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SULFURIZED HYDROCARBON LUBRICANT ADDITIVE

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This invention relates to the production of non-corrosive sulfurized hydrocarbons. More particularly, it concerns the preparation of sulfurized high molecular weight alkyl aromatics useful as multi-functional additives for mineral oil compositions and the like.

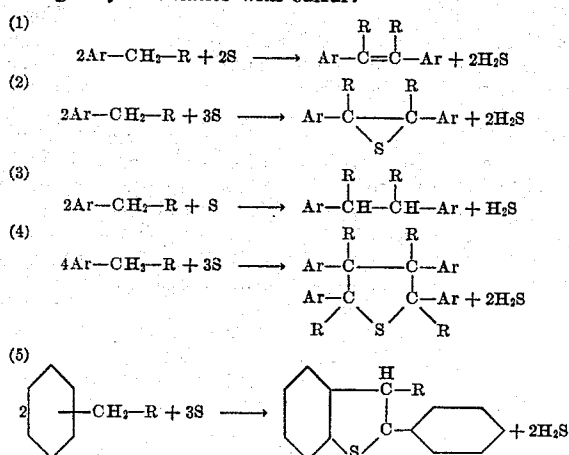
It is well known in the art to treat various types of hydrocarbons with elemental sulfur at elevated temperatures. The resulting sulfurized materials are useful as cutting oils, cutting oil additives and extreme pressure additives, and they impart other beneficial properties to mineral oil compositions. These materials, however, are extremely corrosive to sensitive metals such as copper and silver. While corrosion is not a serious problem in the case of cutting oils, lubricants employed in internal combustion engines must be non-corrosive to protect sensitive metal bearings and other metal parts. For this reason, the extent to which sulfurized hydrocarbons may be used as additives for motor lubricants has been restricted. In some cases, these materials must be used along with potent corrosion inhibitors in order to formulate a non-corrosive oil. Since the sulfurized products become more corrosive as the concentration of sulfur is increased, an additional problem is met in making additives containing enough sulfur to be effective for other purposes and yet being reasonably non-corrosive. It is a principal object of the present invention to produce a sulfurized hydrocarbon free from the above disadvantages, the material finding particular use as an additive for motor lubricants.

In accordance with the present invention, high molecular weight alkyl aromatic hydrocarbons and hydrocarbon compositions comprising substantial quantities of these compounds are treated with elemental sulfur under critical conditions to form a product containing chemically combined sulfur. Oil blends containing the product are substantially non-corrosive to sensitive metals. The products are excellent detergent additives and also inhibit corrosion of metals and oxidation of motor oils under severe engine operating conditions. In addition, they are free from ash-forming constituents. They are consequently very useful as additives for aviation engine lubricants since the formation of ash deposits in aviation engines is generally deleterious. It has also been found that alkyl aromatic pour depressors may be treated in accordance with this invention to obtain products having improved pour stability characteristics and possessing the above desired characteristics as well.

The process of the present invention comprises the step of reacting the high molecular weight alkyl aromatic with elemental sulfur at a high temperature for a time sufficient to form a substantially non-corrosive product that contains less than one-third the originally added sulfur in chemically combined form. The sulfurization is carried out under conditions such that the remaining sulfur is removed as hydrogen sulfide. The surprising feature of this process is the criticalness of the final sulfur content of the product in relation to the original sulfur treat. Invariably, it has been found

that the product must contain in the range of about 18 to 33% by weight, preferably 20 to 30% by weight, of the originally added sulfur in chemically bound form. If the sulfur content is below these values, treating conditions are too severe or the feed stock contains insufficient alkyl aromatics to form stable compounds. If the sulfur content is too high, the product is extremely corrosive. As a general rule, products containing more than about 30% of the original sulfur treat will be excessively corrosive.

The reason for the criticalness of the sulfur content is not clearly understood. It is believed that several of the following types of reactions take place when reacting alkyl aromatics with sulfur:



In these formulas, Ar is an aromatic nucleus such as benzene, naphthalene, anthracene, naphtheno-aromatic nuclei, and the like. R represents a long chain alkyl radical. These reaction mechanisms postulate that polymeric aromatics and substituted thiophenes are produced. If polymers are made, dehydrogenation or condensation takes place and no sulfur enters the product. If substituted thiophenes are made, one-third of the sulfur combines with the alkyl aromatic and two-thirds evolves as H₂S.

Actual experience shows that the products must contain less than one-third the original sulfur in order to be non-corrosive. If the product contains in the order of about 30 to 50% or more of the original sulfur, it contains unstable sulfur-bearing compounds that are extremely corrosive in nature. When the sulfur content is below about 30% of the original sulfur treat, sulfur is combined in a stable useful form. Severe treating conditions tend to produce unuseful bodies having low sulfur contents that may also be corrosive.

Alkyl naphthenes may also be treated in this manner. Apparently, these compounds dehydrogenate to form alkyl aromatics which then react with sulfur to form useful products.

In carrying out the sulfurization reaction, the alkyl aromatic feed stock to be treated may be mixed with the desired amount of sulfur. The mixture is then heated to reaction temperature and maintained at this level for the requisite treating time. If desired, the alkylaromatic may be heated to reaction temperature before sulfur is added. The heated hydrocarbon may be added to hot molten sulfur as an alternative procedure.

Reaction temperatures should be above about 375° F., generally in the range of about 400° to 500° F., preferably about 420° to 480° F. Temperatures substantially below 400° F. are usually too mild, produce unstable products, and excessive treating times are needed. Temperatures well above 500° F. are quite severe and result in unsuitable low-sulfur products.

Treating times will vary depending on the sulfur treat and reaction temperature level. Times in the range of about 0.25 to 15 hours, preferably 0.5 to 10 hours will generally suffice, the longer times being used at lower temperatures. The treating time should be sufficient to complete the reaction whereby the final product contains the critical amount of chemically combined sulfur in non-corrosive form.

The sulfur treat will depend on the final sulfur content desired in the finished product. As a rule, the final product should contain at least 1.5% and preferably above 2% by weight of chemically combined sulfur if potent motor lubricant additives are to be made. Sulfur contents much above 10 to 15% by weight will frequently give oil insoluble products. Therefore, the original sulfur treat, based on the total reactants, should be in the range of about 7 to 40% by weight, preferably 10 to 20% by weight. With the feed stocks of this invention, these amounts of sulfur will react to completion to form sulfur-containing hydrocarbons and H₂S. It is obviously undesirable to use conditions or quantities that permit free sulfur to remain in the finished product since free sulfur is corrosive.

The reaction is preferably carried out at substantially atmospheric pressure with provisions being made in the reactor for removal of hydrogen sulfide. If lower pressures are used, hydrogen sulfide removal is facilitated under some conditions. Pressures above atmospheric should be avoided unless H₂S is removed as heretofore described. Otherwise, the sulfur will remain in the product in unstable corrosive form.

The final product may be filtered to remove insoluble reaction products, etc. It may then be blown with nitrogen or other inert gas to remove dissolved H₂S or may be treated with a basic material to remove free acidic compounds.

Beneficial results may also be obtained by conducting the reaction in the presence of a small amount of a catalyst or stabilizing agent of the rubber vulcanization accelerator type. Such compounds include tertamethyl thiuram disulfide, mercapto benzothiazol, diphenylguanidine, selenium diethyldithiocarbamate, piperidinium pentamethylene dithiocarbamate, etc. and their mixtures. Amounts in the range of about 1 to 20% by weight of the compound, based on the sulfur treat, may be used. These materials help to form a stable product in a shorter time than is needed without them. Lower temperatures, such as in the order of 350° to 400° F. may also be used during the treating operation when using these accelerators.

The hydrocarbon feed stocks used in the practice of the present invention will comprise a substantial proportion of alkyl aromatics or naphthenic compounds, i. e., above about 15 to 25% of such compounds. The term "alkyl aromatics" as used herein refers to single aromatic rings, condensed aromatic rings, naphtheno-aromatic rings and other aromatic systems having at least one long chain alkyl group attached to the ring. Aromatic nuclei such as benzene, biphenyl, naphthalene, anthracene, tetrahydronaphthalene, etc. will be useful. Alkyl groups having above 10, generally above 15, carbon atoms in straight or branched chain configurations may be attached to the ring. Such groups include dodecyl, tetradecyl, octadecyl, and pentacosyl radicals, wax alkyl groups and the like. Hydroaromatic compounds, such as alkylated single and condensed ring naphthenes, that will be dehydrogenated to aromatic compounds under reaction conditions, may also be employed alone or in admixture with alkyl aromatic compounds.

The feed stock should contain only minor amounts or be substantially free of olefinic hydrocarbons such as olefins, olefinic polymers, unsaturated resins and the like. Single and condensed ring aromatic and naphtheno-aromatic hydrocarbons containing no alkyl substituent groups, such as naphthalene, anthracene, diphenyl, etc., should

not be present in more than very small amounts. Compounds of the above types follow a type of reaction mechanism entirely different to alkyl aromatics. They result in the production of materials that are unstable, corrosive, insoluble in oil or extremely low in sulfur content.

The feed stock may contain as diluents certain paraffinic hydrocarbons, although it is generally preferred that waxy constituents be held to a minimum. Substantially pure paraffinic materials do not form satisfactory products when treated with sulfur in accordance with this process; however, their presence is usually not deleterious if the feed comprises at least 20 to 25% alkyl aromatics. Alkyl naphthenes are quite suitable as diluents for reasons mentioned heretofore. It is generally preferred that the feed stock have an average molecular weight of over 200, and preferably over 300, to obtain products of good oil solubility and detergency characteristics.

Mineral oil base stocks provide a convenient source for feed stocks. Particularly desirable are lubricant base stocks having viscosities (Saybolt) above about 50 seconds, preferably in the range of about 75 to 500 seconds, at 210° F., and above about 300 to 750 seconds at 100° F., with A. P. I. gravities below about 30°. The base stock may be derived from mid-continent, coastal, and the like crudes, preferably those relatively rich in aromatic rings. The base stock, either distillates or residua, should be treated to remove waxy, asphaltic and olefinic constituents, if such materials are present in harmful amounts. Bright stocks, prepared by conventional deasphalting, dewaxing and acid-treating and/or clay-contacting of petroleum residua, are quite effective feed stocks.

Solvent extracts or lubricant distillates and bright stocks, prepared by extraction of the materials with solvents such as phenol, furfural, SO₂, and other solvents by procedures well known to the art, are excellent feed stocks. These materials contain high concentrations of alkyl aromatic and naphthenic hydrocarbons. Solvent extracts produced from relatively low boiling lubricant distillates will frequently have the high viscosity and low gravity characteristics needed to produce suitable sulfurized materials. The raffinates produced in solvent extraction, particularly those obtained from the more paraffinic crudes such as Pennsylvania crudes and the like, are generally unsuitable for use in the present invention because of the relatively low content of alkyl aromatics therein.

Alkyl aromatic hydrocarbons prepared by well known synthetic procedures may also be used. Particularly suitable are those produced by catalytic alkylation of aromatics with high molecular weight olefins, employing boron trifluoride, aluminum chloride and other catalysts. Preferred synthetic alkyl aromatic stocks are those produced by a Friedel-Crafts catalytic condensation of long chain aliphatic compounds, such as chlorinated wax, with aromatic compounds such as benzene, naphthalene, and anthracene. The chlorinated material may be derived from materials such as wax distillates, naturally occurring waxes such as palm wax, beeswax, carnauba wax, and the like. Condensation products of this type are well known to the art, particularly for use as pour depressants in waxy lubricants, and may be made by procedures such as those disclosed in U. S. 1,815,022 or by various improved modifications such as those disclosed in U. S. 2,491,683.

One example of a suitable method of preparing this alkyl aromatic compound is to chlorinate paraffin wax to a chlorine content of about 10 to 15% or more, and then condense about 100 parts by weight of the resultant chlorinated paraffin wax with about 10 to 20 parts by weight, preferably about 15 parts by weight, of naphthalene. This may be carried out in the presence of an inert solvent such as a highly refined kerosene, tetrachlorethane, dichlorobenzene, etc. Aluminum chloride may be used as catalyst. These products have molecular weights ranging from about 1000 to 5000, preferably about 1500 to

3000, and have potent pour depressing properties, particularly as judged by the A. S. T. M. pour point test.

It is desired that the above condensation be carried out in such a manner that the resulting product is substantially free of chlorine or other halogen before the sulfurization step is conducted. Chlorine contents of below about 0.1 weight per cent will usually not be detrimental. The sulfurization of the alkyl aromatic condensation products by the present procedure not only results in materials having desirable non-corrosive and detergency characteristics but also improves the pour depressing characteristics thereof in certain respects. If desired the condensation products may be blended with a suitable lubricant base stock before carrying out the sulfurization step, the blend containing at least 20% by weight of the condensation product.

The sulfurized products of the present invention are particularly suitable for use as additives in various mineral and synthetic lubricants such as engine oils, gear oils, greases, and the like where one or more properties such as film strength, oxidation and corrosion resistance, detergency or pour characteristics are important. The amount of the additive to be used in the lubricant may vary over a rather wide range depending on the property to be improved. In the range of about 1 to 10 weight per cent of the sulfurized hydrocarbon, based on the finished oil, may be used to improve detergency and antioxidant characteristics. Up to and about 20% of the additive may be needed to impart mild extreme pressure properties to an oil. In the range of about 0.001 to 2 weight per cent may be used as a pour depressant.

Other agents may be used along with the sulfurized additive in the oil composition. These include dyes, thickeners, viscosity index improvers, oiliness agents, resins, and the like. The lubricant base stock may range from about 35 to 150 seconds Saybolt viscosity at 210° F. and may be derived from mineral oils or prepared synthetically by well known means. Synthetic lubricants such as the conventional polyester and polyether types may be used as base stocks or may be admixed with petroleum-base lubricants.

The sulfurized materials may also be used in other hydrocarbon products such as motor fuels, heating oils, hydraulic fuels, torque converter fuels, turbine oils, process oils, and the like where one or more of the characteristics of the hydrocarbon material needs to be improved.

The following examples will illustrate methods of preparing and using the products of the present invention, but such examples are not to be construed as limiting the scope of the invention in any manner.

EXAMPLE I.—SULFURIZATION VARIABLES

A series of runs were carried out to determine the effect of sulfur treat, treating temperature and treating time on the sulfur content and corrosion characteristics of a lubricant base stock.

The base stock was a bright stock derived from a Mid-continent crude residuum. Waxy and asphaltic constituents were carefully removed from the residuum by de-asphalting, dewaxing, acid treating and clay contacting operations. The finished bright stock had a viscosity index of about 99, a viscosity (Saybolt) at 100° F. of 2658, a viscosity at 210° F. of about 161 seconds, an A. P. I. gravity of 25.9, an average molecular weight of about 400 and an estimated aromatic content of about 20 weight per cent. It consisted almost entirely of aromatic, naphtheno-aromatic and naphthenic ring compounds containing long paraffinic side chains. This material is termed "Bright Stock I." There is no directly quantitative method of analysis for the content of ring compounds in petroleum lubricating oils but the content can be estimated by various empirical methods based on the physical constants of the oils. Those methods are described in an article entitled "Ring Analysis of Hydrocarbon Mixtures"

and published on p. 624 of the Journal of the Institute of Petroleum, vol. 36, No. 322 (October 1950).

Sulfurization treats were carried out by adding the required amount of elemental sulfur to the base stock, heating the mixture up to reaction temperature, and stirring at reaction temperature and atmospheric pressure for the desired treating time. Hydrogen sulfide was evolved in copious quantities as the reaction temperature was approached and during the treatment at reaction temperature. The quantity of H₂S evolved decreased as the reaction proceeded.

Samples were removed from the reaction mixture after reaction temperature was reached and at various times during the treat at reaction temperature. Each sample was analyzed for sulfur and was tested for copper strip corrosion characteristics. Copper strip corrosion was determined as follows:

A blend containing 5% by weight of the sulfurized product in an S. A. E. 20 grade base lubricant was tested by immersing in it a polished metallic copper strip for a period of 3 hours at a temperature of 212° F. The strip was then removed, cleaned and noted for extent of staining. Ratings are given on a scale of "1" to "10" which denotes discoloration ranging from no stain to a black sulfide film. Ratings of "5" and below indicate an essentially non-corrosive material. Ratings of "1" to "2" indicate substantially no corrosion. This test is a modification of the C. R. C. method L-16-445.

Sulfurization treats were carried out with 10, 15 and 20% by weight sulfur, based on the total reaction mixture, at temperatures of 400°, 425°, 450° and 500° F. and for reaction times up to 6 hours. Sulfur in the product, based on the original sulfur treat, was determined by the following formula:

$$\text{Sulfur in product, based on sulfur treat, percent} = 100 \times \frac{(\text{Wt. percent S in product}) (\text{Parts by weight of oil feed})}{(100 - \text{Wt. percent S in product}) (\text{Parts by weight of original S})}$$

Table I, below, presents results obtained when using various sulfur treats at a temperature of 425° F.:

Table I.—Sulfurization of bright stock at 425° F.

Sulfur Treat, Wt. Percent Based on Total Charge	Reaction Time, Hours	Sulfur in Product, Wt. Percent		Copper Strip Rating
		Based on Product	Based on Sulfur Treat	
50	1	4.51	42.5	10
	2	3.20	29.8	6
	3	3.11	29.0	2-3
	4	2.98	27.7	(*)
	5	2.96	27.4	(*)
	6	2.91	27.3	2
55	1	7.24	44.3	10
	2	6.77	41.2	10
	3	5.25	31.4	10
	4	4.68	27.8	6
	5	4.63	27.6	3
	6	9.45	41.7	10
60	1	7.68	32.7	10
	2	7.00	30.1	10
	3	6.40	27.4	6
	4	6.27	26.8	4
	5	6.27	26.8	4
	6	6.23	26.7	3

*Not determined.

In each case, a substantially non-corrosive product was obtained only after the product contained less than one-third the originally added sulfur, the remainder of the sulfur having been evolved as H₂S. The reaction time required to obtain a non-corrosive product increased as the original sulfur treat increased. In the case of the 10% sulfur treat, extending the reaction time for 3 hours after a non-corrosive product was obtained resulted in loss of sulfur and did not improve corrosion characteristics to any appreciable extent.

Table II, below, presents summarized data from the various treats showing the reaction time required to pro-

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duce a substantially non-corrosive product, i. e., one having a copper strip rating below 4:

Table II.—Sulfurization of bright stock at 400°–500° F.

Sulfur Treat, Wt. Percent Based on Total Charge	Reaction Temp., ° F.	Reaction Time to Produce Non-Corrosive Product, Hours	Sulfur in Product, Weight Percent	
			Based on Product	Based on Sulfur Treat
10.....	400	6	3.08	28.6
10.....	425	3	3.11	29.0
10.....	450	1.5	3.11	29.0
15.....	425	5	4.63	27.6
15.....	450	3-4	4.45	26.4
15.....	500	0.5	3.62	21.4
20.....	425	6	6.23	26.7
20.....	450	5	6.10	26.0

The higher the original sulfur treat, the longer the reaction time required to produce a non-corrosive product at a given temperature. At a constant sulfur treat level, shorter reaction times are required as temperature increases. Under the conditions employed, at least 70% of the original sulfur had to be evolved as H₂S before a non-corrosive product was obtained. At a reaction temperature of 500° F., somewhat lower sulfur contents were obtained than were obtained at lower temperatures.

Silver strip corrosion tests were carried out on a number of the products. These tests confirmed the above results; i. e., the final product had to contain below 30 to 33% of the original sulfur before it was substantially non-corrosive to silver.

EXAMPLE II.—TESTING OF SULFURIZED BRIGHT STOCK

Product A.—This product was made by treating 90 parts by weight of bright stock I with 10 parts by weight of elemental sulfur at a temperature of 425° F. for 7 hours. The sulfurization procedure outlined in Example I was employed. The resulting product contained 2.86% by weight of sulfur or about 26.5% by weight of the original sulfur treat. A copper strip rating of "2" was obtained on a 5% blend of the product in an S. A. E. 20 grade lubricant.

An Aviation C. F. R. engine test was carried out on an oil blend containing 5% by weight of product A in an aviation base oil having a viscosity (Saybolt) at 210° F. of 100 seconds. The test was conducted for 50 hours, the C. F. R. engine being operated at 1800 R. P. M. and spark plug base temperature of about 520° F. The oils were rated on the demerit system wherein perfectly clean surfaces are given a rating of 0 while a rating of 10 is given to the worst condition that could be expected with that surface. The results on the unblended and blended oil are shown in Table III, below:

Table III

Wt. Percent Additive in Base Oil	Engine Demerits			
	Overall	Ring Zone	Varnish	Ring Sticking
None.....	2.7	6.7	3.6	2.5
5% Product A.....	1.1	2.4	2.2	0.0

The sulfurized bright stock gave excellent results as a detergent additive. It was particularly effective in keeping the ring zone clean and in eliminating ring sticking. Since it is both non-corrosive and ashless, it is well suited for use in aviation oils.

EXAMPLE III.—SULFURIZATION OF ALKYL NAPHTHALENE

Product B.—This product was an oil solution of an alkyl naphthalene prepared by condensing a chlorinated paraffin wax with naphthalene employing an aluminum

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chloride catalyst and a kerosene solvent. After hydrolyzing to remove catalyst and steam distilling, a wax-alkyl naphthalene was obtained having an average molecular weight of about 2700. Product B consisted of 35% of the wax naphthalene in a paraffinic base oil of S. A. E. 20 grade. The blend had a viscosity (Saybolt) at 210° F. of about 219, and an A. P. I. gravity of about 26.9. The preparation of the wax-naphthalene condensation product was carried out substantially in accordance with the procedure taught in U. S. 2,491,683 to J. C. Munday and Dilworth T. Rogers, issued on December 20, 1949, for making wax-naphthalene pour depressors. This material was sulfurized by the Example I procedure to make the following products.

15 *Product C.*—97 parts by weight of product B were treated with 3 parts by weight of sulfur at 400° F. for 3.5 hours.

20 *Product D.*—90 parts by weight of product B was treated with 10 parts by weight of sulfur at 400° F. for 5.5 hours.

Product E.—90 parts by weight of product B was treated with 10 parts by weight of sulfur at 425° F. for 7 hours.

25 Data from the preparation of these products is shown in Table IV, below:

Table IV.—Sulfurization of wax-naphthalene

Product	Reaction Condition			Sulfur in Product, Wt. Percent		Copper Strip Rating, 5% Blend, 3 Hrs. at 212° F.
	Sulfur Treat, Wt. Percent	Temp., ° F.	Time, Hrs.	Based on Product	Based on Sulfur Treat	
35 C.....	3	400	3.5	1.4	41.0	17
D.....	10	400	5.5	3.96	37.0	10
E.....	10	425	7.0	2.54	23.5	2

¹ Rating on 0.5% blend in base oil.

40 As in the case of the bright stock, the wax alkylated naphthalene had to be sulfurized at conditions sufficiently severe to drive off more than two-thirds of the sulfur before a non-corrosive product was obtained.

EXAMPLE IV.—POUR POINT AND POUR STABILITY TESTS

45 A. S. T. M. pour points were determined on lubricant blends containing the various products of Example III. The wax base mineral lubricant oil consisted of a Mid-Continent S. A. E. 20 grade lubricant having a pour point of about +10° F. Various amounts of products B, C, and D were added thereto and the A. S. T. M. pour points of the resulting blends were then determined as shown in Table V, below:

Table V

Weight Percent Product in Base Oil..	0.10	0.05	0.03	0.01
	60 Product Tested.....	A. S. T. M. Pour Point, ° F.		
Product B (Wax-naphthalene).....	-35	-25	-10	+10
Product C (Prod. B Sulfurized).....	-35	-30	-10	+10
Product D (Prod. B Sulfurized).....	-30	-25	-10	+10

65 It is noted that the pour depressing potency of the alkylated aromatic condensation products was not appreciably changed by mild sulfurization.

70 The A. S. T. M. pour point and pour stability was determined on blends obtained by adding products B and E to a waxy-base mineral lubricating oil. The base oil consisted of an acid-treated, Mid-Continent neutral oil containing 3.5% of conventionally refined Pennsylvania bright stock, the resulting blend having the viscosity of an S. A. E. 10-grade oil and an A. S. T. M. pour point of 75 +30° F. The pour stability of the base stock containing

small concentrations of products B and E were determined by a test in which temperature was varied to simulate winter temperature conditions. The procedure used was Test "V" pour stability test, described in Oil and Gas Journal, vol. 42, No. 7, pp. 103-106 (June 24, 1943). Several cycles of cooling and heating were repeated to determine the solid point of the oil blend. The temperature at which the oil sample became solid under these conditions after one and three cycles of cooling and heating, designated as the solid point, are shown in Table VI, below:

Table VI

Additive Used in Base Oil	Additive Concentration, Wt. Percent	A. S. T. M. Pour, ° F.	Pour Stability Solid Point, ° F.	
			Cycle 1	Cycle 3
Product B.....	0.05	-5	-15	0
Do.....	0.15	-25	-15	-15
Product E.....	0.05	+5	<-20	-20
Do.....	0.15	-15	<-20	<-20

The A. S. T. M. pour potency of the alkylated aromatics was decreased slightly when sulfurized to form a non-corrosive product (product E). The pour stability characteristics of this sulfurized material were markedly superior, however, to those of the unsulfurized material (product B).

EXAMPLE V.—LAUSON ENGINE TESTS

A blend was prepared containing 5.0 weight per cent of product A in a solvent extracted Coastal naphthenic oil having a viscosity (Saybolt) of 60 seconds at 210° F. This blend and a sample of the unblended base oil were employed as crankcase lubricants in tests with a Lauson engine. The engine operated at 300° F. jacket temperature, 295° F. oil temperature, 1800 R. P. M. speed and 1.5 indicated kilowatt load, the tests being conducted for 25 hours each. The loss in weight of the copper-lead bearings and the varnish demerit were determined in each test. The varnish demerit rating was based upon a rating scale in which a perfectly clean piston surface is given a rating of 0 and a demerit of 10 is given to the worst condition which could be expected to exist on that surface. The results are shown in Table VII, below:

Table VII.—High temperature Lauson engine tests

Additive	Additive Concentration in Base Oil, wt. percent	Piston Varnish Demerit	Cu-Pb Bearing wt. Loss (g./bearing)
None.....		6	0.10
Product A (sulfurized Brt. Stock I).....	5.0	2.0	0.03

The sulfurized bright stock imparted excellent corrosion inhibition and detergency characteristics to the lubricant.

EXAMPLE VI.—SULFURIZATION OF ANTHRACENE

85 parts by weight of anthracene and 15 parts by weight of sulfur were stirred and heated at 420-430° F. for 6 hours. Small samples were taken at hourly intervals. All of the samples, including the final product, consisted mainly of a mixture of anthracene and sulfur with a small amount of a hard, black resinous material. On cooling, these materials separated into 3 solid phases.

It is apparent that aromatic hydrocarbons containing no alkyl side chains will not respond to sulfurization in accordance with the present process to produce useful products. This tends to confirm the theory of the reaction as explained heretofore.

EXAMPLE VII.—SULFURIZATION OF PARAFFIN WAX

85 parts by weight of paraffin wax (122° F. melting point) and 15 parts by weight of sulfur were heated and stirred at 400-450° F. for six hours. Small samples were removed after 1, 2, 3 and 6 hours.

The first 3 samples each solidified into two phases, one of which appeared to be substantially pure sulfur. The six-hour sample separated into two solid phases, one being a brown wax, and the other being a heavy black solid that melted well above the melting point of the wax.

The samples were heated above the melting point and filtered and the two fractions analyzed with the following results:

Hours at 400-450° F.	"Wax" Fraction		High Melting Point Fraction	
	Wt. Percent Recovered	Wt. Percent S Present	Wt. Percent Recovered	Wt. Percent S Present
1.....	75	1 2.23	25	63.76
2.....	80	(?)	20	(?)
3.....	75	(?)	25	(?)
6.....	63	3 3.81	37	36.15

¹ 9.7% sulfur based on original sulfur treat.

² Not determined.

³ 14.2% sulfur based on original sulfur treat.

The "wax" fraction from each sample was blended in mineral oil in 5% concentration and tested by the copper strip corrosion test heretofore described. The blends were all very corrosive to copper, giving a copper strip rating of 10+, showing that the sulfur was not combined in a useful form and may have been present as a solid solution. The relatively low sulfur contents of the wax fraction based on sulfur treat, show that the sulfur reacts by a mechanism entirely different to that found in the case of alkyl aromatics.

EXAMPLE VIII.—SULFURIZATION OF VARIOUS LUBRICANT BASE STOCKS

A series of sulfurization treats were carried out on various lubricant base stocks, solvent extracts and solvent raffinates. The sulfur treatments were all carried out at 425° F. for 6 hours using 15% by weight of sulfur based on the total mixture. The sulfurization procedure of Example I was used in all cases.

In one case, the extract used was obtained by phenol extraction of the Bright Stock I. This extract represented a 12 volume percent yield of the bright stock; the extract had a viscosity (Saybolt) at 210° F. of 217, a viscosity at 100° F. of 7633, a viscosity index of 56, an A. P. I. gravity of 17.9°, and an average molecular weight of about 400. This phenol extract comprised the most aromatic and naphthenic constituents of the original Bright Stock I.

Bright Stock II was also sulfurized. This bright stock was a deasphalted and dewaxed Mid-Continent residuum, the bright stock having a viscosity (Saybolt) at 210° F. of 149, a viscosity at 100° F. of 2273, a viscosity index of about 100, an A. P. I. gravity of 26.7°, and an estimated average molecular weight of about 380.

A lubricant distillate, derived from the same crude oil from which Bright Stock II was obtained, was phenol extracted, and the raffinate was dewaxed and clay percolated. The resulting dewaxed raffinate had an A. P. I. gravity of 30.4°, a viscosity (Saybolt) at 100° F. of 392 seconds, a viscosity at 210° F. of 59 seconds, a viscosity index of 105 and an average molecular weight of about 300. This is a very paraffinic stock as can be seen from the high gravity and viscosity index, i. e. it contained relatively few aromatic, naphtheno aromatic and the like rings.

The extract from the phenol extraction of the above lubricant distillate was also sulfurized. This extract had an A. P. I. gravity of 18.3°, and Saybolt viscosities at

100° and 210° F. of about 1250 and 76, respectively, and consisted of the most aromatic and naphthenic constituents of the original distillate.

Both the raffinate and extract of the distillate were sulfurized.

The data from the above sulfurization treats are summarized in Table VIII below:

Table VIII.—Sulfurization at 425° F. for 6 hours with 15 weight percent sulfur

Material Treated	Sulfur in Product, Weight Percent		Copper Strip Rating, 5% Bleed 3 Hrs. at 212° F.
	Based on Product	Based on Original Sulfur Treat	
Bright Stock I.....	4.63	127.6	13
Extract of Bright Stock I.....	4.55	27.0	3
Bright Stock II.....	4.50	26.8	4
Extracted and Dewaxed Distillate from Crude of Bright Stock II:			
Raffinate.....	2.08	12.0	10
Extract.....	3.33	20.0	3

¹ After 5 hours' treating time.

In each case, where the lubricant base stock contained appreciable substituted aromatic rings and naphthenic rings, a non-corrosive product was obtained about 20 to 30% of the original sulfur. The paraffinic raffinate, in common with paraffin wax and non-substituted aromatics, obviously followed an entirely different type of reaction mechanism. This is shown by the fact that even though a much larger amount of sulfur was eliminated, the small amount of remaining sulfur was still in corrosive form.

EXAMPLE IX.—SULFURIZATION OF ALKYL BENZENE

Monoalkyl benzene was prepared by alkylating benzene with C₁₂ polypropylene using an aluminum chloride-hydrocarbon complex catalyst. The bottoms fraction of the product, consisting entirely of C₁₂–C₁₅ alkyl benzenes, having an average molecular weight of about 275 and a boiling range of about 556°–620° F. was sulfurized by the procedure of Example I with 10% sulfur, based on the total reaction mixture, for 2½ hours at 425° F. and then 4 hours at 450° F. The final product contained 2.98 weight percent sulfur, or 27.5 weight percent of the original sulfur treat, and an oil blend containing the product was substantially non-corrosive to copper.

What is claimed is:

1. A process for producing sulfurized alkyl aromatics which comprises the step of reacting a substantially non-olefinic hydrocarbon feed stock comprising alkyl aromatics and having an average molecular weight above about 200 with sulfur at an elevated temperature in the range of about 350° to 500° F. for a time sufficient to form a product containing at least about 1.5% by weight of chemically combined sulfur, said chemically combined sulfur being in the range of about 18 to 33% by weight of the originally added sulfur.

2. A process for producing sulfurized alkyl aromatics which comprises the step of reacting a substantially non-olefinic hydrocarbon feed stock comprising a substantial portion of alkyl aromatics, said feed stock having an average molecular weight of above 200, with elemental sulfur in an amount in the range of about 7 to 40% by weight, based on the total reaction mixture, at a temperature in the range of about 375° to 500° F. to obtain a product containing in the range of about 20 to 30% by weight of the original sulfur in chemically combined form.

3. A process as in claim 2 wherein said hydrocarbon feed stock is a lubricant base stock having a viscosity (Saybolt) at 210° F. above about 75 seconds and an A. P. I. gravity below 30°.

4. A process as in claim 2 wherein said hydrocarbon feed stock includes a chlorinated paraffin wax-aromatic

condensation product having a molecular weight above about 1000.

5. An improved process for producing a sulfurized lubricant which comprises the steps of forming a lubricant base stock comprising substantial amounts of alkyl aromatic and alkyl naphthenic constituents, said base stock being substantially free of olefinic, waxy and asphaltic constituents and having an average molecular weight of at least about 300, and reacting said base stock at an elevated temperature in the range of about 400° to 500° F. with elemental sulfur in an amount in the range of about 10 to 20% weight based on the total reaction mixture, said reaction being continued for a time sufficient to form a product containing in the range of 20 to 30% by weight of the originally added sulfur in chemically bound form, and to drive off the remaining sulfur as hydrogen sulfide.

6. A process as in claim 5 wherein said reaction time is in the range of about 0.25 to 15 hours.

7. As a new composition of matter, the product from the process of claim 1.

8. As a new composition of matter, the product from the process of claim 2.

9. A multi-functional lubricant additive obtained by reacting a substantially non-olefinic hydrocarbon feed stock, having an average molecular weight of at least 200 and containing at least about 20% by weight of alkyl aromatics, with elemental sulfur in an amount in the range of about 7 to 30% by weight based on the total reaction mixture, said reaction being carried out at a temperature in the range of about 400° to 500° F. for a time sufficient to form a product containing in the range of about 20 to 30% by weight of the originally added sulfur in chemically bound form.

10. An additive as in claim 9 wherein said feed stock is a petroleum base stock.

11. An additive as in claim 10 wherein said feed stock is a bright stock derived from a conventionally refined residuum.

12. An additive as in claim 9 wherein said alkyl aromatic is a Friedel-Crafts condensation product of a long chain chlorinated aliphatic hydrocarbon and an aromatic hydrocarbon.

13. A lubricant composition comprising a mineral base lubricant and in the range of about 0.001 to 20% by weight of the product from the process of claim 1.

14. A mineral base lubricant containing in the range of 0.001 to 20% by weight of the product from the process of claim 2.

15. A substantially ashless, non-corrosive motor lubricant consisting essentially of a mineral base lubricant and in the range of 0.001 to 20% by weight of the additive of claim 9.

16. A substantially non-corrosive motor lubricant composition comprising a mineral lubricating oil containing a detergent amount of the product obtained by reacting a substantially non-olefinic petroleum base stock comprising alkyl aromatics and having a viscosity (Saybolt) at 210° F. above 75 seconds, a molecular weight above 200, and an A. P. I. gravity below 30° with elemental sulfur in an amount in the range of about 7 to 30% by weight based on the total reaction mixture, said reaction being carried out at a temperature in the range of about 400° to 500° F. for a time sufficient to form a product containing in chemically bound form in the range of about 20 to 30% by weight of the originally added sulfur.

17. A composition as in claim 16 wherein said base stock is a solvent extract of a petroleum lubricant base stock.

18. A composition as in claim 16 wherein said base stock is a bright stock derived from a conventionally refined residuum.

19. A substantially non-corrosive motor lubricant composition comprising a mineral lubricating oil containing in the range of about 0.001 to 20% by weight

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of the product obtained by reacting a substantially non-olefinic hydrocarbon feed stock containing at least 20% of a Friedel-Crafts condensation product of a long chain chlorinated aliphatic hydrocarbon and an aromatic hydrocarbon with elemental sulfur in an amount in the range of about 7 to 30% by weight based on the total reaction mixture, said reaction being carried out at a temperature in the range of about 400° to 500° F. for a time sufficient to form a product containing in chemically bound form in the range of about 20 to 30% by weight of the originally added sulfur.

20. A composition as in claim 19 wherein said feed

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stock is the condensation product of a chlorinated paraffin wax and naphthalene having a molecular weight in the range of about 1000 to 5000.

References Cited in the file of this patent

UNITED STATES PATENTS

898,378	Kohler -----	Sept. 8, 1908
1,884,762	Lloyd -----	Oct. 25, 1932
1,896,227	Egloff -----	Feb. 7, 1935
2,027,323	Schetelig -----	Jan. 7, 1936
2,112,677	Muskat -----	Mar. 29, 1938