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STABILIZED REFINED PETROLEUM PRODUCT

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19 Claims. (Cl. 252—47)

This invention has to do in a general way with the stabilization of viscous petroleum fractions against the harmful effects of oxidation or deterioration normally encountered in the use of such products. The "viscous petroleum fractions" contemplated by this invention include the viscous oil of the type normally used as lubricants and dielectrics, and in addition this term includes refined paraffin wax. The invention is more specifically related to the improvement or stabilization of such viscous petroleum fractions by the use of addition agents which when admixed with the oil or wax in minor proportions will prevent or delay undesirable changes taking place when the petroleum fraction is exposed to oxidizing conditions.

As is well known to those familiar with the art, substantially all of the various fractions obtained from petroleum or mineral oils and refined for their various uses are susceptible to oxidation. The susceptibility of a viscous oil fraction to oxidation and the manner in which oxidation manifests itself within the oil varies with the type and degree of refinement to which the oil has been subjected and with the conditions under which it is used or tested. In other words, the products formed in a viscous petroleum oil fraction as a result of oxidation and the degree to which they are formed depends upon the extent to which the various unstable constituents which may act as oxidation catalysts have been removed by refining operations and also upon the conditions of use.

A highly refined viscous oil, for example, which is one that has been refined by treatment with fuming sulfuric acid or other means or other combinations such as $AlCl_3$, solvents and acids (or with large quantities of concentrated sulfuric acid), tends to form relatively large amounts of acidic constituents when subjected to oxidizing conditions. The presence of catalytic materials such as copper does not appear to affect appreciably the oxidation of highly refined oils, and such oils are less prone to the formation of colored bodies or of insoluble sludge. The formation of acidic bodies, however, is highly undesirable for most applications of these oils. For example, when used as an insulating or cooling oil in electrical equipment such as transformers or capacitors an increase in acidic bodies tends to lower the dielectric strength of the oil and has other harmful effects which are undesirable. The acids are corrosive to metals and thus reduce the useful life of the oils as lubricants or for other purposes in which they come in contact with metals, and the acidic materials are also injurious in textile lubricants and in spray oils.

Moderately refined oils—that is, oils that have been refined by treatment with only moderate amounts of sulfuric acid or other refining agents—tend to form relatively small amounts of acidic oxidation products as compared with highly refined oils, but they undergo material color depreciation and form considerable amounts of sludge. The changes taking place in these oils are appreciably accelerated by the presence of metal catalysts such as copper. Sufficient acid is generally formed to cause some reduction in the dielectric strength of these oils, but the principal objection to them is their tendency to deposit sludge which interferes with heat transfer in transformers and turbines and also causes plugging of oil feed lines in lubricating systems.

Solvent-refined oils in general, which have been prepared by treatment with selective solvents such as chlorex, phenol, furfural, etc., resemble the moderately refined acid-treated oils in that their oxidation is accelerated by the presence of metals such as copper and further in that it is attended by substantial color depreciation and sludge formation. Acid formation is usually greater than in the case of moderately acid-refined oils, but considerably less than with highly refined oils. Both sludge and acid formation lower their value for many purposes, such as electrical insulation, lubrication, etc. Also, solvent-refined oils have found extensive use as lubricants for internal combustion engines because of their high viscosity index, but under the conditions of use encountered in crankcases such oils develop constituents which are corrosive toward certain metal bearings such as the cadmium-silver bearing, etc., which are sometimes used.

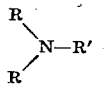
It is to be understood that this classification of viscous oil fractions of the lubricant and dielectric types according to methods of refining treatment is by no means limiting and that there can exist viscous mineral oils whose refining and blending has been such as to make them intermediate in properties between the types set up. Thus, response to inhibitors may be said to depend entirely upon the type of oxidation and end products of oxidation of an oil, which in turn depends largely upon the degree of refining this oil has had. Further, the degree of refining required to produce these types of oils varies with the crude source so that any one refining procedure may produce either a highly refined

oil or a moderately refined oil, depending upon the crude source. Pennsylvania type oils, for example, require much less refining to produce highly refined oils than the Coastal type of oils.

The use of oxidation inhibitors for the purpose of stabilizing a viscous mineral oil fraction against the deleterious effects of oxidation discussed above is well known. Since the action of these inhibiting materials is apparently catalytic, the problem of their development is a difficult one and is evidently influenced to a large degree by the oxidizable constituents which are in the oil following a particular refining treatment. Thus, a particular inhibitor or class of inhibitors may be effective to stabilize a highly refined oil against acid formation while the same inhibitor may have no appreciable effect upon acid, color, or sludge formation in a moderately refined oil and vice versa. This same inhibitor may or may not be effective in inhibiting acid, sludge, and color formation in a solvent-refined oil and may or may not be effective to inhibit the corrosive action of a solvent-refined oil toward metals such as used in cadmium-silver bearings. Furthermore, the behavior of an inhibitor in a non-viscous mineral oil fraction does not necessarily afford any indication as to what its effect will be in a viscous oil fraction.

Refined paraffin wax, which is classified herein as a viscous petroleum fraction, when subjected to oxidizing conditions tends to form acidic products, the formation of which may be retarded by addition agents which apparently act as negative catalysts toward the conversion of potential acidic products in the paraffin wax.

The present invention is predicated upon the discovery of a new class of compounds or reaction products which we have found effective in retarding or inhibiting the deleterious effects of oxidation upon viscous petroleum products. This class of reaction products or compounds may be described as the reaction products obtained by reacting a halide of sulfur, preferably a sulfur chloride, with a nitrogen-substituted dialkyl aromatic amine. More specifically, these products are obtained by reacting sulfur dichloride or sulfur chloride or mixtures of these compounds with a tertiary organic amine having the general formula:

I 

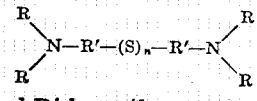
in which R represents an alkyl or an aryl-substituted alkyl (aralkyl) radical and R' represents an aryl radical.

In this regard it is to be understood that the term alkyl, as used herein in connection with the alkyl substituents on these N-substituted aromatic amines, is inclusive of aralkyl groups such as the benzyl group.

The products of reaction obtained by reacting compounds of the type described above are characterized by the fact that they contain tertiary amino groups and sulfur. The sulfur-supplying compound for these reaction products, as indicated above, may in general be any halide of sulfur or mixture thereof, but preference is given to the sulfur chlorides, and particularly sulfur monochloride and sulfur dichloride. The amino compounds contemplated for use in obtaining these products are, as previously indicated, the tertiary dialkyl aromatic amines such as the dialkyl N-substituted phenylamines (dialkyl anilines) and the dialkyl N-substituted alpha and beta naphthylamines.

The general procedure followed in synthesizing these reaction products is to dissolve 2 mol equivalents of dialkyl aromatic amine in an inert solvent such as petroleum ether, cool the solution to a temperature of from about 0° to about 15° C., and then add 1 mol equivalent of sulfur chloride dissolved in the inert solvent. The solvent is removed by evaporation and the residue preferably washed with a sodium hydroxide or sodium sulfide solution to remove free sulfur from the reaction product. The product, which is usually a dark-colored viscous oil, may be used without further treatment as a satisfactory addition agent, or it may be separated into fractions by means of differential solubilities in a solvent such as petroleum ether.

The analysis and physical properties of the reaction products obtained by the foregoing procedure indicate that these products probably contain mixtures of compounds having the general formula:

II 

wherein R and R' have the same significance indicated above and n is a whole number, 1, 2, 3, etc. These analyses and physical properties, however, indicate that in addition to mixtures of the type characterized by the above formula, these products also contain polymers of indefinite chemical composition, and we therefore prefer to designate the addition agents contemplated herein simply as the reaction products of N-substituted dialkyl aromatic amines and sulfur chloride rather than hypothecate what the actual chemical composition of these reaction products may be.

To demonstrate the effectiveness of this class of reaction products contemplated herein as addition agents, we have prepared numerous products using various N-substituted dialkyl aromatic amines and both sulfur monochloride and sulfur dichloride and in at least one instance have separated the products into fractions by means of differential solubility and have subjected such products to various tests in various types of oils to demonstrate their effectiveness. A representative list of the reaction products is given below in Table I, wherein the products are identified by the letters A to G' inclusive, which indicia will be used hereinafter in the examples showing the effectiveness of these products in the various tests. The products are identified by the reactants used and in certain instances such as the products F_1 and F_2 by the fractionating procedure employed in obtaining these special products from the original reaction products.

Table I

A. Dimethyl phenylamine and SCl_2 reaction product

A'. Dimethyl phenylamine and S_2Cl_2 reaction product

B. Diethyl phenylamine and SCl_2 reaction product

B'. Diethyl phenylamine and S_2Cl_2 reaction product

C. Dibutyl phenylamine and SCl_2 reaction product

C'. Dibutyl phenylamine and S_2Cl_2 reaction product

D. Dibenzyl phenylamine and SCl_2 reaction product

D'. Dibenzyl phenylamine and S_2Cl_2 reaction product
E. Dimethyl alpha naphthylamine and SCl_2 reaction product
E'. Dimethyl alpha naphthylamine and S_2Cl_2 reaction product
F. Diethyl alpha naphthylamine and SCl_2 reaction product
F_1. The portion of F which is soluble in petroleum ether (sulfur content 5.88%)
F_2. The portion of F which is insoluble in petroleum ether (sulfur content 12.53%)
F'. Diethyl alpha naphthylamine and S_2Cl_2 reaction product
F'_1. The portion of F' which is soluble in petroleum ether (sulfur content 7.29%)
F'_2. The portion of F' which is insoluble in petroleum ether (sulfur content 19.13%)
G. Dibutyl beta naphthylamine and SCl_2 reaction product
G'. Dibutyl beta naphthylamine and S_2Cl_2 reaction product

The details in the procedure followed in synthesizing reaction products of the type contemplated herein will be better understood from the following specific examples.

Example One

Dibutyl phenylamine-sulfur chloride

Two mol equivalents (41 grams or 0.2 mol) of N-dibutyl phenylamine (N-dibutyl aniline) were dissolved in 400 cc. of petroleum ether, and the solution was cooled in an ice bath. One mol equivalent (13.5 grams or 0.1 mol) of sulfur monochloride dissolved in 200 cc. of petroleum ether was added slowly. The mixture was then allowed to warm up to room temperature and the solvent was removed by evaporation. The residue was extracted with aqueous hydrochloric acid and was then dissolved in benzene and washed with sodium hydroxide solution and with a solution of sodium sulfide to remove any free sulfur present. On evaporation of the benzene a viscous oil was left. This analyzed 14.73 per cent sulfur. When this preparation was repeated except for using an equivalent amount of sulfur dichloride in place of the sulfur monochloride, a product was obtained containing 10.01 per cent sulfur. If we assume that these products are represented by the general Formula II as given above the following relationships would hold:

$n=1$ Per cent sulfur would be 7.28
$n=2$ Per cent sulfur would be 13.56
$n=3$ Per cent sulfur would be 19.05

Therefore, the above products would be considered as being mixtures of mono, di and higher sulfides.

Example Two

Diethyl alpha naphthylamine-sulfur chloride products

Diethyl alpha naphthylamine was reacted in the manner described in Example One with sulfur dichloride and yielded as a product a viscous oil containing 7.71 per cent sulfur. This product was separated into a petroleum ether-soluble portion, which contained 5.88 per cent sulfur, and another portion which was insoluble in petroleum ether, which contained 12.53 per cent sulfur. When sulfur monochloride was used instead of the sulfur dichloride in this preparation, the original product contained 13.17 per cent sulfur and was separated into a fraction soluble in petroleum ether, which contained 7.29 per cent sulfur, and another fraction insoluble in petroleum ether containing 19.13 per cent sulfur.

The procedures described in Examples One and Two above are representative of those which may be used in synthesizing the general class of reaction products contemplated by this invention; and although the fractionation of the reaction products by differential solubilities has been found in certain instances to yield in the fractions special products which show superiority in certain oils and under certain conditions, it is to be understood that the original product as obtained may be used as a satisfactory addition agent and that the fractionation is not an essential requirement to the general utility of these products.

The effectiveness of the reaction products contemplated herein as inhibitors for use in viscous petroleum fractions of the various types hereinabove referred to is demonstrated by the following examples, which give the results of tests conducted on these representative oils with the representative reaction products. In these various examples and the tables therein reference should be made to Table I above for descriptions of the inhibitors or addition agents indicated.

Example Three

Moderately refined oils

(*a*) The oil used in this test was a mixture of Mid-Continent and Coastal distillates which had been refined by treatment with 70 pounds of 98 per cent sulfuric acid per barrel, neutralized, washed, and percolated through clay. It had a specific gravity of 0.879, a flash point of 385° F., and a Saybolt Universal viscosity of 152 seconds at 100° F. This is an oil suitable for use in turbines, and the test used involved heating 25 cc. samples of the oil and oil blends to a temperature of 200° F. with 5 liters of air per hour bubbling therethrough. During the test the oil was maintained in contact with copper and iron by adding 24 inches of 18-gauge copper wire and 1 gram of iron granules to each sample. Also, during the test 2 cc. of distilled water were added each day, and the samples were tested for acidity or neutralization number (N. N.), color and sludge formation at varying periods of time. The results of these tests with this oil and blends of the same oil containing representative addition agents of the type contemplated herein are set forth in Table II below, from which it will be observed that all of these reaction products show an appreciable effect in inhibiting the deterioration of this type of oil.

Table II

Inhibitor	Per cent	Time, hours	N. N.	Lov. color	Sludge mg./25 cc.
None		336	16.0	400	1,282
A	0.10	335	.90	28	52
A'	0.10	1,349	0.92	53	68
B	0.10	303	1.5	45	75
B'	0.10	303	1.0	35	56
C	0.10	303	0.03	43	70
C'	0.10	1,678	0.96	80	49
D	0.10	303	1.35	35	37
D'	0.10	311	0.86	31	21
E	<0.10	329	1.4	35	43
E'	<0.10	492	3.8	70	265
F	<0.10	329	2.9	55	95
F'	<0.10	329	0.16	18	63
G	<0.10	329	12.4	220	693
G'	<0.10	330	5.0	90	282

(*b*) Another test was conducted on moderately refined oil prepared by treating a Coastal crude with 70 pounds of 98 per cent sulfuric acid per

barrel, followed by neutralization and clay percolation. The finished oil had a specific gravity of 0.886, a flash point of 275° F., and a Saybolt viscosity of 56 seconds at 100° F. This was an oil suitable for use in transformers and was tested by heating samples to 120° C. in the presence of copper and bubbling air therethrough. The results obtained in this test using the oil alone and the same oil containing a representative reaction product of the type above referred to are set forth in Table III below.

Table III

Inhibitor	Time, hours	N. N.	Lov. color	Sludge
None	168	.65	59	Very heavy.
A'	168	.24	38	Slight.

EXAMPLE FOUR

Solvent-refined oil

The oil used in this test was a distillate from a Rodessa crude which had been refined by solvent-extraction with furfural, dewaxed, and filtered. The finished oil had a specific gravity of 0.856, a flash point of 420° F., and a Saybolt viscosity of 151 seconds at 100° F. It was tested by the same procedure followed in Example Three (*a*), and the results obtained are set forth in Table IV below.

Table IV

Inhibitor	Percent	Time, hours	N. N.	Lov. color	Sludge mg./25 cc.
None		165	20.3	320	251
A	0.10	1,506	0.01	65	5
B	0.10	305	0.07	6	21
B'	0.10	305	6.7	67	59
C	0.10	305	0.01	3	11
E	<0.10	263	5.8	27	105
E'	<0.10	449	1.4	30	16
F	<0.10	786	0.01	2	19
F_1	0.10	667	3.4	16	23
F_2	<0.10	2,015	0.01	7	3
F'	<0.10	2,177	0.01	3	57
F'_1	0.10	667	4.0	42	22
F'_2	<0.10	2,015	0.01	2	1
G	0.10	210	0.67	10	7
G'	<0.10	425	11.5	72	57

It will be observed from the foregoing results that all of these representative reaction products showed appreciable effectiveness in inhibiting the deterioration of this solvent-refined oil and that outstanding results were obtained with inhibitor A (the reaction product of dimethyl aniline and sulfur dichloride) and the materials F_2 and F'_2 (dialkyl naphthylamine-sulfur chloride reaction products obtained by differential solubility extraction and having a high sulfur content).

EXAMPLE FIVE

Corrosion test

Motor oils, especially those refined by certain solvent-extraction methods, tend to oxidize when submitted to high temperatures and form products that are corrosive to metal bearings. This corrosive action may be quite severe with certain bearing metals such as the hard metal alloys of the cadmium-silver type and alloy metals having similar corrosive susceptibility and may cause the failure of bearings of this type within a comparatively short time.

The present invention, as has been previously indicated, contemplates viscous oils of the type which are normally corrosive to bearing metals of the character just referred to which have been inhibited against such corrosive action by addition agents of the class contemplated herein. Our invention also contemplates a method of lubricating bearings comprising alloys having the corrosion susceptibility characterizing cadmium-silver alloys which consists of applying to the bearing surfaces a hydrocarbon oil film which is normally corrosive to such a bearing and at the same time retarding such corrosive action by maintaining in admixture with the oil film a reaction product obtained by reacting an N-substituted dialkyl aromatic amine with a chloride of sulfur, the product being maintained within the oil film in an amount sufficient to substantially retard this corrosive action.

The following test was employed to demonstrate the effectiveness of the products contemplated herein to inhibit the corrosive action of a motor oil upon an automobile bearing having a cadmium-silver alloy surface. The oil used consisted of Pennsylvania neutral and residuum stocks separately refined and blended to give an S. A. E. No. 20 motor oil with a specific gravity of 0.872, a flash point of 435° F., and a Saybolt viscosity of 318 seconds at 100° F. The test involved placing a section of the bearing weighing about 6 grams in a sample of the oil and heating the oil to a temperature of 175° C. for a period of 22 hours while bubbling a stream of air against the surface of the bearing. The loss in weight of the bearing during this treatment measures the amount of corrosion that has taken place. A sample of the oil containing the addition agent was run simultaneously with a sample of the inhibited oil, and the loss in weight of the bearing section in the inhibited oil compared with the loss in weight of the bearing section in the uninhibited oil indicates the effectiveness of the inhibitor. The results obtained in this test are set forth in Table V below.

Table V

Inhibitor	Per cent	Mg. loss in weight	
		Inhibited	Uninhibited
A	<0.25	0	57
A'	<0.25	0	57
B	0.25	20	61
B'	0.25	21	61
C	0.25	19	61
C'	0.25	0	74
D	0.25	3	61
D'	0.25	7	61
E	<0.25	1	54
E'	<0.25	1	85
F	<0.25	40	61
F_1	0.25	1	40
F_2	<0.25	0	85
F'	<0.25	33	61
F'_1	0.25	1	40
F'_2	<0.25	1	85
G	<0.25	3	54
G'	<0.25	0	85

EXAMPLE SIX

Highly refined oil

The oil used in this test was one suitable for use in transformers, which had been prepared by treating a Coastal distillate with 40 pounds of 98 per cent sulfuric acid and 180 pounds of 103 per cent oleum per barrel, followed by washing and clay percolation. It had a specific gravity of 0.871, a flash point of 310° F., and a Saybolt Universal viscosity of 69 seconds at 100° F. This type of oil tends to form acidic products on oxidation, and it was tested by heating samples to 120° C. and bubbling oxygen therethrough for a period of 70 hours. The acids thus formed were re-

moved by titrating with alcoholic potassium hydroxide, the acidity being indicated by the so-called neutralization number (N. N.), which is the amount in milligrams of KOH required to neutralize the acids formed in 1 gram of the oil. All of the reaction products contemplated herein showed some inhibiting action on the highly refined oil, but outstanding results among the representative products tested were obtained only with those set forth in Table VI below, which were the products obtained from dialkyl alpha naphthylamine and dibutyl beta naphthylamine.

Table VI

Inhibitor	Percent	N. N.
None		25.0
C'	0.10	2.4
F	<0.10	0.0
F'	<0.10	0.01
G	<0.10	0.0
G'	<0.10	0.0

EXAMPLE SEVEN

Refined paraffin wax

As we have previously indicated, refined paraffin wax, when subjected to oxidizing conditions, tends to develop acidic products, and, as has also been indicated herein, paraffin wax is contemplated herein as one of the viscous petroleum products which may be improved by the addition thereto of a reaction product obtained by reacting a chloride of sulfur with an N-substituted dialkyl aromatic amine. To demonstrate this effectiveness, a refined paraffin wax of 126° F. melting point was tested by heating samples thereof alone and containing representative addition agents to a temperature of 120° C. for a period of 70 hours with oxygen gas bubbling therethrough and then determining the neutralization number of the sample. The results obtained with this wax containing representative addition agents are set forth in Table VII below.

Table VII

Inhibitor	Percent	Neutralization number
None		35.6
A	0.10	0.01
A'	0.10	0.00
E'	0.10	0.01
F'	0.10	0.01

It will be apparent from the foregoing examples of tests and the tabulated data presented therein that the reaction products obtained by reacting sulfur chlorides with N-substituted dialkyl aromatic amines are effective to inhibit the deleterious effects of oxidation in refined petroleum fractions. It is true that the effectiveness of individual members of this class will vary somewhat with the types of oil in which they are used; and while the invention contemplates moderately refined and solvent-refined oils as preferred oils in which this class of addition agents find application, the invention also finds application in connection with highly refined oils and waxes.

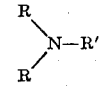
The invention, therefore, in its broadest sense is not restricted to any particular oil but is inclusive of all viscous petroleum fractions in which deterioration under oxidizing conditions is inhibited by addition agents of the class contemplated herein. It is to be understood that while we have attempted to roughly classify the viscous oils according to the refining treatment which they have received, the invention is not confined to the refining treatments described for obtaining oils falling in this classification. This is true because the susceptibility of an oil to oxidation and its response to an inhibitor, which may characterize it as a highly refined oil or a solvent-refined oil under the classification used herein, is dependent not only upon the refining treatment but also upon the crude source of the oil. It is possible, for example, to obtain an oil of the so-called highly refined type from one crude by a refining treatment which would yield an oil having the characteristics of a moderately refined oil from another crude.

The amount of addition agent necessary to obtain the desired results may be varied, depending upon the characteristics of the oil and the conditions under which it is to be used, from about 0.01 per cent to about 1.0 per cent, but in general we have found that satisfactory inhibition can be obtained with average oils and under average conditions by using the addition agents in amounts of around 0.1 per cent to 0.25 per cent.

We claim:

1. An improved petroleum product comprising a refined viscous petroleum fraction normally subject to deterioration under conditions of oxidation and in admixture therewith a minor proportion, sufficient to retard said deterioration, of the reaction product obtained by reacting an N-substituted dialkyl aromatic amine with a halide of sulfur.

2. An improved petroleum product comprising a refined viscous petroleum fraction normally subject to deterioration under conditions of oxidation and in admixture therewith a minor proportion, sufficient to retard said deterioration, of the reaction product obtained by reacting a tertiary amine having the general formula



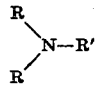
in which R represents a radical selected from the group consisting of alkyl and aryl-substituted alkyl radicals and R' represents an aryl radical, with a chloride of sulfur.

3. An improved petroleum product comprising a refined viscous petroleum fraction normally subject to deterioration under oxidizing conditions and in admixture therewith a minor proportion, sufficient to retard said deterioration, of the reaction product obtained by reacting an N-substituted dialkyl aromatic amine with sulfur monochloride.

4. An improved petroleum product comprising a refined viscous petroleum fraction normally subject to deterioration under oxidizing conditions and in admixture therewith a minor proportion, sufficient to retard said deterioration, of the reaction product obtained by reacting an N-substituted dialkyl aromatic amine with sulfur dichloride.

5. An improved petroleum product comprising a viscous mineral oil selected from the group consisting of moderately refined oils and solvent-refined oils normally subject to deterioration under oxidizing conditions and in admixture therewith a minor proportion, sufficient to retard said deterioration, of the product obtained by reacting an N-substituted dialkyl aromatic amine with a halide of sulfur.

6. An improved petroleum product comprising a viscous mineral oil selected from the group consisting of moderately refined oils and solvent-refined oils normally subject to deterioration under oxidizing conditions and in admixture therewith a minor proportion, sufficient to retard said deterioration, of the product obtained by reacting a tertiary amine having the general formula



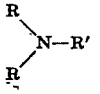
in which R represents a radical selected from the group consisting of alkyl radicals and aryl-substituted alkyl radicals and R′ represents an aryl radical, with a chloride of sulfur.

7. An improved petroleum product comprising a viscous mineral oil selected from the group consisting of moderately refined oils and solvent-refined oils normally subject to deterioration under oxidizing conditions and in admixture therewith a minor proportion, sufficient to retard said deterioration, of the product obtained by reacting an N-substituted dialkyl aromatic amine with sulfur monochloride.

8. An improved petroleum product comprising a viscous mineral oil selected from the group consisting of moderately refined oils and solvent-refined oils normally subject to deterioration under oxidizing conditions and in admixture therewith a minor proportion, sufficient to retard said deterioration, of the product obtained by reacting an N-substituted dialkyl aromatic amine with sulfur dichloride.

9. An improved petroleum product composition comprising a refined viscous petroleum fraction and in admixture therewith from about 0.01 per cent to about 1.0 per cent of the product obtained by reacting an N-substituted dialkyl aromatic amine with a halide of sulfur.

10. An improved petroleum product composition comprising a refined viscous petroleum fraction and in admixture therewith from about 0.01 per cent to about 1.0 per cent of the product obtained by reacting a tertiary amine having the general formula



in which R represents a radical selected from the group consisting of alkyl and aryl-substituted alkyl radicals and R′ represents an aryl radical, with a chloride of sulfur.

11. An improved petroleum product composition comprising a refined viscous petroleum fraction and in admixture therewith from about 0.01 per cent to about 1.0 per cent of the product obtained by reacting an N-substituted dialkyl aromatic amine with sulfur monochloride.

12. An improved petroleum product composition comprising a refined viscous petroleum fraction and in admixture therewith from about 0.01 per cent to about 1.0 per cent of the product obtained by reacting an N-substituted dialkyl aromatic amine with sulfur dichloride.

13. An improved petroleum product comprising a refined viscous petroleum fraction normally subject to deterioration under oxidizing conditions and in admixture therewith a minor proportion, sufficient to retard said deterioration, of the reaction product obtained by reacting a chloride of sulfur with an N-substituted dialkyl aromatic amine selected from the group consisting of: dimethyl phenylamine; diethyl phenylamine; dibutyl phenylamine; dibenzyl phenylamine; dimethyl alpha naphthylamine; diethyl alpha naphthylamine; and dibutyl beta naphthylamine.

14. An improved mineral oil composition comprising a viscous mineral oil selected from the group consisting of moderately refined oils and solvent-refined oils and in admixture therewith from about 0.01 per cent to about 1.0 per cent of the reaction product obtained by reacting a chloride of sulfur with an N-substituted dialkyl aromatic amine selected from the group consisting of: dimethyl phenylamine; diethyl phenylamine; dibutyl phenylamine; dibenzyl phenylamine; dimethyl alpha naphthylamine; diethyl alpha naphthylamine; and dibutyl beta naphthylamine.

15. An improved mineral oil composition comprising a highly refined viscous mineral oil fraction normally subject to the formation of acidic products under oxidizing conditions, and in admixture therewith a minor proportion, sufficient to retard the formation of said acidic products, of the reaction product obtained by reacting a chloride of sulfur with an N-substituted dialkyl aromatic amine selected from the group consisting of diethyl alpha naphthylamine and dibutyl beta naphthylamine.

16. An improved petroleum product consisting of a refined paraffin wax normally subject to the formation of acidic products under oxidizing conditions and in admixture therewith a minor proportion, sufficient to retard acid formation, of the product obtained by reacting a chloride of sulfur with an N-substituted dialkyl aromatic amine.

17. The method of stabilizing normally unstable refined viscous petroleum products which comprises adding thereto a small proportion of the reaction product obtained by reacting a chloride of sulfur with an N-substituted dialkyl aromatic amine.

18. The method of lubricating bearings comprising alloys having substantially the corrosion susceptibility characterizing cadmium-silver alloys which consists in applying to the bearing surfaces a lubricant comprising mineral hydrocarbon oil of a character normally tending to corrode said alloys and having incorporated therein, in proportion sufficient to inhibit the corrosion of said bearing surfaces during the lubrication thereof, the reaction product obtained by reacting a chloride of sulfur with an N-substituted dialkyl aromatic amine.

19. The method of lubricating bearings comprising alloys having substantially the corrosion susceptibility characterizing cadmium-silver alloys which consists in applying to the bearing surfaces a lubricant comprising mineral hydrocarbon oil of a character normally tending to corrode said alloys and having incorporated therein, in proportion sufficient to inhibit the corrosion of said bearing surfaces during the lubrication thereof, the reaction product obtained by reacting a chloride of sulfur with an N-substituted dialkyl aromatic amine selected from the group consisting of dimethyl phenylamine; diethyl phenylamine; dibenzyl phenylamine; dimethyl alpha naphthylamine; diethyl alpha naphthylamine; and dibutyl beta naphthylamine.

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