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LUBRICATING COMPOSITIONS

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This invention relates to sulfur-containing additives used to produce improved lubricants and stabilized organic compositions, to methods of preparing concentrates of naturally-occurring sulfur-containing additives for lubricating oils and greases, and to improved methods of inhibiting oxidative decomposition and lubricating internal combustion engines, particularly those containing corrosion-sensitive alloy bearings.

It was quite generally believed heretofore that relatively high boiling sulfur compounds naturally occurring in petroleum crudes were good inhibitors for lubricating oils, imparting to them anti-corrosive properties and oxidation stability. As a result, several high sulfur-content lubricating oils have appeared on the market for which certain superiorities are claimed. However, in many cases such claims cannot be verified by laboratory and engine tests. Moreover, it was found that as a rule these high sulfur lubricating oils have a very strong and dangerous tendency to form lacquer, sludge and carbon on pistons and piston rings, particularly in high temperature operation.

It has now been discovered however that among the naturally-occurring sulfur compounds in petroleum oils there are beneficially active as well as inactive and even detrimental varieties and that the beneficially active compounds can be extracted from the oils in which they occur to produce concentrates of relatively high non-corrosive sulfur content, which, when added to well refined lubricating oils, impart to them good oxidation stability and anti-corrosive properties without materially increasing their tendency to form lacquer, sludge and carbon.

It is accordingly an object of this invention to produce from crude petroleum, sulfur concentrates which, when added to refined lubricating oils and the like, act as oxidation and corrosion inhibitors without materially increasing the lacquering and sludge depositing tendency of the base oil. A further purpose is to provide lubricating compositions having decreased tendencies to attack modern alloy bearings. Another object

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is to obtain superior aviation and Diesel engine, heavy duty lubricating oils. A still further purpose is to produce novel sulfur-containing petroleum fractions which contribute valuable anti-corrosive, anti-oxidant, anti-wear, high film strength and/or other advantageous properties to organic compositions in which they are incorporated. Other objects will be apparent from the following description.

It has been determined that the anti-corrosive and anti-oxidant properties of the desirable natural petroleum sulfur compounds are associated with the availability or activity of the sulfur in them. If the compounds or mixtures thereof, such as those obtained from petroleum by the hereinafter described methods have low sulfur availabilities, they are themselves substantially non-corrosive to bearing surfaces but may fail to inhibit other types of corrosion. If, however, their sulfur availability is above a certain minimum, they will inhibit against both bearing corrosion and oxidative decomposition and may also contribute other valuable properties to the lubricating oil to which they are added. Some of these additives may produce a brown or colored film on metal bearing surfaces in engine operation. With others, (notably the hereafter described Utanol raffinates) this discoloration of copper surfaces may be substantially absent, but the anti-corrosive and anti-catalytic properties which the sulfur compounds contribute to the lubricating oil are still prominent. Some of these sulfur compositions (e. g. the Utanol raffinates) also possess material anti-wear properties and/or the ability to enhance or prolong the anti-wear properties of other anti-wear agents.

The reactivity or availability of the sulfur in various compounds is defined as the percent sulfur (calculated on the total sulfur content in the compound or mixture) which will react with metallic copper under certain conditions. It is determined by heating at various temperatures samples of the compositions with an excess (over the amount equivalent to the sulfur content) of finely divided metallic copper for a standard pe-

riod of time, here taken at 16 hours. The copper sulfide formed is then determined quantitatively as by oxidizing the sulfide with bromine and precipitating the resultant sulfate with barium chloride. If the percent of sulfur reacted is plotted against the reaction temperatures for various sulfur compounds or high sulfur content oils, a family of curves is obtained which at relatively low temperatures are quite close together. However, at temperatures of say 300° C. the curves separate widely and the availability of the sulfur as determined at this temperature gives a reasonable correlation for various petroleum derived sulfur compounds with their inhibiting efficacy when incorporated in refined lubricating oils. At this particular temperature, compounds having sulfur availabilities below about 15% (for example those in West Texas high-sulfur lubricating oil extracts) are of little if any effect, while certain other natural petroleum sulfur compounds of higher availability, i. e. above about 15% and preferably above about 20% (for example, those in Utanol raffinates) are highly effective.

The availability of these sulfur compounds has been correlated with their anti-corrosiveness in lubricating oils, for example by determining the comparative weight losses of copper-lead bearings subjected to the action of lubricating oils containing standard amounts of these sulfur additives plus a commonly used detergent, which, although contributing other valuable properties, causes or increases corrosiveness of the lubricating oil. Thus various blended oils have been tested and compared by a procedure known as the Thrust Bearing Corrosion test, which was described in the National Petroleum News, September 17, 1941, pp. R 294-296.

Fractions or concentrates of active sulfur compounds may be obtained by various methods from various high sulfur petroleum crudes which contain them. In most crudes, the concentration of these compounds is quite low, and special methods (which are described later) are required in order to recover them in relatively high concentration, so that they may be added to refined lubricating oils in effective amounts without materially changing the desirable properties of the latter. As a rule, it is poor practice to add to a well refined lubricating oil more than about 10% of any addition agent. The effective amounts of sulfur which must be added to various refined lubricating oils in the form of active sulfur compounds usually are on the order of 0.1% to 0.3% by weight of refined oil, although quantities of between 0.02% and 1% may be useful. In a semiplastic composition such as a grease, higher amounts may be employed. Therefore, it is desirable, if not essential, that the sulfur content of a concentrate of active compounds be at least 2% and preferably 5% or higher.

As previously indicated, the indiscriminate addition of natural petroleum sulfur compounds tends to cause an increase in lacquering and sludge depositing tendencies of the blended oils. This however can be minimized by properly refining either the oil from which the active high sulfur concentrates are produced or the concentrates themselves before they are added to lubricating oils. Such refinement includes substantial elimination of asphaltic materials and a treatment capable of separating aromatic from non-aromatic hydrocarbons, for example, by precipitation with gas, such as methane under high pressure as described by Pilat in U. S. Patent

2,315,131, sulfuric acid treatment, solvent extraction, selective hydrogenation, etc., or a combination of such treatments, preferably under conditions not to reduce the sulfur content of the concentrate excessively, i. e. so that not more than about 1/3 of the total sulfur content is lost. In other words, our concentrates are "raffinates," "raffinates" as commonly understood in the petroleum industry being relatively paraffinic petroleum fractions from which naturally associated aromatics have been removed. Whether the sludging tendency is the result of over-activity of certain sulfur compounds (as might well be) or is due to the presence of other associated compounds, is not known at this time. However, this is immaterial, as it is sufficient that a treatment adapted to remove aromatics from hydrocarbon mixtures will achieve the desired result.

In general, crudes which contain the active sulfur compounds in concentration sufficient to recover them in relatively concentrated form, are of highly asphaltic nature such as certain California (particularly Mount Poso, Coalinga, Santa Maria) and Venezuelan crudes.

Outstanding is an oil known to the trade as "Utanol" which is an asphaltic petroleum crude obtained from shallow wells in the Great Salt Lake area and southern Idaho. The oily fraction separated from this material is known as "Utah oil." Utanol varies in sulfur content from about 10% to 15%, has a specific gravity of about 1.0 to 1.1, a saponification number of around 10 to 20, naphtha insolubles of 10% to 15%, and contains about 40% to 70% asphalt as determined by precipitation with about 5 volumes of n-butane at 60° to 100° C. It has no appreciable content of phenols.

Methods for obtaining an oil fraction having the desired concentration of active sulfur compounds from crudes having a sulfur content above 5%, such as Utanol, are relatively simple. One such method specifically applied to Utanol is as follows:

The crude is first de-asphalted by any of the standard de-asphalting methods. This may be achieved by asphalt precipitation or distillation, or both. The precipitation method is preferred because of the extremely high asphalt content of the Utanol which may interfere with the proper distillation and result in cracking of the asphalt and the inclusion of harmful cracked material in the distillate.

The precipitation may be carried out by mixing the Utanol with several volumes of a liquid light hydrocarbon oil comprising predominantly or consisting of C₃ to C₆ hydrocarbons, preferably at a temperature within about 75° to 100° C. of the critical temperature of the latter. Thus propane or propylenes at normal room temperature, butanes or butylenes at temperatures of 60° C. or above are well suited. Dissolving in benzene and precipitating with isopentane also proved successful. If desired, the crude may be dissolved in a liquid C₄ to C₁₂ hydrocarbon, naphtha, light kerosene, etc., and gaseous methane, ethane, natural gas, propane, fuel gas, water gas, CO, CO₂ or other gases may be introduced at high pressures to effect or complete the asphalt precipitation. Moreover, selective so-called "naphthenic" solvents may be present, such as liquid SO₂, furfural, nitrobenzene, beta,beta'-dichlor-diethyl ether, phenol, cresylic acids, aniline, methylsulfolane, dimethylsulfolane, or a large number of others or their mixtures.

If the crude oil contains relatively low boiling components, as gasoline, kerosene, etc., they may be flashed from the crude prior to the precipitation or else may be separated later by fractional distillation of the deasphalted raffinate oil.

The supernatant liquid layer, i. e. the raffinate phase resulting from asphalt precipitation and containing the desired oil, is now separated from the precipitated asphalt. This oil must be further refined to reduce its lacquer-imparting tendencies.

Depending on the conditions of the precipitation, the nature of the solvents employed and the nature of the crude itself, one of several ways may be followed. Obviously the more drastic the precipitation conditions are, the less drastic need be the second treating step which involves (as previously indicated) a treatment adapted to remove aromatic hydrocarbons. Solvent extraction may be employed with any one of the well known selective "naphthenic" solvents previously mentioned. Treatment with strong, i. e. 93 to 100% sulfuric acid is usually desirable and effective. Amounts of sulfuric acid ranging anywhere from 5 to 100 pounds per barrel of the raffinate oil may be employed.

Several treatments may be combined and the second refining treatment may be carried out in the presence or absence of the light hydrocarbon liquid employed in the precipitation; generally its presence may be helpful in the second step. The undesirable components, if any (which may be in the form of sludge, extract, etc.), produced in the second refining treatment, are now separated. Solvent, if present, is removed in the usual manner as by distillation or washing with water or wash solvent, and the recovered high sulfur oil may be given a finishing treatment with clay (such as fuller's earth, acid activated clay, etc.), bauxite, zeolite, silica gel or other adsorbents.

The specific dispersion of the treated high sulfur raffinate oil is often a fair indication of its lacquer imparting tendencies. It is desirable that the specific dispersion be below about 160, more preferably below about 140 or 145. Also, the color may be an indication if taken together with the specific dispersion. Preferably, the color should be better than 6 (A. S. T. M. or National Petroleum Association Scale).

Samples of treated Utanol raffinate oils from

Ability of Utanol raffinates to decrease wear was determined on a Multiple Four Ball machine similar in principle to the Boerlage apparatus described in the magazine Engineering, volume 136, July 14, 1933. This apparatus comprises four steel balls arranged in pyramid formation. The top ball is rotated by a spindle against the three bottom balls which are clamped in a stationary ball holder. All balls are immersed in the oil to be tested. The tests are run for two hours at 700 R. P. M. under a 7 kg. load and at a controlled temperature of 130° C. Diameters of the wear scars worn on the three balls forming the base of the pyramid are then measured, and the average taken as the true indication of wear. Results were as follows:

	Lubricant	Scar diameter in millimeters
1	Refined aviation lubricating oil, API gravity about 26, SU at 210° F. about 115-125	0.7
2	Oil #1 containing clay treated Utanol Pilat raffinate, ΔS=0.10%	0.47
3	Oil #1 containing clay treated Utanol Pilat raffinate, ΔS=0.30%	0.36

Oxidation tests were made with the same oil to determine the time required for the absorption of 1800 cc. of oxygen by 100 g. of oil in the presence of 1 cm.² of copper surface/gram of oil at 150° C. The following data are typical:

	Hours
Oil No. 1 (as above)	9.3
Oil No. 2 (as above)	48

This Utanol raffinate was also tested in the Thrust Bearing Corrosion test, referred to earlier, employing a compounded heavy duty truck and bus or Diesel lubricating oil. It contained in each case 1% of the magnesium salt of lauryl salicylate which has been a widely used lubricating oil detergent, but which, although otherwise beneficial, imparts corrosive properties to the lubricant. In 20 hour tests at 125 lbs. thrust and 2400 R. P. M. with this oil, the copper-lead bearings showed a weight loss at 130° C. of 15 mg./cm.². When tested with this same oil, to which had been added a clay treated Utanol Pilat raffinate, ΔS=0.10%, the bearings showed no weight loss at 160° C.

Chevrolet engine tests using procedure L-4-243 of the Cooperative Lubricants Test Program were also made using a corrosive S. A. E. reference oil. Results were as follows:

	Varnish rating	Sludge rating	Bearing wt. loss, mg./cm. ²	Used oil properties	
				Sap. No. mg. KOH/g.	Neut. No. mg. KOH/g.
Base oil	105	73	84.0	22.2	3.6
Base oil + Utanol raffinate ΔS=0.10%	106.5	70.5	33.4	25.1	4.6
Base oil + Utanol raffinate ΔS=0.10%	109.5	72	21.7	26.8	4.2
Base oil + Utanol raffinate ΔS=0.30%	104.5	73	3.2	9.98	2.8

different batches had the following properties:

	General range	One acid treated Pilat raffinate
Gravity, °	0.98-1.0	0.9880
Viscosity at 100° F.	950-1400	1,018
Viscosity at 210° F.	34-39	34.7
Viscosity index	40-55	53
Specific dispersion	130-145	132
Color	4-7.5	4½
Saponification number, mg. KOH/g.	0-8	0.9
Ultimate analysis:	A clay treated Pilat raffinate	
Carbon.....per cent weight	78.27	
Hydrogen.....do.	10.90	
Sulfur.....do.	12.7	11.9
Nitrogen.....do.	0.14	0.06

The action of a Utanol raffinate in increasing the efficiency of an anti-wear agent, the calcium salt of methylene bis p-isooctylphenol, may be seen from the following data of piston ring weight loss in a CFR-Diesel engine. Test conditions: 1400 R. P. M.; load, 68 lbs./in.² brake mean effective pressure; jacket temp. 100° C.; oil temperature 70° C.; compression ratio 16:1; 47 cetane number commercial Diesel fuel; base oil, commercial Diesel lubricating oil S. A. E. 30; test length, 4 runs of 13 hours, results reported for overall period.

Additive	Piston ring weight loss, mg.
None	73.4
Ca salt of methylene bis p-isooctylphenol 0.10% ash	31.6
Ca salt of methylene bis p-isooctylphenol 0.10% ash plus Utanol raffinate AS-0.10%	29.6

The Utanol raffinates also possess other desirable characteristics when incorporated in a lubricating oil, such as anti-scuffing and anti-scratching properties in Diesel engines. Their beneficial activity may also be enhanced by utilization in the presence of small amounts of synthetic organic sulfur-containing anti-oxidants, e. g. dibenzyl sulfide or disulfide, wax disulfide, diphenyl sulfide, sulfurized sperm oil, sulfurized olefin polymers, sulfurized wax olefins (obtained in the cracking, or by chlorination and dehydrochlori-

relatively high specific dispersion or content of aromatics, the former often being considerably above 160, unless the solvent extraction and additional treatment preparatory to the solvent extraction was very drastic. If the specific dispersion of the sulfur concentrate is above about 145, the concentrate may again be solvent-extracted or sulfuric acid treated, etc., to further reduce its aromaticity and specific dispersion to below about 140 in order to produce an addition agent for lubricating oils which has the least lacquer imparting tendencies.

In the table below, a comparison is made of the effect of the several sulfur concentrates on the oxidation stability (Dornite type oxygen absorption apparatus at 150° C.) in the presence of 1 square centimeter of copper per gram of oil of an S. A. E. 60 lubricating oil when added thereto in amounts to raise the sulfur content by 0.1%:

Source of petroleum material	Method of obtaining sulfur conc.	Spec. dispersion of sulfur concentrate $\frac{W_1 - W_2}{d} \times 10^4$	Time to absorb 1800 ml. of O ₂ /100 g. oil
			Hours
Utanol	None added		9.2
Mt. Poso lubricating distillate, furfural raffinate, 55 V. I.	Asphalt precipitation-acid treating	132	47.7
Mt. Poso lubricating distillate, acid treated furfural raffinate, 60 V. I.	Mercuric acetate in acetic acid	126	52.0
	SbCl ₅ -AlCl ₃	143	32.1
Mt. Poso lubricating distillate, furfural raffinate, 55 V. I.	Aluminum chloride	158	21.3
West Texas distillate	Acid treat+extraction with HgAc ₂ in HAc	196	13
Do.	Duosol extraction followed by acid treat	200+	9.8

nation, of paraffin wax), bis-(methylene aryl or alkaryl sulfides), etc.

As indicated before, when starting with crudes or fractions thereof having sulfur contents materially below about 5%, such as California and Venezuelan oils, different methods for recovering the active sulfur compounds must be employed than that described for Utanol. Since oils having a relatively low sulfur content may display a ratio of aromatics to sulfur that is higher, for example, than with Utanols, it is necessary to first remove from these oils some of the aromatics, as by selective solvent extraction with a "naphthenic" solvent of the type described earlier, and if necessary augment this treatment with others such as sulfuric acid treatment. Likewise, crudes relatively low in asphalt and aromatic content do not show the desired concentration of the sulfur compounds by the removal of their smaller amounts of undesirable constituents. The sulfur components, however, can be concentrated by methods such as the following:

Extraction with acetic acid containing a soluble mercury salt such as mercuric acetate, mercuric chloride, etc. to form a mercury complex extract which is then worked up to recover the extract oil and if necessary further refine the latter.

Extraction with a liquid mixture of SbCl₅ and AlCl₃ to form a complex which may be separated and decomposed to recover the oil.

Extraction with AlCl₃ at temperatures between about 0 to 80° C. as described in U. S. Patent 2,309,337 to form a complex which may be decomposed to recover the oil.

All three of these extraction methods yield relatively dark oils, even though the starting raffinate may have been of light color. Moreover, the SbCl₅-AlCl₃ extraction, as well as the AlCl₃ extraction, tend to cause accumulation in the sulfur concentrate of whatever aromatics have been left over from the preceding solvent extraction, and therefore result in sulfur concentrates of

The method of concentrating sulfur compounds with the aid of mercuric acetate in acetic acid is described below in greater detail:

A sample of 50 V. I. Mt. Poso furfural raffinate was first extracted with glacial acetic acid to remove nitrogen bases. Glacial acetic acid saturated with mercuric acetate was then added to the oil, with stirring, in the amounts shown in the table below. The mixture was allowed to settle and the lower layer drawn off. This extraction may be performed several times on a sample (as shown in the table) and the remaining oil then washed with acetic acid to remove the remaining mercury compounds. It is also advantageous to carry out the extraction in the presence of an inert, oxygen-excluding agent such as nitrogen or natural gas which may be bubbled through the liquid to minimize oxidation. The extracts and acetic acid end-wash are then combined. The acetic acid may be distilled off and the mercury then released from the oil, for example, by heating say to 100° C. with dilute acid (e. g. 2 vols. of 15% HCl) or by saturating with H₂S, the oil then being diluted with isopentane or other suitable solvent, water-washed, dried and clay-treated before removal of solvent.

The variables for several such runs are shown in the following table:

	Run number		
	I	II	III
Weight of oil used, gms.	620	901	738
No. of dumps of reagents	3	3	3
Volume of acetic acid, mls.	190	215	150
Volume of HgAc ₂ plus acetic acid, mls.	485	660	540
Temperature of treatment, ° C.	30	18	50
Total treating time, minutes	90	135	165
Weight per cent yield of extract (on oil)	4.3	4.3	5.4
Per cent sulfur remaining in oil	0.15	0.14 (7)	0.16 (4)
Per cent sulfur in extract oil (average)	2.80	2.98	2.82

Extract from Run No. II was incorporated in white oil to the extent of 3%. This increased the time required for 100 g. to absorb 1800 ml. of oxygen from less than 2 to 236 hours. Corresponding extracts obtained at higher (e. g. reflux) temperatures were considerably less effective.

It has been found that when this mercuric acetate extraction of the oil is carried out at room temperature or lower (i. e. below about 20° C. and preferably near the melting point of acetic acid) the content of desirable sulfur constituents in the extract is greater than if the oil is refluxed or maintained at a higher temperature while treating with the mercury salt. In general, any mercury salt, particularly the mercuric salts soluble in acetic acid such as the oxalate, carbonate, chloride, sulfate, etc. or their mixtures, may be employed in like manner as the mercuric acetate, since these salts will give mercuric acetate in the acetic acid solution. The solubility of the acetate is considerably greater than for the other salts, hence it is generally more advantageous to start with the mercuric acetate. As compared with salts of other metals, the mercury salts are definitely superior for this purpose as shown by the foregoing data.

The herein described compositions possessing the required amount of available or reactive sulfur may also be incorporated advantageously in extreme pressure lubricants, cutting oils, roll oils, wire drawing lubricants, greases, hypoid gear lubricants, etc. They may also be used to impart anti-wear and/or anti-oxidant properties to lubricants not necessarily subject to high pressure, such as turbine oil, refrigerator oil, lubricants for bearings, in particular, modern alloy bearings comprising cadmium-silver, cadmium-nickel, copper-lead, "high lead" alloys, as well as Babbit metal, and the like. The lubricating media also need not be derived in whole or in part from mineral oil but may consist in whole or part of vegetable or animal lubricants such as palm oil, cottonseed oil, fish oil, animal wax, phosphatides, etc., as well as the so-called synthetic lubricants (e. g. polymers of olefins derived from cracked wax). In addition, by reason of their anti-oxidant properties, such additives may be incorporated advantageously in organic substances not intended for use as lubricants at all, such as gasoline, kerosene, spray oil, medicinal oil, transformer or electrical insulating oil, cleaning fluid, synthetic or natural rubber, Diesel fuel, photographic developers, etc.

Particular reference may be made to the inclusion of the herein described anti-oxidants as additives for coating materials such as asphalt, resins, oils, waxes, varnish, insulating or moisture-protective substances such as oiled or "waxed" paper, etc. Such plastic or semi-plastic vehicles may also contain, for example, anti-rusting agents and be applied to metal surfaces to provide a corrosion-resistant coating. Also such oxidation inhibited adhesive coatings may be applied to wood, paper, cardboard, felt, stone, laminated glass, fabric, concrete, plastic compositions, Transite board, etc., by such methods as roller coating, dipping, brushing, spraying and the like.

When the sulfur compounds of this invention are intended for addition to lubricating oils, they or the concentrates which contain them should have boiling temperatures above gas oil range and preferably within or above lubricating oil range.

These compounds may also be advantageously

used in connection with other additives in lubricating media, for example, detergents formed from the oil-soluble salts of various bases with detergent forming acids. Such bases include metallic as well as organic bases. Metallic bases include those of the alkali metals, as well as Cu, Mg, Ca, Sr, Ba, Zn, Cd, Al, Sn, Pb, Cr, Mn, Fe, Ni, Co, etc. Organic bases include various nitrogen bases as primary, secondary, tertiary and quaternary amines.

Examples of detergent forming acids are the various fatty acids of, say, 10 to 30 carbon atoms, wool fat acids, paraffin wax acids (produced by oxidation of paraffin wax), chlorinated fatty acids, aromatic carboxylic acids including aryl fatty acids, aryl hydroxy fatty acids, paraffin wax benzoic acids, various alkyl salicylic acids, phthalic acid mono esters, aromatic keto acids, aromatic ether acids; diphenols as di-(alkyl phenol) sulfides and disulfides, methylene bis alkylphenols; sulfonic acids such as may be produced by treatment of alkyl aromatic hydrocarbons or high boiling petroleum oils with sulfuric acid; sulfuric acid mono esters; phosphoric acid mono and di-esters, including the corresponding thiophosphoric acids; phosphonic and arsonic acids, etc.

Non-metallic detergents include compounds such as the phosphatides (e. g. lecithin), certain fatty oils as rapeseed oils, voltolized fatty or mineral oils.

Other detergents are the alkali earth phosphate di-esters, including the thiophosphate di-esters; the alkali earth diphenolates, specifically the calcium and barium salts of diphenol mono and poly sulfides; etc.

Our sulfur additives may also be used in association with other anti-oxidants, for example alkyl phenols such as 2,4,6-trimethylphenol, pentamethylphenol, 2,4-dimethyl-6-tertiary-butylphenol, 2,4-dimethyl-6-octylphenol, 2,6-di-tertiary-butyl-4-methylphenol, 2,4,6-tri-tertiary-butylphenol, etc.; amino phenols as benzyl amino phenols; amines such as dibutylphenylene-diamine, diphenylamine, phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, dinaphthyl amines; etc.

Other corrosion inhibitors may also be present such as dicarboxylic acids of 16 and more carbon atoms, alkali metal and alkali earth salts of sulfonic acids and fatty acids, etc.

Likewise, other additives may be present in a lubricating oil or grease such as blooming agents, anti-foaming agents, viscosity index improvers, etc.

Instead of first producing the herein described additive and then adding it to a lubricating oil, a high sulfur asphaltic crude such as raw Utanol may be added to a crude petroleum, for example a topped crude suitable for the manufacture of lubricants, and the mixture then subjected to one or several treatments adapted to remove substantially all asphaltenes and at least a portion of aromatic hydrocarbons such as previously described. Amounts of this high sulfur oil which may be added to the crude lubricating stock vary with the amount and availability of the sulfur content of the former, as explained before, and may range preferably from about 2% to 15%.

We claim as our invention:

1. A process for obtaining a sulfur-containing fraction possessing anti-oxidant and other valuable properties, which process comprises extracting a substantially paraffinic lubricating oil

raffinate with a mercury salt under temperature conditions to produce a mercury salt-sulfur compound complex and breaking the resulting mercury salt-sulfur compound complex to regenerate and recover the extracted sulfur compounds.

2. A process for obtaining a sulfur-containing fraction possessing antioxidant and other valuable properties, which process comprises extracting a substantially paraffinic lubricating oil raffinate with a mercury salt under conditions of atmosphere and temperature to substantially avoid any oxidation and to produce a mercury salt-sulfur compound complex, and breaking the resulting complex to regenerate and recover the extracted compounds.

3. A process for obtaining a sulfur-containing fraction possessing antioxidant and other valuable properties, which process comprises extracting a substantially paraffinic lubricating oil raffinate with a mercury salt at a temperature below about 20° C. and breaking the resulting sulfur complex to recover the extracted sulfur compounds.

4. A process for obtaining a sulfur-containing fraction possessing antioxidant and other valuable properties, which process comprises extracting a substantially paraffinic lubricating oil raffinate with glacial acetic acid saturated with mercuric acetate and breaking the resulting sulfur complex to recover the extracted sulfur compounds.

5. A process for obtaining a sulfur-containing fraction possessing antioxidant and other valuable properties, which process comprises extracting a substantially paraffinic lubricating oil raffinate with a mercury salt at a temperature not above about 50° C., thereby producing a mercury salt-sulfur compound complex, and breaking the resulting complex to regenerate and recover the extracted compounds.

6. A process for obtaining a composition possessing antioxidant and other valuable properties, which process comprises extracting a substantially paraffinic lubricating oil raffinate with a mercury salt at a temperature not above about 50° C., thereby producing a mercury salt addition compound, and breaking the resulting addition compound to regenerate and recover the extracted compounds.

7. A process for obtaining a composition possessing antioxidant and other valuable properties, which process comprises treating a substantially paraffinic lubricating oil raffinate with glacial acetic acid saturated with mercuric acetate, thereby producing a mercuric acetate addition compound, and breaking the resulting addition compound to regenerate and recover the extracted compounds.

8. An organic composition comprising a predominant amount of an organic substance which is unstable against oxidative deterioration and which is responsive to sulfur-containing antioxidants, and an added beneficial amount of natural-occurring sulfur-containing compounds from petroleum oil possessing antioxidant and other valuable properties prepared by the process which comprises extracting a substantially

paraffinic lubricating oil raffinate with a mercury salt under temperature conditions to produce a mercury salt-sulfur compound complex and breaking the resulting mercury salt-sulfur compound complex to regenerate and recover therefrom the extracted compounds.

9. An organic composition comprising a predominant amount of a mixture of hydrocarbons, which mixture is unstable against oxidative deterioration and which is responsive to sulfur-containing antioxidants, and an added antioxidant amount of a concentrate of natural-occurring sulfur containing compounds from petroleum oil possessing antioxidant and other valuable properties prepared by the process which comprises extracting a substantially paraffinic lubricating oil raffinate with a mercury salt under temperature conditions to produce a mercury salt-sulfur compound complex and breaking the resulting complex to regenerate and recover the extracted compound.

10. An oleaginous composition comprising a predominant amount of an oleaginous material which is unstable against oxidative deterioration and which is responsive to sulfur-containing antioxidants, and an added antioxidant amount of a concentrate of natural-occurring sulfur-containing compounds from petroleum oil possessing antioxidant and other valuable properties prepared by the process which comprises extracting a substantially paraffinic lubricating oil raffinate with a mercury salt under temperature conditions to produce a mercury salt-sulfur compound complex and breaking the resulting complex to regenerate and recover the extracted compound.

11. A lubricant comprising a predominant amount of a refined mineral oil, a small added amount of a normally corrosive detergent, and an added small amount sufficient to render the resultant mixture substantially non-corrosive of a concentrate of natural-occurring sulfur-containing compounds from petroleum oil possessing antioxidant and other valuable properties prepared by the process which comprises extracting a substantially paraffinic lubricating oil raffinate with a mercury salt under temperature conditions to produce a mercury salt-sulfur compound complex and breaking the resulting complex to regenerate and recover the extracted compound.

12. A lubricant comprising a predominant amount of a refined mineral oil and characterized by a normal tendency to corrode metal bearing surfaces, and an added corrosion-inhibiting amount of a concentrate of natural-occurring sulfur-containing compounds from petroleum oil possessing anticorrosive and other valuable properties prepared by the process which comprises extracting a substantially paraffinic lubricating oil raffinate with a mercury salt under temperature conditions to produce a mercury salt-sulfur compound complex and breaking the resulting complex to regenerate and recover the extracted compound.

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