Patented Dec. 3, 1940 2,223,411

UNITED STATES PATENT OFFICE

2,223,411

MINERAL OIL COMPOSITION

Everett W. Fuller, Woodbury, and Lyle A. Hamilton, Wenonah, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, New York, N. Y., a corporation of New York

No Drawing. Application September 28, 1940, Serial No. 358,832

17 Claims. (Cl. 252—50)

This invention is concerned in a general way with the stabilization of viscous mineral oil fractions by the use of a novel class of compounds or reaction products which when admixed with such a mineral oil in minor proportions will prevent or delay undesirable changes taking place in the oil.

As is well known to those familiar with the art, substantially all the various fractions obtained from mineral oils and refined for their various uses are susceptible to oxidation. The susceptibility of an 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 an 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 or 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 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 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 is by no means limiting and that there can exist 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 or 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.

As indicated above, it is not uncommon to find an inhibiting agent or a class of inhibiting agents which is of practical effectiveness in only one of the various types of oil indicated above. One of the outstanding characteristics of the compounds or reaction products contemplated by the present invention, however, is that this class of compounds is effective to inhibit the deleterious effects of oxidation in each of the various types of viscous oils mentioned. They are also effective to inhibit acid formation in paraffin wax. Our invention, therefore, is directed broadly to petroleum products selected from the group consisting of viscous oils and paraffin wax as the mineral oil constituent of the composition of matter contemplated herein.

The particular field which shows the greatest promise for the immediate future and therefore constitutes the preferred class of compositions contemplated herein embraces viscous mineral oil fractions which have been refined to meet turbine oil or transformer oil specifications by one of the cheaper methods of refining such as light acid treatment or solvent-refining, which normally produce an oil of the so-called sludging type. As a preferred class of mineral oil compositions, therefore, our invention contemplates a normally sludging oil of the turbine or transformer type which contains a minor proportion of the novel inhibitor contemplated herein in an amount sufficient to retard the sludge formation.

The compounds or products contemplated herein as inhibitors for petroleum products fall into the general class of condensation products obtained by reacting amines with aldehydes. We are aware of the fact that this broad general class of compounds or reaction products has heretofore been suggested for use as inhibitors for mineral oils. Patent No. 1,594,983 discloses and claims the broad general class of condensation products obtained by reacting an aldehyde with a nitrogenous base, or more specifically, by reacting an aldehyde with an amine. The patent discloses these products as inhibitors for mineral oils. Although the patent contains a generic disclosure of the type just discussed, the only examples of amines used to illustrate the class of compounds contemplated by the patentee are primary amines; also the patentee indicates that all of the aldehydes are effective when reacted with amines to produce products of equivalent inhibiting powers.

Our invention is predicated upon the discovery that a specific aldehyde (formaldehyde) when reacted with a specific group of amines (secondary amines) produces inhibitors of surprisingly superior effectiveness as compared with the broad class represented by the primary amine reaction products of the type disclosed in the patent above referred to. More specifically, our invention contemplates the use of the condensation products obtained by reacting formaldehye with N-substituted arylamines. Novelty and distinction over the patent above referred to is predicated upon the discovery, first, that formaldehyde when reacted with N-substituted arylamines produces products superior in their inhibiting properties to the products obtained with the same amines and higher aldehydes, and, second, that the N-substituted arylamines when reacted with formaldehyde produce condensation products superior in their inhibiting properties to those obtained by reacting formaldehyde with primary amines.

The N-substituted arylamines are compounds having the general formula

I.



in which R represents an aryl radical and R' represents a radical selected from the group consisting of alkyl, alkaryl, aryl and aralkyl radicals. Examples of the N-substituted arylamines typified by the above general formula and contemplated herein for use as reactants with formaldehydes to obtain the novel class of inhibitors are: N-methyl phenylamine, N-ethyl phenylamine, N-propyl phenylamine, N-butyl phenylamine, N-amyl phenylamine, N-butyl alpha-naphthylamine, N-benzyl phenylamine, diphenylamine, N-phenyl alpha-naphthylamine, N-phenyl beta-naphthylamine, and N-tolyl phenylamine.

The general procedure preferred for preparing the condensation products contemplated herein as inhibitors for petroleum compositions consists in first dissolving the secondary aromatic amine (N-substituted arylamine) in an alcohol and adding approximately one mole equivalent of hydrochloric acid. The mixture is then heated to a temperature of from 60 to 80° C. and from one to two mole equivalents of formaldehyde are added. The heating is continued for a few hours, after which the reaction mixture is poured into water containing an excess of alkali such as NaOH, KOH or NH_4OH. The condensation product, which may be a solid or an oil, depending upon the amine used, separates from the water solution and may be purified by ordinary methods.

Modifications in the foregoing procedure may be made by changing the relative proportions of the reactants, by using other solvents or by carrying out the reaction under alkaline or neutral conditions rather than under acid conditions. For example, a typical modified procedure which we have employed in making highly effective oil addition agents of the type contemplated herein involves reacting about one mole equivalent of an N-substituted arylamine with about one-half mole equivalent of formaldehyde in an aqueous solution containing about one mole equivalent of hydrochloric acid. The reaction is preferably carried out at elevated temperature. The temperature of the reaction may, of course, be varied, as, for example, by permitting the reaction to proceed over a period of several days at room temperature. Further details in the procedure followed in synthesizing these products may be gathered from the following examples describing the synthesis of typical reaction products of the type which we have prepared to illustrate the effectiveness of these compounds.

EXAMPLE I

10.7 grams of N-methyl aniline (0.1 mole) were dissolved in 200 cc. of ethyl alcohol. Fourteen grams of concentrated HCl (0.1+ mole) were added with stirring. 8.1 grams of formaldehyde solution (0.1 mole) were added and the mixture stirred. After 2 hours the white precipitate that had formed was filtered off and washed with a little alcohol. The precipitate was then suspended in 200 cc. of ethyl alcohol, and 50 cc. of 5 per cent NH_4OH were added with stirring. The precipitate was filtered, washed with a little alcohol and then with water and dried. It gave a white powder that melted at about 205° C.

EXAMPLE II

81.5 grams of N-amylaniline (0.5 male) were dissolved in 350 cc. of methyl alcohol. Seventy-five grams of concentrated HCl (0.5+ mole) were added, and the mixture was heated to a gentle reflux in a 1-liter flask with a stirrer, a water-cooled condenser and a dropping funnel. Eighty-two grams of 37 per cent formaldehyde (approx. 1.0 mole of CH_2O) were added from the dropping funnel in the course of ½ hour, and the mixture was then further heated to gentle reflux for 5 hours. The contents of the flask were poured into 1000 cc. of distilled water containing 200 cc. of NH_4OH solution. The oil that separated was extracted with benzene, washed with water, dried over $CaCl_2$, and the solvent was then removed by distillation. This left 81 grams of a rather viscous brown oil that was miscible with petroleum oils.

The effectiveness of the condensation products contemplated herein as inhibitors of oxidation in various petroleum products, including various types of viscous mineral oils and paraffin wax, is illustrated by the following examples:

EXAMPLE III

Highly Refined (Non-sludging) Oils

The oil used in this test was of the type suitable for use in transformers which had been highly refined from a Coastal distillate by treatment with 40 pounds of 98 per cent sulfuric acid, followed by 180 pounds of 103 per cent Oleum per barrel, after which it was neutralized, washed, etc. It had a specific gravity of 0.871, a flash point of 310° F., and a Saybolt viscosity of 69 seconds at 100° F. The test involved heating the oil samples to 120° C., then bubbling oxygen gas through them for 70 hours, after which the neutralization number of the oil sample was obtained. Table 1 below shows the results obtained in the foregoing test using the oil alone and the same oil containing the specified proportion of a condensation product obtained by reacting formaldehyde with the N-substituted arylamine indicated.

Table 1

Oil sample	Neutralization number
Oil alone	25.00
Oil+<.10% product from N-methyl phenylamine	.01
Oil+.10% product from N-isoamyl phenylamine	.01
Oil+<.10% product from N-benzyl phenylamine	.01
Oil+<.10% product from N-phenyl alpha-naphthylamine	.02
Oil+<.10% product from N-phenyl beta-napthylamine	.01
Oil+.10% product from N-butyl alpha-naphthylamine	.00

EXAMPLE IV

Moderately Refined (Sludging) Oils

The oil used in this test was one obtained from a mixture of Mid-Continent and Coastal distillates which had been refined to meet turbine oil specifications by treatment with 70 pounds of 98 per cent sulfuric acid per barrel, followed by neutralization, water-washing and clay percolation. The oil had a specific gravity of 0.879, a flash point of 385°, and a Saybolt viscosity of 152 seconds at 100° F.

The test involved heating a 25 cc. sample of the oil to a temperature of 200° F. with 5 liters of air per hour bubbling therethrough. Twenty-four inches of 18-gauge copper wire and 1 gram of iron granules were added to the oil sample, and 2 cc. of distilled water were added each day. The samples were tested for acidity, color and sludging after varying intervals of time. The effectiveness of the inhibitor can be observed by comparing the time interval and the observed properties of the inhibited oils and the oil alone in Table 2 below. It will be observed, for example, that this oil containing 0.10 per cent of the condensation product obtained by reacting formaldehyde with N-iso-amyl phenylamine, at the end of 1349 hours had a neutralization number (N. N.) of .32, a Lovibond color of 22, and precipitated 23 milligrams of sludge in the 25 cc. sample, as compared with the oil alone, which at the end of only 89 hours had a neutralization number of 1.1, a Lovibond color of 34, and precipitated 54 milligrams or more than twice as much sludge as was formed in the inhibited sample during a time interval many times greater.

Table 2

Oil sample	Time in hours	N. N.	Lovi. color	Sludge mg./25 cc.
Oil alone	89	1.1	34	54
	305	3.6	100	148
Oil+.10% product from formaldehyde and N-isoamyl phenylamine	366	.02	2.5	3
	1349	.32	22	23
Oil+<.10% product from N-methyl phenylamine	645	.34	35	16
Oil+<.10% product from diphenylamine	307	.06	7	16
Oil+<.10% product from N-benzyl phenylamine	307	.01	2	8
Oil+<.10% product from N-phenyl alpha-naphthylamine	645	.16	35	12
Oil+<.10% product from N-phenyl beta-naphthylamine	307	.01	10	14

EXAMPLE V

Solvent-Refined (Sludging) Oils

The oil used in this test was one obtained from a mixture of Mid-Continent and Coastal distillates which had been solvent-refined with furfural to a 25 per cent loss. It had an A. P. I. gravity of 31.8 and a Saybolt viscosity of 136 seconds at 100° F. The test employed was the same as that described under Example IV above, and the results thereof are recorded in Table 3 below.

Table 3

Oil sample	Time in hours	N. N.	Lovi. color	Sludge mg./25 cc.
Oil alone	96	1.0	10	81
	167	8.2	68	127
	237	21.2	285	799
Oil+.10% of product from formaldehyde and N-isoamyl phenylamine	366	.02	2	4
	721	.03	2.3	5
	1349	1.6	35	47
Oil+<.10% product from formaldehyde and N-methyl phenylamine	645	1.4	26	32
Oil+<.10% product from formaldehyde and diphenylamine	307	2.4	42	37
Oil+<.10% product from formaldehyde and N-benzyl phenylamine	307	.07	2.4	15
Oil+<.10% product from formaldehyde and N-phenyl alpha-naphthylamine	645	.75	27	173
Oil+<.10% product from formaldehyde and N-phenyl beta-naphthylamine	307	.01	7	13

EXAMPLE VI

Solvent-Refined Motor Oils

A further example of the stabilizing action of the condensation products obtained by reacting

formaldehyde with N-substituted arylamines is shown by the following test results. The oil used in this test was an S. A. E. 20 motor oil made by solvent-extracting a Pennsylvania neutral stock and a Pennsylvania residual stock with chlorex and then blending to the required viscosity. The test procedure involved immersing a section of a connecting rod bearing containing a cadmium-silver alloy surface and weighing about 6.0 grams in 30 grams of oil. The oil was heated to a temperature of 175° F. for 22 hours while a stream of air was bubbled against the surface of the bearing. The weight loss of the bearing during this treatment measures the amount of corrosion that has taken place. In carrying out these tests a sample of the oil containing one of the specified reaction products was run simultaneously with a sample of the uninhibited oil, each sample containing a section cut from the same bearing. The loss in weight of the bearing in the inhibited sample of oil can thus be compared directly with the loss of weight in the bearing in the corresponding uninhibited sample. The results of this test are tabulated below in Table 4, in which it will be observed that tests were in several instances conducted with the same inhibitor in different proportions.

Table 4

Inhibited oil sample	Mg. loss in weight	
	Inhibited	Uninhibited
Oil+.10% product from formaldehyde and N-methyl phenylamine	0	52
Oil+.05% product from N-methyl phenylamine and formaldehyde	0.2	69
Oil+.10% product from formaldehyde and N-iso-amyl phenylamine	0	52
Oil+.05% product from formaldehyde and N-iso-amyl phenylamine	0.2	69
Oil+.10% product from formaldehyde and N-phenyl beta-napthylamine	0	52
Oil+.05% product from formaldehyde and N-phenyl beta-naphthylamine	3	69
Oil+<.10% product from formaldehyde and N-benzyl phenylamine	0	74
Oil+<.10% product from formaldehyde and diphenylamine	0	74
Oil+<.25% product from formaldehyde and N-phenyl alpha-naphthylamine	1	74

As was pointed out above, the present invention is predicated upon the discovery of the fact that the narrow class of condensation products obtained by reacting formaldehyde with N-substituted arylamines is far superior to the broad class of products obtained by reacting aldehydes generally with amines generally. This superiority will be indicated in the following examples, wherein secondary amines, and specifically N-substituted arylamines, have been reacted with formaldehyde to obtain products which are compared in tests of the type discussed above with condensation products obtained from formaldehyde and typical primary amines.

EXAMPLE VII

In this test the procedure followed was the same as that described above in Example III, and the oil used had been refined in the same way to meet the same specifications. The oil alone had a neutralization number in the neighborhood of 25, and the results obtained from blends of this oil containing reaction products of formaldehyde and typical primary amines are listed in Table 5A below, the corresponding results obtained with the same oil containing reaction products of formaldehyde and typical N-substituted arylamines being listed in Table 5B below. It will be observed from the results in these tables that the reaction products of the primary amines are in three instances practically ineffective to inhibit acid formation in the highly refined oil, and in the case of the reaction product of the ring-substituted tertiary amyl aniline the neutralization number of the oil after the test was from 50 to 100 times greater than the neutralization number of the samples containing the secondary amine reaction products.

Table 5A

Oil sample	Naturalization number
Oil+<.10% product from formaldehyde and aniline	20.7
Oil+<.10% product from formaldehyde and alpha-naphthylamine	20.9
Oil+.10% product from formaldehyde and C-p-tert.-amyl aniline	1.1
Oil+.10% product from formaldehyde and C-dodecyl aniline	19.6

Table 5B

Oil sample	Neutralization number
Oil+<.10% product from formaldehyde and N-methyl phenylamine	0.01
Oil+.10% product from formaldehyde and N-iso-amyl phenylamine	0.01
Oil+<.10% product from N-benzyl phenylamine and formaldehyde	0.01
Oil+<.10% product from formaldehyde and N-phenyl alpha-naphthylamine	0.02
Oil+<.10% product from formaldehyde and N-phenyl beta-naphthylamine	0.01
Oil+.10% product from formaldehyde and N-butyl alpha-naphthylamine	0.00

EXAMPLE VIII

In this test a solvent-refined turbine oil obtained by furfural extraction of Rodessa crude and having a specific gravity of .865, a flash point of 420° F., and Saybolt viscosity of 157 seconds at 100° F. was subjected to the same test described in Example IV. The results of this test for the oil alone are given below in Table 6A, the results for the same oil containing reaction products of formaldehyde with representative primary amines being given in Table 6B, and the results for oil blends containing reaction products of formaldehyde with secondary amylamines or N-substituted arylamines are given in Table 6C below.

Table 6A

Oil sample	Time in hours	N. N.	Lovi. color	Sludge mg./25 cc.
Oil alone	92	0.91	9	33
	165	20.3	320	251

Table 6B

Oil sample	Time in hours	N. N.	Lovi. color	Sludge mg./25 cc.
Oil+.10% product from formaldehyde and C-p-tert-amyl aniline	68	0.43	8	172
	163	25.2	250	180
Oil+.10% product from formaldehyde and C-dodecyl aniline	68	0.49	8	216
	163	23.0	400	206

Table 6C

Oil sample	Time in hours	N. N.	Lovi. color	Sludge mg./25 cc.
Oil+.10% product from formaldehyde and N-ethyl phenylamine	163	0.01	1	5
	499	0.06	2	52
	643	3.1	8.5	19
Oil+.10% product from formaldehyde and N-mixed amyl phenylamine	500	0.01	1	7
	836	3.0	8	153
Oil+.10% product from formaldehyde and N-butyl alpha-naphthylamine	167	0.01	2	17
	498	0.01	3.5	63

From the results in the tables above it will be observed that the reaction products from the primary arylamines have little or no effect as inhibitors of the oil in question under this test. The sample containing the ring-substituted dodecyl aniline, for example, at the end of 163 hours had an acidity and a Lovibond color each greater than the corresponding values in the oil alone at the end of 165 hours. The amount of sludge formed in the oil containing the ring-substituted dodecyl aniline was nearly as great as the sludge formed in the oil alone. When these results are compared with those obtained in Table 6C over comparative or even much greater time intervals, it will be apparent that the condensation products contemplated herein are many times more effective as inhibitors of oxidation than the general class of products disclosed in the patent referred to above.

EXAMPLE IX

In this test the procedure followed and the oil used were similar to those described in connection with Example VI above. Table 7A below shows the corrosion test results on solvent-refined motor oil containing the reaction products of formaldehyde and typical primary amines, and Table 7B shows the corresponding results obtained with the reaction products of formaldehyde and the N-substituted amines. It is interesting to observe in connection with the data in these tables that the reaction products obtained from the primary amines actually accelerated the corrosion of the cadmium-silver bearing surfaces, as compared with the reaction products of the secondary amines (N-substituted arylamines), which in several instances completely eliminated corrosion over the period of the test and in all instances effected a material retardation of corrosion.

Table 7A

Oil sample	Mg. loss in weight	
	Inhibited	Uninhibited
Oil+.25% of product from formaldehyde and C-p-tert-amyl aniline	9	37
Oil+.10% of product from formaldehyde and C-p-tert-amyl aniline	78	37
Oil+.25% of product from formaldehyde and C-dodecyl aniline	59	37
Oil+.10% of product from formaldehyde and C-dodecyl aniline	52	37

Table 7B

Oil sample	Mg. loss in wt.	
	Inhibited	Uninhibited
Oil+.05% product from formaldehyde and N-methyl phenylamine	0.2	69
Oil+.05% product from formaldehyde and N-ethyl phenylamine	0	55
Oil+.01% product from formaldehyde and N-ethyl phenylamine	16	66
Oil+.05% product from formaldehyde and N-iso-amyl phenylamine	0.2	69
Oil+<.10% product from formaldehyde and diphenylamine	0	74
Oil+.10% product from formaldehyde and N-phenyl alpha-naphthylamine	1	74
Oil+.25% product from formaldehyde and N-phenyl betanaphthylamine	0	78
Oil+.10% product from formaldehyde and N-butyl alphanaphthylamine	2	62
Oil+.05% product from formaldehyde and N-butyl alphanaphthylamine	5	74

EXAMPLE X

As was pointed out above, we have discovered that the reaction products obtained with formaldehyde and N-substituted arylamines are of outstanding superiority over corresponding reaction products obtained with the N-substituted arylamines and the higher aldehydes. This is demonstrated by the results obtained with an oil and a test similar to those described in Example III above using N-ethyl phenylamine as the amine reactant and formaldehyde, acetaldehyde and octylaldehyde, respectively, as the aldehyde reactants.

The results of this comparative test are set forth in Table 8 below. The oil, it will be recalled, gave a neutralization number at the end of the test in the neighborhood of 25, and it will be observed from the data that the condensation product using formaldehyde is far superior in its inhibiting power to the corresponding condensation products obtained with the higher aldehydes.

Table 8

Oil sample	N. N.
Oil+.10% product from formaldehyde and N-ethyl phenylamine	.02
Oil+.10% product from acetaldehyde and N-ethyl phenylamine	14.8
Oil+.10% product from octylaldehyde and N-ethyl phenylamine	16.2

EXAMPLE XI

A similar comparative test using the same oil described under Example IV and the procedure described in Example IV above was carried out to obtain the results indicated in Table 9 below, and another test employing a solvent-refined oil of the type described in Example V above was carried out to obtain the comparative results shown in Table 10 below.

Table 9

Oil sample	Time in hours	N. N.	Lovi. color	Sludge mg./25 cc.
Oil alone	89	1.1	34	54
	305	3.6	100	148
Oil+.10% product from formaldehyde and N-ethyl phenylamine	163	.01	3	6
	499	1.3	27	64
Oil+.10% product from acetaldehyde and N-ethyl phenylamine	162	1.3	30	15
	306	3.8	65	94
Oil+.10% product from octylaldehyde and N-ethyl phenylamine	306	4.6	75	238

Table 10

Oil sample	Time in hours	N. N.	Lovi. color	Sludge mg./25 cc.
Oil alone	92	0.91	9	33
	165	20.3	320	251
Oil+.10% product from formaldehyde and N-ethyl phenylamine	163	.01	1	5
	499	.06	2	52
	643	3.1	8.5	19
Oil+.10% product from acetaldehyde and N-ethyl phenylamine	168	4.1	30	20
	190	15.1	193	57
Oil+.10% product from octylaldehyde and N-ethyl phenylamine	168	11.5	147	42

From the data presented above in Tables 9 and 10 it will be observed that the condensation products employing formaldehyde are much more effective as inhibitors of sludge formation in the normally sludging turbine oils than are the corresponding condensation products obtained with the higher aldehydes.

EXAMPLE XII

To demonstrate the effectiveness of the condensation products contemplated herein as inhibitors of the deleterious effects of oxidation upon paraffin wax, a refined paraffin wax having a melting point of 126° F. was tested by heating to 120° C. for 70 hours with oxygen bubbling therethrough, after which the neutralization number of the wax was determined. In this test the uninhibited wax gave a neutralization number of 35.6 at the end of the test as compared with a sample of the same wax containing .10 per cent of N-n-butyl alpha-naphthylamine-formaldehyde condensation product, which showed no acidity at the end of the test. A sample of the same wax containing 0.10 per cent of N-amyl phenylamine-formaldehyde condensation product showed an acidity of 0.01 at the end of the test.

In the methods of preparation described in Examples I and II it will be observed that the reactants (the N-substituted arylamine and the formaldehyde) were used in about equal molecular proportions and that the solvent medium for the reaction mixture was an alcohol. As aforesaid, the procedure may be altered by varying the relative proportions of the reactants, by using other solvents, etc.; and reference was made hereinabove to a modification in which the reaction is carried out in aqueous solution and the ratio of mole equivalents of N-substituted arylamine to formaldehyde in the reaction mixture was of the order of one to one-half.

Preparations have been made following the general procedure last described above. The products are equal, if not superior, to the products obtained by the procedures of Examples I and II in their effectiveness as addition agents for petroleum fractions. Materials obtained by this procedure have an advantage over those described in the foregoing examples in that, being made without the use of organic solvents, they may be more easily synthesized, and their cost of manufacture is considerably less. Materials made by this procedure consist partly of bis-alkylamino-diphenyl methane (when made from N-alkyl phenylamine or N-alkyl aniline) and partly of higher boiling materials of unknown composition. However, the unknown constituent of these products is equally effective in its stabilizing effect as the substituted diphenyl methane, and for that reason this aspect of the invention is not confined to a particular compound or class of compounds as the addition agents but, as aforesaid, is directed to, and is defined as, a reaction product.

Further details in the procedure which may be followed in preparing these reaction products without the use of an organic solvent may be obtained from the following example.

EXAMPLE XIII

The reaction mixture was prepared by dissolving 48.4 grams (.4 mole) of N-ethyl aniline in 100 cc. of water containing 80 cc. of hydrochloric acid (specific gravity 1.19) and then adding 16 grams of formaldehyde solution (.2 mole of CH_2O). The mixture was heated on a steam bath for 31 hours, during which time a white precipitate formed during the first hour and then gradually dissolved, leaving a clear solution. The mixture was then made alkaline with 10 per cent NaOH solution and steam-distilled to remove any excess of ethyl aniline. The residue was extracted with benzene, washed with water, dried over $CaCl_2$ and the solvent distilled off to yield 48 grams of reaction product, which was a viscous oil.

In a second preparation the same reaction mixture was heated to reflux temperature for 10 hours, then neutralized, washed and dried as above to yield 46 grams of a similar product.

When 40 grams of the first product described above was distilled under a vacuum of 2 mm., 28 grams of an oil was obtained that boiled at 210°–215° C. and contained 10.88 per cent nitrogen. The residue consisting of 12 grams of higher boiling materials contained 9.54 per cent nitrogen on analysis. The first fraction consisted essentially of 4, 4' bis-ethylamino-diphenyl methane, but the residue was a condensation product of unknown structure. Since both fractions are effective antioxidants, the term "reaction product" as used herein includes either the reaction product in its entirety or an individual fraction thereof of the type obtained by a fractionation of the type last described above.

Typical reaction products obtained by the procedure of Example XIII have been blended with typical mineral oil fractions and tested for their stabilizing effect upon the oxidation of various viscous oils. The results obtained from these tests are set forth in Tables 11, 12, 13 and 14, wherein the oils used and test procedures followed were the same as those described in Examples III, IV, V and VI respectively.

Table 11

(HIGHLY REFINED, NON-SLUDGING OIL)

Oil sample	Neutralization number
Oil alone	25.00
Oil+.10% N-methyl phenylamine-formaldehyde product	.03
Oil+.10% N-ethyl phenylamine-formaldehyde product (fraction boiling 210° to 215° C. at 2 mm.)	.02
Oil+.10% N-ethyl phenylamine-formaldehyde product (fraction boiling above 215° at 2 mm.)	.02
Oil+.10% N-amyl phenylamine-formaldehyde product	.01
Oil+.10% N-butyl alpha-naphthylamine-formaldehyde product	.01

Table 12

(MODERATELY REFINED (SLUDGING) OIL)

Oil sample	Time, hrs.	N. N.	Lov. color	Sludge mg./25 cc.
Oil alone	168	.99	25	17
	240	2.5	110	246
	336	16.0	400	1282
Oil+.10% N-methyl-phenylamine - formaldehyde product	164	.01	1	
	524	.01	2	18
Oil+.10% N-ethyl-phenylamine - formaldehyde product (fraction boiling 210-215° C. at 2 mm.)	164	.01	2	15
	500	.4	12	31
	1004	2.1	52	108
Oil+.10% N-ethyl-phenylamine - formaldehyde product (fraction boiling above 215° C. at 2 mm.)	164	.01	1	10
	500	.01	2	51
	1004	2.0	50	133
Oil+.10% N-amyl-phenylamine-formaldehyde product	164	.02	2	14
	500	1.4	50	68
Oil+.10% N-buytl-alpha-naphthylamine - formaldehyde product	162	.02	1	
	666	1.6	45	45

Table 13

(SOLVENT-REFINED (SLUDGING OILS)

Oil sample	Time, hrs.	N. N.	Lov. color	Sludge mg./25 cc.
Oil alone	92	.91	9	33
	165	20.3	320	251
Oil+.10% N-methyl phenylamine - formaldehyde product	164	.01	1	
	524	.01	1	25
Oil+.05% N-ethyl phenylamine - formaldehyde product (fraction boiling 210-215 ° C. at 2 mm.)	500	.01	1	
	2012	.01	1	8
Oil+.05% N-ethyl phenylamine - formaldehyde product (fraction boiling above 215° C. at 2 mm.)	500	0.0	1	19
	2012	0.0	1	11
Oil+.05% N-amyl phenylamine - formaldehyde product	500	.01	1	40
	2014	.03	2	1
Oil+.02% N-butyl alpha-naphthylamine - formaldehyde product	498	.01	1	56
	666	1.0	10	13

Table 14

SOLVENT-REFINED MOTOR OILS

Reaction product in oil	Percent conc.	Mg. loss in weight	
		Inhibited	Uninhibited
N-methyl phenylamine-formaldehyde	.25	0	28
N-ethyl phenylamine-formaldehyde (fraction boiling 210-215° C.)	.25	0	30
N-ethyl phenylamine-formaldehyde (fraction boiling above 215° C.)	.25	0	30
N-amyl phenylamine-formaldehyde	.25	0	33
N-butyl alpha-naphthylamine-formaldehyde	.25	0	33

As indicated by the foregoing examples, the proportion of the improving agents or condensation products contemplated herein necessary to effect the desired inhibition of oxidation effects is small. The amounts used may of course be varied, depending upon the oil, the conditions of use, etc., but in general the desired results can be obtained with an amount of inhibitor ranging from about 0.01 per cent to about 1.0 per cent by weight of the oil.

As will appear from the foregoing data, the condensation products obtained by reacting formaldehyde with N-substituted arylamines are of outstanding superiority to the general class of amine-aldehyde reaction products as represented by products obtained from aldehydes generally and primary amines. It is upon this discovery that we base our claim to novelty and patentability, and while we have herein described certain preferred procedures for obtaining these condensation products and have illustrated the products with those obtained by several typical N-substituted arylamines, our invention is not limited to any specific procedure or any specific N-substituted arylamine but includes within its scope such changes or modifications either in procedure or in reactants as may fairly come within the spirit of the appended claims.

This application is a continuation-in-part of applicants' copending application Serial No. 290,499, filed August 16, 1939.

We claim:

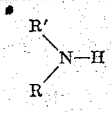
1. A composition of matter comprising: a petroleum product selected from the group consisting of viscous mineral oil fractions and paraffin wax, and in admixture therewith a minor proportion, sufficient to inhibit the deleterious effects of oxidation upon said petroleum product, of the condensation product obtained by reacting formaldehyde with an N-substituted arylamine.

2. A composition of matter comprising: a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to inhibit the deleterious effects of oxidation upon said mineral oil, of the condensation product obtained by reacting formaldehyde with an N-substituted arylamine.

3. A composition of matter comprising: a paraffin wax and in admixture therewith a minor proportion, sufficient to inhibit the deleterious effects of oxidation upon said wax, of the condensation product obtained by reacting formaldehyde with an N-substituted arylamine.

4. A composition of matter comprising: a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to inhibit the deleterious effects of oxidation upon said mineral oil, of the condensation product obtained by reacting formaldehyde with an N-substituted arylamine selected from the group consisting of N-methyl phenylamine; N-ethyl phenylamine; N-amyl phenylamine; N-butyl alpha-naphthylamine; N-benzyl phenylamine; diphenyl-amine; phenyl alpha-naphthylamine; and phenyl beta-naphthylamine.

5. A composition of matter comprising: a petroleum product selected from the group consisting of viscous mineral oil fractions and paraffin wax, and in admixture therewith a minor proportion, sufficient to inhibit the deleterious effects of oxidation upon said petroleum product, of the condensation product obtained by reacting formaldehyde with an organic amine having the general formula



in which R represents an aryl radical and R' represents a radical selected from the group consisting of alkyl, alkaryl, aryl and aralkyl radicals.

6. A composition of matter comprising: a viscous mineral oil fraction and in admixture there-

with a minor proportion, sufficient to inhibit the deleterious effects of oxidation upon said oil, of the condensation product obtained by reacting formaldehyde with an amine having the general formula



in which R represents an aryl radical and R' represents a radical selected from the group consisting of alkyl, alkaryl, aryl and aralkyl radicals.

7. A composition of matter comprising: a paraffin wax and in admixture therewith a minor proportion, sufficient to inhibit the deleterious effects of oxidation upon said wax, of the condensation product obtained by reacting formaldehyde with an amine having the general formula



in which R represents an aryl radical and R' represents a radical selected from the group consisting of alkyl, alkaryl, aryl and aralkyl radicals.

8. A composition of matter comprising: a petroleum product selected from the group consisting of viscous mineral oil fractions and paraffin wax, and in admixture therewith a minor proportion, from about 0.01 per cent to about 1.0 per cent, of the condensation product obtained by reacting formaldehyde with an N-substituted arylamine.

9. A composition of matter comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, from about 0.01 per cent to about 1.0 per cent, of the condensation product obtained by reacting formaldehyde with an amine selected from the group consisting of N-methyl phenylamine; N-ethyl phenylamine; N-amyl phenylamine; N-butyl alpha-naphthylamine; N-benzyl phenylamine; diphenylamine; phenyl alpha-naphthylamine; and phenyl beta-naphthylamine.

10. A composition of matter comprising: a petroleum product selected from the group consisting of viscous mineral oil fractions and paraffin wax, and in admixture therewith a minor proportion, from about 0.1 per cent to about 1.0 per cent, of the condensation product obtained by reacting formaldehyde with an organic amine having the general formula



in which R represents an aryl radical and R' represents a radical selected from the group consisting of alkyl, alkaryl, aryl and aralkyl radicals.

11. A mineral oil composition of the type adapted for use in turbines and transformers comprising a refined mineral oil fraction normally susceptible to the formation of sludge under the conditions of use normally encountered in turbines and transformers and a minor proportion of the condensation product obtained by the reaction of formaldehyde with an N-substituted aromatic amine.

12. A mineral oil composition of the type adapted for use in turbines and transformers comprising a refined mineral oil fraction normally susceptible to the formation of sludge under the conditions of use normally encountered in turbines and transformers and a minor proportion of the condensation product obtained by the reaction of formaldehyde with an N-substituted aromatic amine selected from the group consisting of N-methyl phenylamine; N-ethyl phenylamine; N-amyl phenylamine; N-butyl alpha-naphthylamine; N-benzyl phenylamine; diphenylamine; phenyl alpha-naphthylamine; and phenyl beta-naphthylamine.

13. A mineral oil composition of the type adapted for use in turbines and transformers comprising a refined mineral oil fraction normally susceptible to the formation of sludge under the conditions of use normally encountered in turbines and transformers and a minor proportion of the condensation product obtained by the reaction of formaldehyde with an organic amine having the general formula



in which R represents an aryl radical and R' represents a radical selected from the group consisting of alkyl, alkaryl, aryl and aralkyl radicals.

14. A composition of matter comprising: a petroleum product selected from the group consisting of viscous mineral oil fractions and paraffin wax, and in admixture therewith a minor proportion, sufficient to inhibit the deleterious effects of oxidation upon said petroleum product, of the condensation product obtained by reacting at elevated temperature about one mole equivalent of an N-substituted aryl amine and from one to two mole equivalents of formaldehyde in an alcohol solution containing about one mole equivalent of a mineral acid.

15. A composition of matter comprising: a petroleum product selected from the group consisting of viscous mineral oil fractions and paraffin wax, and in admixture therewith a minor proportion, sufficient to inhibit the deleterious effects of oxidation upon said petroleum product, of the condensation product obtained by reacting at elevated temperature about one mole equivalent of an N-substituted aryl amine and about one half mole equivalent of formaldehyde in an aqueous solution containing about one mole equivalent of a mineral acid.

16. A composition of matter comprising: a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to inhibit the deleterious effects of oxidation upon said oil, of the condensation product obtained by reacting at elevated temperature about one mole equivalent of an N-substituted aryl amine and from one to two mole equivalents of formaldehyde in an alcohol solution containing about one mole equivalent of a mineral acid.

17. A composition of matter comprising: a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to inhibit the deleterious effects of oxidation upon said oil, of the condensation product obtained by reacting at elevated temperature about one mole equivalent of an N-substituted aryl amine and about one-half mole equivalent of formaldehyde in an aqueous solution containing about one mole equivalent of a mineral acid.

EVERETT W. FULLER.
LYLE A. HAMILTON.