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LUBRICANT

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This invention relates to lubricants and particularly to lubricating oils designed for heavy-duty service in internal combustion engines.

The production of a satisfactory lubricant, and particularly the production of a suitable lubricating oil for use in internal combustion engines, has presented a very difficult problem and has been the subject of a great deal of research. The problems presented are primarily due to deterioration of the lubricating oil under the conditions of use, which deterioration is primarily the result of oxidation accelerated by heat and the presence of the various metals in contact therewith. The products of such deterioration tend to form sludge, increase the viscosity of the oil, deposit on the parts of the engine and corrode sensitive bearing metals, such as those composed of alloys or mixtures of copper or lead, cadmium and nickel, silver and cadmium, and cadmium and tin. The increase in viscosity, the sludge and the deposits on the parts of the engine impede and may even arrest circulation of the lubricant. Corrosion of the sensitive bearing metals may proceed to such an extent as to cause mechanical failure of the engine. Accordingly, frequent and expensive changes of the oil, reconditioning of the engine and replacement of bearings are necessary. This is particularly true in so called heavy-duty service, that is, in the operation of trucks, buses, stationary and mobile power units and the like, where heavy loads are applied to the engines and deterioration of the oil is accelerated.

Many compounds have been proposed for addition to lubricating oils for the purpose of curing one or more of the defects of the ordinary petroleum lubricating oil. Amongst materials which have been proposed for addition to lubricating oils are sulfur and sulfur compounds. Sulfur and its compounds are generally added to increase the film strength of the oils. This requires the addition of relatively large proportions of the sulfur and its compounds with sacrifice of other desirable properties of the oil. Usually the sulfur and its compounds tend to increase the corrosion of sensitive bearing metals and to have other deleterious effects, so that they are not ordinarily used, except where high bearing pressures are encountered and it is essential that the oil have a high film strength. Under these circumstances, the disadvantageous properties of the additions are less important and, in some cases, may be overcome by the addition of other materials.

Those skilled in the art have also proposed the addition of soaps and soap-like materials to lubricating oils so as to take advantage of the detergent properties thereof for removing deposits from the parts of the engines and for maintaining the products of deterioration in suspension in the oils. Some of these materials are alleged to inhibit deterioration of the oils, and others are alleged to inhibit corrosion of sensitive bearing metals. Such soaps and soap-like materials are organic compounds containing metals in chemical combination and may generally be referred to as organo-metallic compounds. Generally, the disclosures of the organo-metallic compounds in the art are quite broad and frequently indicate a large number of different metals as being suitable, some of them even indicating that copper compounds would be suitable. Copper and its compounds are notorious as catalysts for the oxidation of organic compounds. Those skilled in the art have generally found that many copper compounds, when employed in lubricating oils in the proportions ordinarily recommended for organo-metallic compounds, actually accelerate oxidation of the oils and/or corrosion of sensitive bearing metals. In the case of those copper compounds which apparently inhibit the formation of sludge and like deterioration products, it has been generally necessary to add relatively large amounts of the copper compound to the oil in order to obtain practical and optimum results. However, such large amounts of such copper compounds generally accelerate corrosion of sensitive bearing metals. Also, while many compounds appear to have very desirable properties when subjected to some laboratory tests, they do not exhibit such properties when tested in an engine, particularly under conditions of heavy-duty service.

It is an object of this invention to provide new, improved and more stable lubricants. Another object is to provide lubricating oils for internal combustion engines and particularly for heavy-duty service. A further object is to provide more stable lubricants which can be employed in internal combustion engines over longer periods of time with the formation of less deposits on the engine and with less corrosion of sensitive bearing metals. A still further object is to provide a lubricant which is more satisfactory in internal combustion engines under heavy-duty service. Other objects are to provide new compositions of matter and to advance the art.

The above and other objects of our invention may be accomplished by dissolving in a petroleum lubricating oil from 50 to about 500 parts of copper per million parts of oil, hereinafter abbreviated P. P. M., in the form of oil-soluble compounds of copper and from about 0.1% to about 0.5% of sulfur in the form of oil-soluble sulfur compounds. We have found that, when such copper and sulfur compounds are employed in such proportions, the deterioration of the lubricating oil is largely inhibited and a greatly improved lubricant is obtained. This is particularly apparent when such lubricants of our invention are employed in internal combustion engines under heavy-duty service, wherein the copper and the sulfur cooperate to stabilize the oil against deterioration so that the engines can be operated with such lubricants over long periods of time without causing objectionable increase in the viscosity of the oils, objectionable corrosion of sensitive bearing metals and the formation of objectionable amounts of deposits on the parts of the engines.

The proportions employed in accordance with our invention are critical. Smaller amounts of copper are substantially ineffective for the purpose. When the amount of copper is increased above 500 P. P. M., the bearing corrosion increases and if the amount of copper is materially increased above 500 P. P. M., it may actually accelerate, rather than inhibit, corrosion of sensitive bearing metals. The sulfur is essential since, if the oil contains substantially less than 0.1% of sulfur and less than 200 P. P. M. of copper, no substantial stabilizing effect will be obtained and deterioration of the oil may even be accelerated in some cases. Increase of sulfur beyond 0.5% does not materially increase the stabilizing effect and substantial amounts of sulfur, in excess of 0.5%, may even be detrimental to the extent of accelerating deterioration of the oil and/or accelerating corrosion of sensitive bearing metals.

It should be noted that all oil-soluble copper compounds are not equally effective on a copper basis for use in conjunction with sulfur compounds. Similarly, all oil-soluble sulfur compounds are not equally effective on a sulfur basis for use in conjunction with copper compounds. The optimum concentration of copper and sulfur depends on the nature of the copper compound, the sulfur compound and the lubricating oil employed and must be determined experimentally in each case. We have found, however, that the optimum concentrations for all the compounds that we have tested fall within the range of 50 to 500 P. P. M. copper and 0.10 to 0.50% sulfur. Usually the optimum concentrations fall within the range of from about 100 to about 300 P. P. M. of copper and from about 0.2% to about 0.4% of sulfur.

The oil, to be employed as the lubricant, may be any of the usual mineral oils, such as the petroleum lubricating oils ordinarily employed in the lubrication of the internal combustion engines. It is not essential that the lubricating oil be highly refined, as partially refined and mildly refined oils will respond to the treatment of our invention.

Oil-soluble copper compounds, that may be employed in conjunction with sulfur compounds in accordance with our invention, include compounds of both cupric and cuprous copper. By an oil-soluble copper compound, we mean one that is soluble in a lubricating oil to such an extent that at least 50 P. P. M. copper may be dissolved in the oil. These compounds may be simple salts or may be of the more complex type in which the copper is partially held by residual valences and may contain one or more chelate rings. Useful compounds include copper derivatives of carboxylic acids, mono-thio carboxylic acids, di-thio carboxylic aicds, mercaptans, phenols, thiophenols, amines, hydroxy-aldehydes, hydroxy-ketones, diketones, organic substituted acids of sulfur, organic substituted acids of phosphorus, mono-thio carbonates, di-thio carbonates, tri-thio carbonates, mono-thiocarbamates, di-thiocarbamates, glyoximes, xanthates and complexes of an organic compound with an organic or inorganic salt of copper. The preferred copper compounds are the copper soaps, such as copper naphthenates, and copper-treated sulfurized unsaturated compounds. Some representative oil-soluble copper compounds are:

Cupric naphthenate
Cupric oleate
Cupric linoleate
Basic cupric naphthenate
Cuprous pentadecanethiol-8
Cupric propionyl acetonate
Cupric ethyl acetoacetate
Cupric diethyl 3-ketoglutarate
Cupric salicylal isobutylamine complex
Cupric diundecyl glyoxime
Cupric dibutyl dithiocarbamate
Cuprous pinane trithiocarbonate
Complex of cuprous chloride with tributyl phosphite
Complex of cupric nonene phosphonate with isobutylamine
Complex of cupric tetradecylsulfonate with butylamine
Cupric di(tetradecylsulfonamido) ethane

Oil-soluble sulfur compounds, that may be used in conjunction with copper compounds in accordance with our invention, include mercaptans, sulfides, disulfides, polysulfides, thioethers, thiophenols, thiocarbamates, xanthates, thio acids, dithio acids, sulphones, thioamides, and mixtures thereof. Specific examples of some of these types include dibenzyl disulfide, dipinane disulfide, dicyclohexyl disulfide, dibenzyl sulfide, dioctyl sulfide, dibutyl sulfone, pinane mercaptan, pentadecane-thiol-8, triphenyl phosphine sulfide, 1,2-bis (benzylthio) ethane, dithio-bis-diamyl formate, and dithiobis (dibutyl thio formamide). Most lubricating oils contain an appreciable quantity of dissolved naturally occurring sulfur compounds. We have found that these naturally occurring sulfur compounds are also effective when used in conjunction with copper compounds in accordance with our invention. Accordingly, we include the natural sulfur content in the oil when speaking of our preferred concentrations of sulfur. By an oil-soluble sulfur compound, we mean a compound that is sufficiently soluble in a lubricating oil to give a permanent solution at ordinary temperatures containing at least 0.10% sulfur. It should be noted that sulfur compounds behave differently from elemental sulfur. The former enhance the stabilizing action of copper compounds, while the latter detracts from such stabilizing action. Accordingly, we specifically exclude elemental sulfur as a sulfur compound.

The products, obtained by sulfurizing unsaturated compounds, are particularly useful oil-soluble sulfur compounds, when employed in accordance with our invention. It will be understood that an unsaturated compound is an organic compound which contains one or more olefinic double bonds. These compounds include the sulfurized natural oils from vegetable, fish, and animal sources, as well as sulfurized synthetic unsaturated compounds. Sulfurized sperm, lard, corn and menhaden oils and sulfurized terpenes may be mentioned as examples of sulfurized natural oils. Examples of sulfurized synthetic unsaturated compounds include the products obtained by sulfurizing cetene, abietene, cyclohexene, dihydronaphthalene, menthene, dipentene, terpinene, terpinolene, oleyl alcohol, abietyl alcohol, methyl oleate and methyl abietate. Mixtures of sulfurized unsaturated compounds are equally suitable. The exact chemical structure of these sulfurized unsaturated compounds is not definitely known. It is known, however, that each double bond of such an unsaturated compound will ordinarily react with one, two, or three atoms of sulfur. We prefer to employ compounds which contain not more than one atom of sulfur for each double bond present. Sulfur, in excess of this quantity, tends to function as elemental sulfur in detracting from the stabilizing action of copper compounds and hence is undesirable.

The preferred sulfurized unsaturated compounds to be employed in combination with the copper compounds in accordanc with our invention are sulfurized unsaturated dehydrated alcohols prepared as described in the co-pending application of F. B. Downing and R. G. Clarkson Serial No. 440,201, filed on even date herewith. The process, described in more detail in such application, comprises dehydrating unsaturated long chain alcohols in the presence of catalysts, such as fuller's earth, at temperatures of from about 200° C. to about 300° C., whereby the alcohols are largely converted to unsaturated ethers. The resulting dehydrated products are then sulfurized by treatment with sulfur in the presence of a catalyst at temperatures of from about 130° C. to about 200° C. By "long chain," we mean compounds containing a carbon chain of at least 10 carbon atoms. The preferred compounds are the sulfurized dehydrated unsaturated "Ocenols." The term "Ocenols" is generally employed by those skilled in the art to designate the mixture of unsaturated long chain alcohols obtained by the hydrolytic reduction of unsaturated natural oils from vegetable, fish and animal sources, representative oils being sperm oil, beef tallow, lard oil, cottonseed oil, olive oil, corn oil, rapeseed oil, menhaden oil, soyabean oil, linseed oil and Chinawood oil.

The most satisfactory method for determining the stability of a lubricant in an internal combustion engine is by actual use of the lubricant in the engine. We employ the following engine test, which correlates well with results obtained in the field. Six-cylinder 1940 and 1941 model Chevrolet engines (in some cases fitted with one copper-lead bearing) are operated on a block mounting at a speed of 3150 R. P. M. (equivalent to a road speed of 60 miles per hour) against a load of 35 brake horse power (equivalent to that obtained in road operation) applied by means of a dynamometer. The oil in the sump is maintained at 280° F. and the cooling jacket liquid at 200° F. The test is run for 66⅔ hours (corresponding to road operation for 4000 miles), except in cases where the oil deterioration is so extensive that such lengthy operation is impractical. The degree of deterioration of the oil in this test corresponds directly to that obtained in equal periods of heavy-duty service and is indicative of that observed in longer periods of less severe service.

The following ratings are employed to determine the stability of the oil and its effect on the engine. Samples of the oil used are removed from the crankcase at intervals and analyzed for total sludge (naphtha insolubles) and asphaltenes (chloroform solubles) by the method described in J. Ind. Eng. Chem., anal. ed. 6, 419 (1934) and for viscosity rise and neutralization number by the well-known A. S. T. M. methods. On the basis of these analyses, the condition of the oils is rated as excellent, good, fair, poor or bad. At the end of the run, the engine is disassembled, inspected and rated as to cleanliness. In the system of cleanliness rating employed, a clean engine would score 100 points. Points are deducted from this score based on the quantity and quality of sludge and other deposits in various parts of the engine. An engine with a score of about 50 points by this system would be so badly fouled as to be in imminent danger of mechanical failure due to impaired lubricant circulation caused by the presence of large amounts of sludge or other deposits or due to seizure of valve mechanisms or other moving parts. The copper-lead bearing is weighed before and at the end of the test to determine the loss in weight of sensitive bearing metals. The engine scores are more accurate and reproducible for relatively clean engines with scores of 90–100 than for dirty engines with scores of 50–70 because it is difficult to determine the exact degree of dirtiness of a very dirty engine. Conversely, low bearing corrosions of the order of 0.10 to 0.20 gram per bearing are more accurate and reproducible than high bearing corrosions of the order of 0.5 to 1.0 gram per bearing.

The following oils, each obtained from a different refiner and selected as being typical of the types employed in ignition-engine lubrication, were used in the tests.

Oil	Type	S. A. E. grade	Viscosity index
A	Solvent extracted Mid-Continent base.	20	92
B	Solvent extracted Pennsylvania base.	10	107
C	Solvent extracted Pennsylvania base.	20	107
D	Acid treated Coastal base	30	7
E	Solvent extracted Mid-Continent base.	20	94
F	Distilled Pennsylvania base	20	105

The tests in Table I demonstrate the effective action of oil-soluble copper and sulfur compounds in improving oil condition and engine cleanliness and retarding bearing corrosion. The corrosion of copper-lead bearings is given as the weight in grams lost by the bearing during the engine test. This figure also includes the weight loss due to wear.

The amount of sulfur, naturally present in the oils used, was determined by the burner test. In this test, a sample of oil is blended with 3 parts by weight of naphtha. The mixture is burned, and the combustion products are absorbed by a sodium carbonate solution. On addition of a barium chloride solution to the sodium carbonate solution, barium sulfate precipitates. From the quantity of barium sulfate obtained (corrected for traces of sulfur in the naphtha and reagents), the per cent sulfur present in the oil is calculated.

in the product and the nature of the sulfurized unsaturated compound. It is preferable to add the copper or copper salt slowly in small portions rather than in one batch. When the sulfurized unsaturated compound contains appreciable quantities of unreacted or loosely bound sulfur, the first portions of copper added react with this sulfur and remove it, presumably as copper sulfide, and only a little copper is introduced into the sulfurized unsaturated compound. When all the unreacted or loosely bound sulfur has

TABLE I

Effect of copper and sulfur compounds on oil condition, engine cleanliness and bearing corrosion

Oil	Additive	P. P. M. Cu in oil	Total per cent S in oil	Hours tested	Oil condition rating	Engine cleanliness rating	Cu-Pb corrosion
A	None (avg. 4 runs)	0	0.24	66⅔	Bad	55.0	1.05
A	Copper dibutyl dithiocarbamate	120	0.27	66⅔	Good	91.5	0.97
A	do	200	0.29	66⅔	Excellent	91.5	0.20
A	do	485	0.34	66⅔	do	92.5	0.33
A	Copper pinane trithiocarbonate	200	0.27	66⅔	do	92.0	0.35
A	Cuprous chloride-tributyl phosphite complex	120	0.24	66⅔	do	95.5	0.93
A	Copper propionyl acetonate	120	0.24	66⅔	Poor	68.0	0.66
A	Copper propionyl acetonate plus sulfurized dehydrated "Ocenol"	120	0.38	66⅔	Good	89.5	(1)
A	Copper naphthenate plus sulfurized dehydrated "Ocenol"	120	0.38	66⅔	do	98.0	(1)
A	Copper naphthenate+sulfurized sperm oil	120	0.38	66⅔	Fair	84.5	(1)
A	Copper naphthenate+sulfurized terpenes	120	0.38	66⅔	Good	87.0	0.76
A	Copper pentadecyl-8 mercaptide plus pentadecyl-8 disulfide	120	0.27	66⅔	do	91.0	0.97
A	Copper pentadecyl-8 mercaptide plus pentadecyl-8 disulfide plus sulfurized dehydrated "Ocenol".	120	0.39	66⅔	Excellent	89.5	0.57
A	Copper naphthenate-butyl amine complex plus sulfurized dehydrated "Ocenol".	240	0.39	66⅔	do	97.0	0.66
D	None	0	0.307	33⅓	Bad	53.0	(2)
D	Copper naphthenate	200	0.307	66⅔	Fair	85.0	(2)
F	None	0	0.109	66⅔	Bad	66.0	1.90
F	Copper naphthenate	240	0.109	66⅔	Excellent	90.5	0.13

[1] Not determined.
[2] Oil D was non-corrosive.

Oil-soluble compounds, containing both copper and sulfur, may be employed in accordance with our invention. The ratio of sulfur to copper in such compounds is ordinarily so small, however, that optimum results cannot be obtained with them. Accordingly, it will usually be desirable to employ the optimum quantity of copper in the form of a compound containing copper and sulfur or copper only and to supply whatever additional sulfur is needed in the form of a separate sulfur compound. As an alternate to this procedure, a composition, in which the ratio of sulfur to copper is relatively high, may be employed. Such compositions should contain at least four parts by weight of sulfur per part by weight of copper and are best obtained by treating a sulfurized unsaturated compound, such as has been previously described, with metallic copper or a copper salt. The amount of sulfur in such compositions, together with the sulfur naturally occurring in the oil, will usually be sufficiently large so that optimum concentrations of copper and sulfur may be obtained without the addition of any other sulfur compound.

The copper treatment of a sulfurized unsaturated compound has the dual advantage of introducing copper into the compound and of removing any unreacted or loosely-bound sulfur that may be present. The copper treatment may be accomplished at temperatures as low as 60° C. or as high as 200° C., but temperatures of about 100° C. will usually be preferred. It is usually sufficient to stir the sulfurized compound with powdered copper or a copper salt at a temperature of about 100° C. The amount of copper employed and the time and temperature of heating will depend on the amount of copper desired

been removed, further additions of copper rapidly increase the copper content of the sulfurized unsaturated compound. Copper compounds, that may be employed instead of copper powder, include cuprous chloride, cupric acetate, cupric oxide and cuprous cyanide. When the desired amount of copper has been introduced into the sulfurized unsaturated compound, the mixture is filtered or centrifuged from any copper sulfide or unreacted copper and is then ready for use as an additive for lubricating oils.

We do not know the structure of the oil-soluble copper compounds, obtained by treating sulfurized unsaturated compounds with copper or a copper salt. Oil-soluble compositions, containing about 0.25–3.0% copper and about 6–20% sulfur, are easily obtainable by this method, however, and such compositions are highly effective when employed in accordance with our invention. This is demonstrated in the following tests. All parts are by weight.

One hundred and thirty-nine parts of "Ocenol," obtained by sodium and alcohol reduction of sperm oil, was dehydrated by heating and stirring with 8 parts of fuller's earth. The temperature of the mixture was slowly raised to 295° C. during 7 hours. After stirring for 3 hours longer at 295° C., dehydration was essentially complete. The mixture was then cooled to 200° C. and sulfurized by stirring with 15 parts of sulfur for 3 hours at 195–205° C. This product is representative of the sulfurized unsaturated compounds disclosed and claimed in the co-pending application of F. B. Downing and R. G. Clarkson, hereinbefore referred to. The product, thus obtained, was then copper-treated. This was accomplished by slowly adding 16 parts of copper powder with stirring during 10 hours at 100–110° C. The mixture was then filtered from fuller's earth, copper sulfide and unreacted copper powder. The filtrate was copper-treated sulfurized dehydrated "Ocenol" as a dark-red oil containing 7.43% S and 0.63% Cu. This material is designated I. Two other samples of copper-treated sulfurized dehydrated "Ocenol," prepared in a similar manner, are designated II and III. II contained 8.77% S and 1.19% Cu, and III contained 8.89% S and 2.15% Cu. These materials were tested in Chevrolet engines, as previously described, and the results of the tests are given in Table II.

TABLE II

Effect of copper-treated sulfurized dehydrated "Ocenol" on oil condition, engine cleanliness and bearing corrosion

Oil	Additive	P. P. M. Cu in oil	Total percent S in oil	Hours tested	Oil condition rating	Engine cleanliness rating	Cu-Pb corrosion
A	None	0	0.23	66⅔	Bad	56.5	1.05
A	2.05% I	129	0.38	66⅔	Excellent	94.0	0.59
B	None	0	0.06	33⅓	Bad	63.0	1.20
B	2.05% I	129	0.21	66⅔	Excellent	94.5	0.08
C	None I	0	0.26	33⅓	Bad	60.5	0.03
C	2.05%	129	0.41	66⅔	Good	86.0	0.11
D	None	0	0.31	33⅓	Bad	53.0	(1)
D	1.71% II	203	0.46	66⅔	Good	85.5	(1)
E	None	0	0.16	50	Bad	42.0	0.85
E	0.75% III	154	0.23	66⅔	Good	82.0	0.95
F	None	0	0.11	66⅔	Bad	66.0	1.90
F	2.05% I	129	0.26	66⅔	Good	83.0	0.10

[1] Oil D was non-corrosive.

The critical effect of concentration on the behavior of copper may be seen from results obtained in the well-known Underwood test. In this test, oil, at 325° F., is sprayed over a section of bearing metal. Means are provided for recirculating the sprayed oil so that a limited quantity is used in a given test, thus simulating service conditions in an engine. The bearing metals are removed and weighed at intervals to determine the extent of corrosion, and samples of the oil are removed and analyzed at intervals to determine the extent of oil deterioration. The method used was essentially that described in a pamphlet dated August 1, 1938, of the Research Laboratories Division of the General Motors Corp., entitled "Underwood Oxidation Testing Apparatus," with the exception that the apparatus was thoroughly cleaned before each test and 70 P. P. M. iron, as iron naphthenate, was added to the oil as a catalyst to make the test more severe. Table III shows the effect of a series of concentrations of copper, as copper naphthenate, on oil A containing 0.24% S.

TABLE III

15-hour Underwood test data

	P. p. m. Cu in oil				
	0	60	120	360	800
Mg. loss in weight of copper-lead bearing section	314	68	63	196	438
Total sludge (mg./10 g. oil)	257	135	80	4	3
Viscosity rise (S. U. S. at 210° F.)	62	11	12	3.0	3.7
A. S. T. M. neutralization No	7.3	4.4	2.1	0.9	1.5

Concentrations of sulfur less than 0.10% have no substantial action on the behavior of copper in stabilizing lubricants for internal combustion engines. This may be seen from Table IV, which shows results obtained in oil B, using the previously described Chevrolet engine test.

TABLE IV

Effect of sulfur compounds on copper compounds in improving oil condition, engine cleanliness and bearing corrosion

Additive	P. P. M. Cu in oil	Total per cent S in oil	Hours tested	Oil condition rating	Engine cleanliness rating	Cu-Pb corrosion
None	0	0.06	33⅓	Bad	65.0	0.78
Copper naphthenate	120	0.06	33⅓	do	62.5	0.64
Copper naphthenate+sulfurized dehydrated "Ocenol."	120	0.11	66⅔	Fair	70.0	0.42
Sulfurized dehydrated "Ocenol"	0	0.17	66⅔	Poor	55.0	0.48

The oil, which contained 0.06% S, was run only 33⅓ hours because of extensive oil deterioration and engine fouling. For the same period of time, 120 P. P. M. of copper in the oil gave an even dirtier engine. When the total sulfur was raised to 0.11%, however, the use of 120 P. P. M. copper gave a better engine condition at 66⅔ hours than was obtained at 33⅓ hours at the lower sulfur concentration. Increased concentration of sulfur alone was itself beneficial, an increase in sulfur concentration to 0.17% giving an engine cleanliness of 55.0 for a 66⅔ hour test. The combination of 120 P. P. M. copper and 0.11% sulfur was much superior, however, showing that the beneficial action of these components together is greater than would be expected from their individual behaviors.

We do not know the exact nature of the effect that the copper and the sulfur have upon each other. However, they do seem to have some very profound effect, one upon the other. The combination, when employed in the proportions hereinbefore given, appears to be extremely effective for inhibiting deterioration of the oil and, at concentrations of copper below those at which any of the copper compounds will accelerate corrosion of sensitive bearing metals, the combination is very effective to inhibit corrosion of bearing metals. While we do not wish to be limited to any theory, it appears that the function of the copper and sulfur compounds, in inhibiting oil deterioration and bearing corrosion and promoting engine cleanliness, is primarily, if not entirely, the result of protection of the oil from oxidation during its use in the engine. The concentrations of copper compounds and sulfur compounds employed are insufficient to produce any marked detergency or lubricity in the oil. In other words, the combination of copper and sulfur compounds, in the concentrations employed, appear to function as antioxidants, rather than as detergents or film strength improvers. The amounts of the copper and sulfur compounds employed are insufficient to materially affect the viscosity of the oils and the resulting compositions are free-flowing liquid lubricants suitable for use in the crankcases of internal combustion engines.

While our lubricants exhibit their desirable properties in engines operating on any of the usual motor fuels, it has been found that, when a motor fuel containing tetra ethyl lead is employed in an engine wherein our lubricants are also employed, the effect of our compounds is very materially improved. The tests, the results of which are shown in Tables I, II and IV, were conducted with the engines operating on gasoline having incorporated therein 1 cc. per gallon of tetra ethyl lead as a well known standard commercial composition which also contained alkyl halides. The discovery of the effect of motor fuels, containing tetra ethyl lead, on the lubricants of our invention constitutes the invention of J. H. Fuller and John R. Sabina and is disclosed more specifically and is claimed in the copending application of J. H. Fuller and John R. Sabina, Serial No. 440,250 filed April 23, 1942, for "Method of operating internal combustion engines."

While the stabilizing and corrosion-inhibiting properties, imparted to lubricating oils used in internal combustion engines by the addition of copper and sulfur as previously described, are most striking in so-called heavy-duty service, a similar effect is also obtained in less severe service. Internal combustion engines, in which these additives may be employed with beneficial results, include engines designed for use in passenger automobiles, trucks, tanks, buses, tractors, aircraft, and stationary and semi-stationary power plants. Furthermore, the beneficial action of these additives is not limited to any particular type or kind of oil. Excellent results can be obtained in mildly refined oils as well as in highly refined oils and in paraffinic base oils as well as in naphthenic and asphaltic base oils. These additives may also be employed in conjunction with other additives such as pour point depressants, viscosity index improvers, thickeners, detergents and the like.

The copper may be provided by a mixture of two or more different copper compounds. We believe that the copper treated sulfurized unsaturated compounds, and particularly the copper treated sulfurized dehydrated "Ocenols," comprise mixtures of copper compounds. Also, the sulfur will be, and usually is, provided by a mixture of sulfur compounds part of which are naturally present in the oil.

Part of the invention disclosed herein is more specifically disclosed and claimed in our co-pending application for "Lubricating oils" filed April 23, 1942, as Serial No. 440,200. Such application specifically discloses and claims lubricating oils containing copper compounds which do not readily liberate copper ions and which are represented by the oil-soluble copper mercaptides, dithiocarbamates and trithiocarbonates.

While we have disclosed the preferred embodiments of our invention, it will be understood that such specific embodiments are given for illustrative purposes only and that various modifications may be made without departing from the spirit or scope of our invention. Accordingly, we intend to cover our invention broadly as in the appended claims.

We claim:

1. A lubricant comprising a petroleum lubricating oil having dissolved therein from 50 to about 500 P. P. M. of copper in the form of an oil-soluble compound of copper and from about 0.1% to about 0.5% of sulfur in the form of oil-soluble sulfur compounds.

2. A lubricant comprising a petroleum lubricating oil having dissolved therein from 50 to about 500 P. P. M. of copper in the form of an oil-soluble organic compound of copper and from about 0.1% to about 0.5% of sulfur in the form of oil-soluble organic sulfur-containing compounds.

3. A lubricant comprising a petroleum lubricating oil having dissolved therein from 50 to about 500 P. P. M. of copper in the form of an oil-soluble organic compound of copper and from about 0.1% to about 0.5% of sulfur in the form of oil-soluble organic sulfur-containing compounds at least a substantial part of which are sulfurized unsaturated organic compounds containing a maximum of one sulfur atom for each double bond.

4. A lubricant comprising a petroleum lubricating oil having dissolved therein from 50 to about 500 P. P. M. of copper in the form of an oil-soluble organic compound of copper and from about 0.1% to about 0.5% of sulfur in the form of oil-soluble organic sulfur-containing compounds at least a substantial proportion of which are sulfurized unsaturated ethers containing a maximum of one sulfur atom for each double bond.

5. A lubricant comprising a petroleum lubricating oil having dissolved therein from 50 to about 500 P. P. M. of copper in the form of an oil-soluble organic compound of copper and from about 0.1% to about 0.5% of sulfur in the form of oil-soluble organic sulfur-containing compounds at least a substantial proportion of which are sulfurized unsaturated dehydrated alcohols obtained by the reduction of sperm oil which sulfurized dehydrated alcohols contain a maximum of one sulfur atom for each double bond.

6. A lubricant comprising a petroleum lubricating oil having dissolved therein from 50 to about 500 P. P. M. of copper in the form of an oil-soluble copper soap and from about 0.1% to about 0.5% of sulfur in the form of oil-soluble organic sulfur-containing compounds.

7. A lubricant comprising a petroleum lubricating oil having dissolved therein from about

100 to about 300 P. P. M. of copper in the form of an oil-soluble copper soap and from about 0.2% to about 0.4% of sulfur in the form of oil-soluble organic sulfur-containing compounds.

8. A lubricant comprising a petroleum lubricating oil having dissolved therein from about 100 to about 300 P. P. M. of copper in the form of an oil-soluble copper soap and from about 0.2% to about 0.4% of sulfur in the form of oil-soluble organic sulfur-containing compounds at least a substantial part of which are sulfurized unsaturated organic compounds containing a maximum of one sulfur atom for each double bond.

9. A lubricant comprising a petroleum lubricating oil having dissolved therein from about 100 to about 300 P. P. M. of copper in the form of an oil-soluble copper soap and from about 0.2% to about 0.4% of sulfur in the form of oil-soluble organic sulfur-containing compounds at least a substantial proportion of which are sulfurized unsaturated ethers containing a maximum of one sulfur atom for each double bond.

10. A lubricant comprising a petroleum lubricating oil having dissolved therein from about 100 to about 300 P. P. M. of copper in the form of an oil-soluble copper naphthenate and from about 0.2% to about 0.4% of sulfur in the form of oil-soluble organic sulfur-containing compounds.

11. A lubricant comprising a petroleum lubricating oil having dissolved therein from about 100 to about 300 P. P. M. of copper in the form of an oil-soluble copper naphthenate and from about 0.2% to about 0.4% of sulfur in the form of oil-soluble organic sulfur-containing compounds at least a substantial part of which are sulfurized unsaturated organic compounds containing a maximum of one sulfur atom for each double bond.

12. A lubricant comprising a petroleum lubricating oil having dissolved therein from about 100 to about 300 P. P. M. of copper in the form of an oil-soluble copper naphthenate and from about 0.2% to about 0.4% of sulfur in the form of oil-soluble organic sulfur-containing compounds at least a substantial proportion of which are sulfurized unsaturated dehydrated alcohols obtained by the reduction of sperm oil which sulfurized dehydrated alcohols contain a maximum of one sulfur atom for each double bond.

13. A heavy-duty internal combustion engine lubricant comprising a petroleum lubricating oil having dissolved therein from 50 to about 500 P. P. M. of copper in the form of an oil-soluble organic compound of copper and from about 0.1% to about 0.5% of sulfur in the form of oil-soluble organic sulfur-containing compounds.

14. A heavy-duty internal combustion engine lubricant comprising a petroleum lubricating oil having dissolved therein from 50 to about 500 P. P. M. of copper in the form of an oil-soluble organic compound of copper and from about 0.1% to about 0.5% of sulfur in the form of oil-soluble organic sulfur-containing compounds at least a substantial part of which are sulfurized unsaturated organic compounds containing a maximum of one sulfur atom for each double bond.

15. A heavy-duty internal combustion engine lubricant comprising a petroleum lubricating oil having dissolved therein from about 100 to about 300 P. P. M. of copper in the form of an oil-soluble copper soap and from about 0.2% to about 0.4% of sulfur in the form of oil-soluble organic sulfur-containing compounds at least a substantial part of which are sulfurized unsaturated organic compounds containing a maximum of one sulfur atom for each double bond.

16. A lubricant comprising a petroleum lubricating oil having dissolved therein from about 100 to about 300 P. P. M. of copper in the form of an oil-soluble copper naphthenate and from about 0.2% to about 0.4% of sulfur in the form of oil-soluble organic sulfur-containing compounds at least a substantial proportion of which consists of sulfurized sperm oil containing a maximum of one sulfur atom for each double bond.

17. A lubricant comprising a petroleum lubricating oil having dissolved therein from about 100 to about 300 P. P. M. of copper in the form of an oil-soluble copper naphthenate and from about 0.2% to about 0.4% of sulfur in the form of oil-soluble organic sulfur-containing compounds at least a substantial proportion of which consists of sulfurized terpenes containing a maximum of one sulfur atom for each double bond.

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