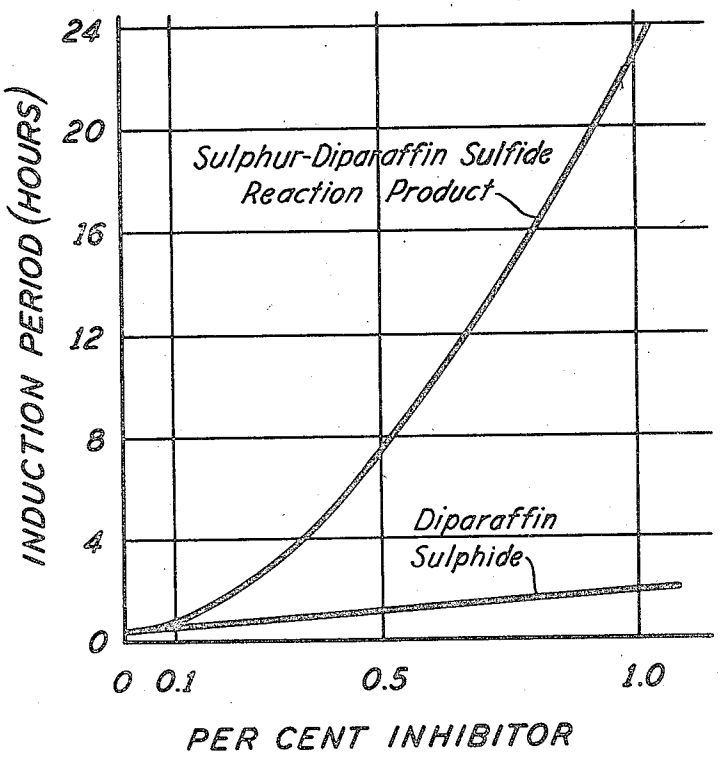
July 11, 1950 T. I. CLAUSEN ET AL 2,514,625

LUBRICATING OIL COMPOSITION

Filed Dec. 13, 1945

OXIDATOR TESTS
WHITE OIL PLUS INHIBITOR



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LUBRICATING OIL COMPOSITION

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7 Claims. (Cl. 252—32.7)

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This invention relates to new and useful sulfur compounds, to a process of making the same and to mineral lubricating oils and the like containing these sulfur compounds as improvement agents.

It is known that small amounts of aliphatic sulfides, i. e., compounds of the general formula

$$R—S_n—R'$$

wherein R and R′ are aliphatic radicals and n is 1, 2 or 3, function in mineral lubricating oils as antioxidants, corrosion inhibitors (especially to inhibit corrosion of cadmium-silver and copper-lead type alloy bearings) and, when used in somewhat larger amounts, as extreme pressure agents. However, these sulfides are limited in their effectiveness, and relatively large amounts must be used to accomplish the desired result.

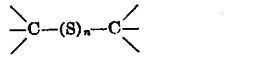
It is an object of the present invention to provide aliphatic sulfur compounds that are more effective than those of the prior art, and to provide a means of preparing these improved aliphatic sulfur compounds.

It is a further object of the invention to provide derivatives of high molecular weight aliphatic sulfur compounds, starting with available aliphatic sulfides, which derivatives are superior to the aforesaid available aliphatic sulfides as antioxidants for mineral lubricating oils.

Still further objects will be apparent from the ensuing description and the appended claims.

We have discovered that by heating a high molecular weight aliphatic sulfide with free sulfur, a stable product (stable in the sense that sulfur does not precipitate out from the reaction mass after it has been cooled), is obtained and which exhibits a marked improvement over the original sulfide as an improvement agent for mineral lubricating oils.

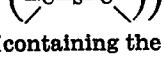
The starting materials are sulfur and a high molecular weight aliphatic sulfide, although selenium may be substituted for part or all of the sulfur. The high molecular weight aliphatic sulfide is a sulfide containing in the molecule one or more groups



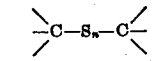
wherein the carbon atoms are aliphatic and n is a small integer, which is preferably 1 or 2 but

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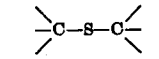
may be as high as 3. This sulfide contains not less than 14 carbon atoms, preferably not less than 20 carbon atoms. As indicated, the sulfide constituting one of the starting materials may be a monosulfide (containing the group



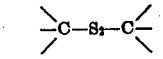
or a polysulfide (containing the group



where n=2 or 3). Moreover, there may be a plurality of such groups in one molecule; e. g., the poly-monosulfides, containing two or more groups



and the poly-disulfides, containing two or more groups



Examples of monosulfides are cetyl ethyl monosulfide ($C_{16}H_{33}—S—C_2H_5$), didecyl monosulfide ($C_{10}H_{21}—S—C_{10}H_{21}$), dilauryl monosulfide ($C_{12}H_{25}—S—C_{12}H_{25}$), dicetyl monosulfide ($C_{16}H_{33}—S—C_{16}H_{33}$) and dibenzyl monosulfide ($C_6H_5.CH_2—S—CH_2.C_6H_5$). Examples of polysulfides are didecyl, dilauryl, dibenzyl and dicetyl disulfides (R—S_2—R, where the R's are decyl, lauryl, benzyl of cetyl radicals, respectively). Examples of poly-monosulfides are didodecyl ethylene dithioether ($C_{12}H_{25}—S—CH_2—CH_2—S—C_{12}H_{25}$), other di-monosulfides (di-thioethers) of the type R—S—$(CH_2)_n$—S—R, where the R's are aliphatic groups, and the products of condensing polychlorinated aliphatic hydrocarbons with sodium monosulfide. Examples of poly-disulfides are didodecyl ethylene di-disulfide ($C_{12}H_{25}S_2—CH_2—CH_2—S_2—C_{12}H_{25}$), other di-disulfides of the type R—S_2—$(CH_2)_n$—S_2—R, where the R's are aliphatic groups, and the products of condensing polychlorinated aliphatic hydrocarbons with sodium disulfide, i. e., the products described in Farrington et al. Patent No. 2,346,157 as "multi-bridged thioalkyl compounds."

Preferably, however, the aliphatic sulfides used as starting materials in the process of this in-

vention are the complex products of condensing chlorinated paraffin wax with sodium monosulfide, sodium polysulfide or a mixture of sodium monosulfide and sulfur. Such complex products, hereinafter referred to as "diparaffin sulfides," are described in Farrington et al., U. S. Patent No. 2,346,157, wherein they are designated as "paraffin wax thiomers." In the Farrington patent, the preparation of suitable aliphatic sulfides is described in detail, beginning at page 5, column 2, line 5 with the preparation of chlorinated paraffin wax and continuing with Examples 1, 2 and 3 on pages 5 and 6.

Any form of free sulfur (or selenium) may be used as the other starting material; e. g., flowers of sulfur, roll sulfur and red selenium.

The sulfur and aliphatic sulfide may be reacted in widely varying proportions. Since it is a primary object of the invention to effect a substantial improvement of the aliphatic sulfide as an antioxidant, a substantial amount of sulfur relative to aliphatic sulfide will be used ordinarily; usually at least 15% of sulfur based on the weight of sulfur originally present in the aliphatic sulfide will be employed. The upper limit of the proportion of sulfur will be governed by two factors, namely, the degree of improvement desired in the end product (the more sulfur incorporated, the better the product) and the capacity of the original sulfide to combine with sulfur. The latter factor (capacity of the original sulfide to combine with sulfur), is in turn governed by two factors, namely, the total amount of sulfur originally present in the sulfide and the form in which it is present. An example will suffice to illustrate this principle.

Assume three aliphatic sulfides, as follows: (1) R—S—R; (2) R—S—R—S—R and (3) R—S_2—R. The second sulfide (R—S—R—S—R) will combine with more sulfur than the first sulfide (R—S—R) because the second sulfide contains two monosulfide or thioether groups (C—S—C), each of which is capable of combining with sulfur, whereas the first sulfide contains only one such group. The third sulfide (R—S_2—R), contains more sulfur per molecule than the first and as much sulfur per molecule as the second sulfide, but it will not combine with as much sulfur as either the first sulfide or the second sulfide, because its capacity to combine with sulfur is already partly satisfied by the second sulfur atom in the disulfide group.

This theoretical explanation is given by way of a guide in the practice of the invention. It is probably over-simplified since the form in which sulfur exists in complex sulfides such as the diparaffin sulfides is not known with certainty. The guiding principles in the practice of the invention may be re-stated thus: Most aliphatic sulfides, such as are produced by condensing sodium or potassium monosulfide or polysulfide with a chlorinated aliphatic hydrocarbon or mixture of hydrocarbons, are capable of combining with sulfur. There is strong evidence that this combination is a chemical combination, as distinguished from a mere physical dissolution or dispersion of sulfur in the aliphatic sulfide, in that (provided not too much sulfur is added and provided the mixture is heated sufficiently) a substantial amount of sulfur can be incorporated in the sulfide without any tendency for the sulfur to precipitate out when the product is cooled. The capacity of the original sulfide so to combine with sulfur is governed by the nature of the original sulfide. By empirical means, it is possible

to determine how much sulfur can be stably combined with the sulfide.

For example, we have found that diparaffin sulfide prepared as described in Example 1 below and containing 12.4% sulfur, will combine stably with about 35% of sulfur based on weight of sulfur originally present in the sulfide, while diparaffin sulfide prepared as described in Example 1 below, and containing about 15% sulfur, will combine stably with about 45% of sulfur based on the weight of sulfur originally present in the sulfide.

In the preferred embodiment of the invention, sulfur and diparaffin sulfide are used as the starting materials; the diparaffin sulfide is prepared by chlorinating paraffin wax of about 120° to 160° F. melting point to about 15 to 25% chlorine content and the chlorinated wax is condensed with sodium monosulfide, sodium monosulfide and sulfur or sodium polysulfide to produce a material containing about 10 to 20% sulfur; and the diparaffin sulfide and sulfur are reacted in proportions and under such conditions of time and temperature as stably to incorporate about 15 to 45% of sulfur based on the weight of sulfur originally present in the diparaffin sulfide.

Selenium may be substituted for sulfur, or mixtures of selenium and sulfur in varying proportions may be used. In either case, principles similar to those governing the use of sulfur apply. However, higher temperatures are required to incorporate selenium in the aliphatic sulfide than are required with sulfur.

The temperature of reaction is controlled mainly by two factors: getting the sulfur dissolved in the aliphatic sulfide and evolution of hydrogen sulfide. Desirably, a temperature is employed sufficient to dissolve the sulfur in the sulfide. Since the melting point of sulfur is 275° F., the minimum temperature of reaction is preferably 275° F., but by use of eutectic or other low melting mixtures, accompanied by correspondingly longer reaction periods, lower temperatures may be employed. Desirably, also, the temperature is kept below that at which hydrogen sulfide is evolved in substantial amount, usually below about 400° F. Preferably, a reaction temperature of about 275° to 350° F. is employed.

The time of reaction will be governed by factors such as the temperature of reaction, the nature of the aliphatic sulfide and the amount of sulfur which it is desired to combine with the sulfide. Generally, about six hours heating at 300° F., correspondingly more and less at lower and higher temperatures, is sufficient to combine all the sulfur that is capable of combining with the sulfide to produce a stable product.

It is known to incorporate sulfur directly into hydrocarbon materials in varying amounts, as by reacting sulfur with unsaturated hydrocarbons, condensing alkali metal sulfides, polysulfides and hydrosulfides with chlorinated hydrocarbons, etc. These methods are, however, distinguished from and inferior to the method of the present invention in at least the following respects: The principal object of this invention is to convert an aliphatic sulfide of relatively low activity (as measured, for example, by its capacity to inhibit oxidation of mineral lubricating oils) to a sulfur compound of relatively high activity. This object is desirably accomplished by an inexpensive procedure which is readily susceptible to control, and the final product is desirably stable in the sense that the sulfur is stably combined and does not tend to precipitate

out when cooled to, say, 77° F. These objects are accomplished by the method of the invention; the aliphatic sulfide is converted to a higher sulfur product of increased activity, the conversion can be readily controlled and is inexpensive, and the product is stable. The methods of the prior art, even if so carried out as to produce a high sulfur product, fail in one or more of these important respects; the product does not have high sulfur activity, or the process of making it is expensive or difficult to control, or the product is unstable, or the method and its product are deficient in several of these respects.

The following specific examples will serve further to illustrate the practice and advantages of the invention.

EXAMPLE 1.—PREPARATION OF ALIPHATIC SULFIDES AND SULFURIZATION OF SAME

Chlorinated paraffin wax is prepared by chlorinating a 130° F. melting point paraffin wax to 20% chlorine content by bubbling chlorine through the wax at 190° to 200° F. 1875 pounds of this chlorinated wax, 710 pounds of sodium monosulfide (60–62% Na_2S), 172 pounds of sulfur, 450 gallons of alcohol and 450 gallons of petroleum thinner were taken. The alcohol, sodium sulfide and sulfur were charged to a jacketed pressure reaction vessel, the vessel was closed and heated to refluxing temperature and the chlorinated wax was added slowly over a period of one hour, the reaction mixture being meanwhile refluxed and agitated. After the reaction had proceeded for a considerable time (substantially to completion), the pressure was increased by application of heat until the temperature rose to 270° F. and the pressure was increased to about 100 pounds gauge. The total reaction time was 8 hours. The pressure was then released, alcohol was removed by distillation and the reaction mixture was diluted with the petroleum thinner and allowed to settle to deposit sodium chloride. The thinner solution was then filtered to remove insoluble matter and the thinner was removed by distillation. The residue constituted the desired diparaffin sulfide. It contained 14% sulfur and 2.5% chlorine.

Next, 14,000 pounds of the diparaffin sulfide prepared as described above were charged to a jacketed steel mixer and heated to 300° F. 588 pounds of flowers of sulfur were added to the charge, slowly and with agitation of the mixture. The mixture was then stirred vigorously for six hours while being maintained at 300° F. During the period of agitation and heating, samples of the reaction mixture were taken and tested by immersing a copper strip in the sample for five minutes at 212° F. At first the copper strip was black and flaky, but as the reaction approached completion the copper strip (a fresh strip being used each time) would lose its flaky appearance. Finally, upon completion of the reaction, the strip appeared blue-black in color and smooth in appearance.

The product was bright in appearance and required no further processing. On cooling, no sulfur separated, even on long standing. It contained 17.5% sulfur, 2.5% chlorine and was a dark colored viscous oil. The yield was quantitative.

EXAMPLE 2.—PERFORMANCE OF SULFUR COMPOUNDS OF THE INVENTION

A. *Oxidator tests.*—These tests were carried out in apparatus of the type described by Dornte in "Industrial and Engineering Chemistry," vol. 28, page 26 (1936). In this test, oxygen at atmospheric pressure is bubbled through the oil, which is maintained at 340° F. The extent of oxidation of the oil is measured by the amount of oxygen absorbed by the oil, and the time in hours required for 100 grams of oil to absorb 1200 cc. of oxygen (S. T. P.) is called the "induction period." Results are noted in Table I below:

Table I

Test Oil	Induction Period
Heavy White Oil	0.05
Heavy White Oil + 0.1% of final product of Example 1	0.85
Heavy White Oil + 0.5% of final product of Example 1	7.4
Heavy White Oil + 1% of final product of Example 1	23
Heavy White Oil + 1% of diparaffin sulfide (intermediate product of Example 1)	2

The induction period of white oil+1% of diparaffin sulfide is inserted for comparative purposes, to show the phenomenal improvement imparted by combining sulfur therewith. Thus, white oil containing 1% of the final product of Example 1 contained only 1.25 times as much sulfur as white oil containing 1% of diparaffin sulfide, yet the first oil was about ten times as stable to oxidation as the second oil. This comparison is shown even more clearly by the curves of Figure 1 of the drawing, in which abscissae represent amount of inhibitor and ordinates represent induction period.

B. *Engine performance.*—The test employed was that test designated by the Co-ordinating Research Council as the L–4–545 Test. It is described in a circular entitled "Test Procedure for Determining Oxidation Characteristics of Heavy-Duty Crankcase Oils," which can be obtained from the Co-ordinating Research Council, 30 Rockefeller Plaza, New York, N. Y. This test employs a Chevrolet engine and will be referred to hereafter as the "Chevrolet Test." The engine is run for 36 hours at a jacket temperature of 200° F., sump temperature of 280° F. Bearings are weighed before and after the test and the average bearing weight loss is recorded as the corrosion. Other details of the test will be found in the aforesaid circular.

Several oils were submitted to the Chevrolet Test. These oils were:

Oil A_1.—S. A. E. 30 blend of solvent refined California paraffinic and naphthenic oils, containing a small amount each of a thiophosphate (calcium di-cetylphenyl dithiophosphate), a phenate (product of heating sulfur with the calcium salt of an alkylated phenol produced by alkylating phenol with a butene polymer of average molecular weight 196) and 1% of diparaffin sulfide (intermediate product of Example 1, above).

Oil A_2.—Same as A_1, except that it contained 0.33% of the sulfur-diparaffin sulfide reaction product of Example 1, instead of 1% of diparaffin sulfide.

Oil B_1.—Same as A_1, except that base oil was an S. A. E. 30 solvent refined California paraffinic oil.

Oil B_2.—Same base oil as B_1, same compounding as A_2.

Oil C_1.—S. A. E. 30 highly refined mixed base oil, same compounding as A_1.

Oil C_2.—Same base oil as C_1, same compounding as A_2.

Oil D_1.—S. A. E. 30 highly refined mixed base oil (different from base oil of B_1 and B_2), same compounding as A_1.

Oil D_2.—Same base oil as D_1, same compounding as A_2.

Test results are given in Table II below:

Table II

Test Oil	A_1	A_2	B_1	B_2	C_1	C_2	D_1	D_2
Percent Diparaffin Sulfide	1		1		1		1	
Percent Sulfur-diparaffin sulfide reaction product		0.33		0.33		0.33		0.33
Cu-Pb bearing wt. loss mgs./half bearing	163	129	65	34	93	89	80	31
Varnish rating	44	45	46	47	46	46	44	47
Sludge rating	49	48	47	50	47	50	48	50
Engine rating (=varnish rating+sludge rating)	93	93	93	97	93	96	92	97

EXAMPLE 3.—SUBSTITUTION OF SELENIUM FOR SULFUR

492.5 grams of diparaffin sulfide prepared as described in Example 1 above and containing 13.9% sulfur, were heated with 7.5 grams of selenium at 375° F. for two hours, yielding a dark brown product containing 1½% selenium based on weight of reaction product. This reaction product was dissolved in medicinal grade of white oil in the amount of 1% by weight based on the oil and was subjected to the above-mentioned oxidator test. The induction period exceeded 50 hours (i. e., at the end of 50 hours, less than 1200 mls. of oxygen had been absorbed per 100 grams of oil, in contrast to induction periods of 23 hours for 1% sulfurized diparaffin sulfide (product of Example 1), and 2 hours for 1% diparaffin sulfide; see Table I above.

The sulfur-sulfide and selenium-sulfide reaction products of the invention may be used to stabilize oxidizable organic substances generally but they are most useful in stabilizing hydrocarbon and nonhydrocarbon lubricating oils; e. g., light to heavy petroleum lubricating oils of naphthenic, paraffinic and mixed base origins, vegetable oils and viscous, oily polymers of propylene oxide. They may be used in amounts of 0.1% or less to 2% or more, preferably 0.2 to 1%, by weight based on the finished composition, or greater quantities, e. g. 2 to 25%, may be used to produce concentrates or stock solution for later blending with more oil to produce a finished composition. These sulfur-sulfide and selenium-sulfide products may also be used advantageously in lubricating oils in conjunction with oil-soluble metal salts such as the phenate and the thiophosphate of the engine tests above. These metal salts, which promote piston cleanliness and act as sludge inhibitors or dispersants in crankcase oils, may be used in finished oils in amounts of 0.1 to 2% or more or in concentrates in amounts of 2 to 25%, in conjunction with the sulfur-sulfide and selenium-sulfide products of the invention. Further examples of metal salts which may be used advantageously with the aforesaid sulfur-sulfide and selenium-sulfide products are: phenates such as calcium, barium and aluminum salts of cetyl phenol and diamyl diphenol monosulfides; sulfonates such as calcium, barium and aluminum mahogany sulfonates and oil-soluble calcium, barium and aluminum alkyl benzene sulfonates; phosphates and thiophosphates such as calcium and zinc salts of dicetyl phosphoric acid, and di-methylcyclohexyl dithiophosphoric acid and di-cetylphenyl dithiophosphoric acid; calcium, barium and aluminum naphthenates; and calcium and barium salts of aliphatic carboxylic acids such as α-phenyl stearic acid, α-cetyl succinic acid and the acid lauryl ester of succinic acid. In other words, the oil-soluble metal salts of organic acids or organo-substituted inorganic acids may be advantageously used in conjunction with the present aliphatic sulfur-containing reaction products.

By "aliphatic sulfides" as used in the appended claims without qualification, it is intended to include, as radicals attached to the sulfur, open chain and cyclic aliphatic radicals, which may be saturated or unsaturated and which may be substituted by polar groups or by aromatic radicals.

We claim:

1. A lubricating oil comprising a major amount of an oxidizable lubricating oil and a small amount, sufficient to inhibit substantially said oxidative deterioration, of the aliphatic sulfur-containing reaction product produced by heating an element selected from the group consisting of sulfur and selenium with a dialkyl sulfide of relatively low inhibitor activity and containing at least 14 carbon atoms in the molecule, to about 275–400° F., said product containing about 15–45% of said added element, based on the weight of sulfur present in said dialkyl sulfide before heating, said added element being stably combined with said dialkyl sulfide and exhibiting substantially no tendency to separate at 77° F., said reaction product having a greatly increased inhibitor activity as compared to said original dialkyl sulfide.

2. A lubricating oil comprising a major amount of an oxidizable lubricating oil and a small amount, sufficient to inhibit substantially oxidative deterioration of said oil, of the aliphatic sulfur-containing reaction product produced by heating to about 275–400° F. an element selected from the group consisting of sulfur and selenium with a multi-(thio-bridged) dialkyl sulfide containing at least 14 carbon atoms, said product containing about 15–45% of said added element based on the weight of sulfur present in said dialkyl sulfide before heating, said added element being stably combined with said dialkyl sulfide and exhibiting substantially no tendency to separate at 77° F.

3. A lubricating oil composition comprising a major proportion of an oxidizable organic lubricating oil and a small amount, sufficient to inhibit substantially oxidative deterioration of said oil, of the aliphatic sulfur-containing reaction product produced by heating sulfur with a diparaffin wax thiomer at about 275–350° F., said product containing about 25–35% added sulfur based on the weight of sulfur present in the diparaffin wax thiomer before heating with sulfur, said added sulfur being stably combined with said diparaffin wax thiomer and exhibiting substantially no tendency to separate at 77° F.

4. A lubricating oil composition comprising a major proportion of an oxidizable mineral lubricating oil, stabilized against oxidation by a small amount of the aliphatic sulfur-containing reaction product produced by heating sulfur with a dialkyl sulfide of relatively low inhibitor activity and containing not less than 14 carbon atoms in the molecule, said product containing about 15%

to 45% of added sulfur based on the weight of sulfur present in said dialkyl sulfide before heating with sulfur, said added sulfur being stably combined with said sulfide and exhibiting substantially no tendency to separate at 77° F., said reaction product having a greatly increased inhibitor activity as compared to said original dialkyl sulfide.

5. A lubricating oil containing about 0.1–2% by weight of the aliphatic sulfur-containing reaction product produced by heating sulfur with diparaffin wax thiomer at about 275–350° F., said product containing about 25–35% added sulfur based on the weight of sulfur present in said thiomer before heating with sulfur, said added sulfur being stably combined with said thiomer and exhibiting substantially no tendency to separate at 77° F.

6. A lubricating oil composition comprising a major proportion of an oxidizable organic lubricating oil stabilized against oxidation by a small amount of the aliphatic sulfur-containing reaction product produced by heating at about 275–400° F. sulfur with a multi-(thio-bridged) dialkyl sulfide containing not less than 14 carbon atoms in the molecule, said product containing about 15–45% of added sulfur based upon the weight of sulfur present in said dialkyl sulfide before heating with said sulfur, said added sulfur being stably combined with said dialkyl sulfide and exhibiting substantially no tendency to separate at 77° F.

7. A lubricating oil composition comprising a major proportion of an oxidizable organic lubricating oil and a small amount, sufficient to inhibit oxidation of said oil, of the reaction product produced by first condensing polychlorinated paraffin wax with an alkali metal sulfide and then heating the resultant diparaffin wax thiomer with sulfur at about 275° to 350° F. to combine stably with said thiomer about 25 to 35% by weight of sulfur based on the sulfur originally present in said thiomer.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,110,281	Adams et al.	Mar. 8, 1938
2,192,874	Smith et al.	Mar. 5, 1940
2,337,473	Knowles	Dec. 21, 1943
2,338,829	Werntz	Jan. 11, 1944
2,342,572	Cook	Feb. 22, 1944
2,344,392	Cook	Mar. 14, 1944
2,344,393	Cook	Mar. 14, 1944
2,346,155	Denison	Apr. 11, 1944
2,346,157	Farrington	Apr. 11, 1944
2,398,415	Denison	Apr. 16, 1946
2,398,416	Denison	Apr. 16, 1946