---|
| | 19 | 20 | 21 | 22 | 23 | 24 |
| Calcium phenyl stearate per cent | 1.33 | 0.67 | 1.33 | 0.67 | 1.33 | 1.33 |
| Lauryl alcohol do | 1.0 | None | 0.5 | 0.5 | 1.0 | 1.0 |
| Alizarin monostearate per cent | 0.75 | 0.5 | None | 0.375 | None | None |
| Alizarin distearate do | None | None | None | None | 0.75 | None |
| Alizarin do | None | None | None | None | None | 0.2 |
| Indiana sludging time hours | 28 | 15 | 36.5 | ------ | ------ | 26 |
| 1% A. S. T. M. naphtha insoluble hours | 45 | 40 | 49 | ------ | ------ | 39 |
| Viscosity at 210° F.—end of 50 hours | 69 | 72 | 73.8 | ------ | ------ | 69 |
| Viscosity rise at 210° F. in 50 hours | 17.3 | 17.6 | 17.6 | ------ | ------ | 14.2 |
| 100 milligram induction period: | | | | | | |
| Copper-lead alloy hours | 45 | 56+ | 4 | ------ | 36 | 11 |
| Cadmium-silver alloy hours | 7 | 56+ | 0.5 | ------ | 41.5 | 30.5 |

In compounding the above-referred-to samples designated No. 19 and No. 20, the neutral calcium phenyl stearate was used while Samples Nos. 21 to 24, inclusive, were compounded with basic calcium phenyl stearate.

The corrosive characteristics of various compounds included in Table VI, determined as in the tests previously described, are graphically illustrated on Figs. V and VI of the drawings with respect to copper-lead and cadmium-silver alloy bearings, respectively—including for ready comparison the curve for Sample 8 previously identified.

Though the combined use of alizarin and alizarin distearate increases the tendency to form a precipitate over that present when the distearate is used alone, this tendency is not particularly objectionable in most cases. Further, the presence of alizarin appears to have an activating effect upon the alizarin distearate which increases the corrosion-inhibiting ability of the distearate. For example, a compounded oil consisting of 1.33% basic calcium phenyl stearate, 1% lauryl alcohol and 1% alizarin distearate in the above-mentioned South Texas pale oil, when subjected to the "hot box" test in a standard one-cylinder Diesel Caterpillar test engine, resulted in a cop-

per-lead alloy bearing corrosion loss of 105 milligrams. In a similar compounded oil wherein the alizarin distearate proportion was reduced to 0.75% and 0.1% of alizarin added, the copper-lead alloy bearing corrosion loss was only 50 milligrams. In both cases the piston and ring condition was excellent with respect to carbon deposition. However, when the proportion of alizarin distearate in this compound was reduced to only 0.5%, the bearing corrosion loss increased decidedly.

In the regular Caterpillar one-cylinder engine test, the copper-lead alloy bearing corrosion losses, using the alizarin-free Samples No. 7 and No. 13, were, respectively, 11,900 milligrams and 2860 milligrams while that for Sample No. 8, which contained alizarin monostearate, was 420 milligrams. In the more severe hot-box Caterpillar engine test, these losses for compounded oils containing alizarin or alizarin stearate were as follows:

70 milligrams for Sample No. 19
40 milligrams for Sample No. 20
65 milligrams for Sample No. 22
170 milligrams for Sample No. 23
100 milligrams for Sample No. 24

For the purpose of more clearly illustrating the advantages derived from my invention, the base lubricating oil used in the foregoing specific examples has in each case been a South Texas pale oil such as previously identified. However, it will be understood that my invention is not limited to a particular lubricating oil but is applicable to lubricating oils generally.

For example, a mixture of 62.5% phenol-solvent-treated neutral oil and 37.5% slightly solvent-treated bright stock from a Pennsylvania crude compounded with 1.33% neutral calcium phenyl stearate, 0.75% alizarin distearate and 0.1% alizarin caused a copper-lead alloy bearing corrosion loss in the above-mentioned hot box Caterpillar engine test of only 60 milligrams. Its Indiana sludging time was 108 hours; its 1% A. S. T. M. naphtha insoluble was 127 hours; and its viscosity rise at 210° F. for 50 hours and 100 hours was, respectively, 4.9 and 24.7 seconds. Similarly a mixture of 75% of the previously mentioned Texas pale oil and 25% of an acid-treated high sulfur lubricating oil fraction compounded with 1.33% basic calcium phenyl stearate, 1.0% lauryl alcohol, 0.75% alizarin distearate and 0.1% alizarin, when tested on a four-cylinder Caterpillar test engine (hot box test) resulted in an average copper-lead alloy bearing corrosion loss of only 43 milligrams. In this test, the piston skirt was clean, the rings were free and there was only a very light carbon deposit in the top groove. Its 100 milligram induction period with copper-lead alloy bearings was 40 hours.

Nor is the utility of my invention limited to calcium phenyl stearate lubricating oil compounds. I have found it of decided advantage where the calcium phenyl stearate is supplemented by still further addition agents and also where the calcium phenyl stearate is replaced by other corrosion-inducing addition agents. For example, decidedly beneficial results have been obtained by compounding with the previously referred to South Texas pale oil 1.33% basic calcium phenyl stearate, 1.0% lauryl alcohol, 0.75% alizarin distearate, 0.1% alizarin and 2.0% sulfurized sperm oil. This compound had a 100 milligram induction period with copper-lead alloy bearings of 47 hours. On a four-cylinder Caterpillar test engine (hot box test) the average copper-lead alloy bearing corrosion loss was 117 milligrams and the piston condition with respect to carbon deposit was good.

Similarly, a compound consisting of South Texas pale oil, 4% of a solution in mineral oil of the calcium soap of oxidized mineral oil about equal in calcium content to 1.33% of calcium phenyl stearate, 0.75% alizarin distearate, 0.1% alizarin and 2% sulfurized sperm oil was found to have a 100 milligram copper-lead alloy bearing induction period in excess of 51 hours. In a four-cylinder Caterpillar test engine hot box test, using this latter compound, the copper-lead alloy bearing corrosion loss was 55 milligrams and the piston condition with respect to carbon deposition was excellent.

I will further illustrate my invention with respect to lubricating oil compounds wherein aluminum phenyl stearate or phenyl stearic acid is substituted for the calcium phenyl stearate previously referred to. With aluminum phenyl stearate, the above-mentioned tendency for the formation of a precipitate under certain conditions is substantially reduced and a more stable composition under such conditions is obtained.

The application of my invention with respect to the inhibition of oxidation and corrosion by the addition of alizarin to aluminum phenyl stearate or free phenyl stearic acid lubricating oil compounds is illustrated by the following Table VII. In the compounded oils illustrated, the lubricating oil constituent was the previously mentioned South Texas pale oil. Tests of samples containing no alizarin are included for comparison:

*Table VII*

| | Sample No. | | | | | | |
|---|---|---|---|---|---|---|---|
| | 25 | 26 | 27 | 28 | 29 | 30 | 31 |
| Aluminum phenyl stearate...per cent... | None | 1.0 | None | None | None | None | None |
| Phenyl stearic acid per cent... | None | None | None | 1.0 | 1.0 | 1.9 | 5.0 |
| Alizarin.....do.... | None | 0.3 | None | None | 0.3 | 0.3 | 0.1 |
| Total oxygen absorbed per 100 grams of compounded oil: | | | | | | | |
| 300 min. at 300° F. cc.. | 166 | 716 | ------ | ------ | ------ | ------ | ------ |
| 120 min. at 300° F. cc.. | ------ | ------ | 208 | 637 | 99 | 104 | 404 |
| Bearing metal in oil.. | No | Yes | Yes | Yes | Yes | Yes | Yes |
| Bearing loss—copper-lead.....mgs.. | (1) | −0.2 | 2.3 | 49.8 | 0.3 | 0.0 | 6.7 |

[1] Not determined.

Also, a compounded oil consisting of the South Texas pale oil with 1% aluminum phenyl stearate and 0.5% alizarin showed no appreciable signs of corrosion of copper-lead alloy bearings by the Chrysler bearing corrosion test.

Though alizarin is only slightly soluble in lubricating oil at room temperatures, it was in complete solution at the temperatures of these tests.

Lubricating oil compounds containing aluminum phenyl stearate or phenyl stearic acid are normally decidedly corrosive but, as appears from the above-tabulated results, the inclusion of very small proportions of alizarin materially inhibits corrosion. It appears that the alizarin acts as a true corrosion-inhibitor in such compounded oils. However, alizarin does not appear to act as an anti-oxidant in the compounds of Table VII as the oxidation rate was reduced by the addition of alizarin only to about that of the base oil with-

out the bearing metal present. For instance, a further test of the compounded oil containing 1.0% phenyl stearic acid but no alizarin showed a metal loss of 49.8 milligrams due to corrosion and a total oxygen absorption of about 640 c. c. as compared with 90 c. c. for the oil without the metal present. Also, Sample 31 above had a reduced oxidation rate during the first part of the test, but closely approximated that of the alizarin-free compound during the latter part of the oxidation period.

While I do not predicate my invention upon any theory of the action of alizarin, it would appear that alizarin protects the metal from the corrosive action of the addition agent. I have observed that metal which has previously been subjected to the action of compounded oils containing alizarin is much more resistant to corrosion than bearings which have not been so treated. For example, the same copper-lead alloy bearing used in the above test of Sample 30 was subsequently tested with Sample 28 and the resulting bearing corrosion loss was only 16 milligrams as compared with 49.8 milligrams loss of the bearing not so treated.

The corrosion-inhibiting power of alizarin with respect to normally corrosive compounded oils containing aluminum phenyl stearate is graphically illustrated by Figure VII of the drawings as to copper-lead and cadmium-silver alloy bearings. The curves for the alizarin-free oils are also included for ready comparison.

In addition to the advantages derived from my invention with respect to corrosion, the lubricating oil compound is frequently also improved with respect to its sludging and film-strength characteristics. For instance, the addition of 0.5% of alizarin monostearate to a compounded oil consisting of a highly refined steam-distilled double-solvent-treated residual oil from a Pennsylvania crude, having a viscosity of approximately 126 seconds at 210° F. Saybolt Universal and 1.25% of the methyl ester of a fatty acid produced by the oxidation of mineral oil, was found to improve materially the sludging characteristics of said compounded oil and substantially to decrease the viscosity rise of the compounded oil when subjected to the Indiana sludging test.

The film strength of Sample 13, for instance, was 18 pounds as determined by the Timken breakdown test. The addition of 0.2% alizarin increased this breakdown load to 22 pounds and the addition of 0.75% alizarin stearate, together with 0.2% alizarin, further increased the breakdown load to 24 pounds. Similarly, Sample 24 which contained 0.2% alizarin had a Timken breakdown load of 22 pounds as compared with 18 pounds for Sample 13.

I claim:

1. An improved lubricating oil compound comprising a petroleum lubricating oil, a metal soap of an aromatic fatty acid in an amount sufficient to impart corrosiveness to said lubricating oil compound and a compound of the group consisting of alizarin and fatty acid esters thereof in an amount sufficient to inhibit said corrosiveness.

2. An improved lubricating oil compound comprising a petroleum lubricating oil, a metal phenyl stearate in an amount sufficient to impart corrosiveness to said lubricating oil compound and a compound of the group consisting of alizarin and fatty acid esters thereof, in an amount sufficient to inhibit said corrosiveness.

3. An improved lubricating oil compound comprising a petroleum lubricating oil, phenyl stearic acid in an amount sufficient to impart corrosiveness to said lubricating oil compound and a compound of the group consisting of alizarin and fatty acid esters thereof in an amount sufficient to inhibit said corrosiveness.

4. An improved lubricating oil compound comprising a petroleum lubricating oil, calcium phenyl stearate in an amount sufficient to impart corrosiveness to said lubricating oil compound and a compound of the group consisting of alizarin and fatty acid esters thereof in an amount sufficient to inhibit said corrosiveness.

5. An improved lubricating oil compound comprising a petroleum lubricating oil, calcium phenyl stearate in an amount sufficient to impart corrosiveness to said lubricating oil compound and a compound of the group consisting of alizarin, alizarin monostearate and alizarin distearate in an amount sufficient to inhibit said corrosiveness.

6. An improved lubricating oil compound comprising a petroleum lubricating oil, aluminum phenyl stearate in an amount sufficient to impart corrosiveness to said lubricating oil compound and a compound of the group consisting of alizarin, alizarin monostearate and alizarin distearate in an amount sufficient to inhibit said corrosiveness.

7. An improved lubricating oil compound comprising a petroleum lubricating oil, phenyl stearic acid in an amount sufficient to impart corrosiveness to said lubricating oil compound and a compound of the group consisting of alizarin, alizarin monostearate and alizarin distearate in an amount sufficient to inhibit said corrosiveness.

8. An improved lubricating oil compound comprising a petroleum lubricating oil, calcium phenyl stearate in an amount sufficient to impart corrosiveness to said lubricating oil compound, a solubilizer and a compound of the group consisting of alizarin, alizarin monostearate and alizarin distearate in an amount sufficient to inhibit said corrosiveness.

9. An improved lubricating oil compound comprising a petroleum lubricating oil and an addition agent which imparts corrosiveness to said lubricating oil compound, the corrosiveness of the compounded oil being substantially inhibited by the addition of an effective amount of an alizarin stearate.

10. An improved lubricating oil compound comprising a petroleum lubricating oil and an addition agent which imparts corrosiveness to said lubricating oil compound, the corrosiveness of the compounded oil being substantially inhibited by the addition of effective amounts of alizarin and a fatty acid ester of alizarin.

11. An improved lubricating compound comprising a petroleum lubricating oil, a metal soap of an aromatic fatty acid in an amount sufficient to impart corrosiveness to said lubricating oil compound, the corrosiveness of the compounded oil being substantially inhibited by the addition of an effective amount of an alizarin stearate.

12. An improved lubricating oil compound comprising a petroleum lubricating oil, and a metal soap of an aromatic fatty acid in an amount sufficient to impart corrosiveness to said lubricating oil compound, the corrosiveness of the compounded oil being substantially inhibited by the addition of effective amounts of alizarin and a fatty acid ester of alizarin.

LEONARD E. BEARE.