Patented Oct. 25, 1938 2,134,436

UNITED STATES PATENT OFFICE

2,134,436

EXTREME PRESSURE LUBRICATION

Troy Lee Cantrell and James Otho Turner, Lansdowne, Pa., assignors to Gulf Oil Corporation, Pittsburgh, Pa., a corporation of Pennsylvania

No Drawing. Application April 24, 1937, Serial No. 138,860

14 Claims. (Cl. 87—9)

This invention relates to improved lubricating oils and in particular to lubricating oil compositions containing an oil-soluble agent or agents effective to impart so called "extreme-pressure" characteristics thereto, said agent being an alkyl-phenyl oxy-ether of 2:4-dinitrobenzene, and said compositions also having certain additional advantages as set forth hereinbelow.

This application is a continuation-in-part of our prior application, Serial No. 98,828, filed August 31, 1936. That application relates to the manufacture of ortho-substituted aryl ethers, including ethers of 2:4-dinitrobenzene. As disclosed in that application, such ortho-nitro-phenyl ethers generally are miscible with mineral lubricating oils, and when dissolved in such oils give improved lubricants.

This is also true of the ethers of 2:4-dinitrobenzene made by the general methods of our prior application, particularly the alkyl-phenyl oxy-ethers. In another continuation of Serial No. 98,828, filed simultaneously with the present application, we describe and claim alkyl-phenyl oxy-ethers of 2:4-dinitrobenzene and improved methods of making such ethers, namely, application Serial No. 138,853. The alky-phenyl ethers there disclosed are useful for various purposes.

The present application is directed to improving mineral lubricating oils and lubricants containing such oils, with these oil-soluble alkyl-phenyl oxy-ethers, particularly ortho-alkyl-phenyl ethers of 2:4-nitrobenzene, as the improvement agent in such lubricating compositions. By the present invention, improved lubrication is obtained, particularly in lubricating metal bearing surfaces at high pressures, speeds and temperatures.

Despite the many technical advances which have been made in the arts of refining and applying lubricating oils, modern lubricating oils and bearings often fail to perform satisfactorily. It is well known in the art that straight petroleum lubricants have fairly well defined limits of bearing speeds, pressures and temperatures, within which they will give acceptable service. These limitations are often reached and even exceeded in modern engines, gears and the like, resulting in unsatisfactory lubrication by straight mineral oils. Such modern designs have been brought about through constant attempts on the part of engineers to improve engines and machines with respect to compactness, speed, power and acceleration. In order to provide satisfactory lubrication for modern designs and keep pace with new mechanical improvements in design, it is necessary to provide lubricating compositions having improved lubricating value as compared with straight lubricating oils and which will give satisfactory service under drastic lubricating conditions under which straight mineral oils would fail to perform satisfactorily.

Thus, considerable attention is being paid to the development of lubricating oil compositions which are capable of giving satisfactory service under high pressures, such compositions being generally known in the art as "extreme-pressure" or "EP" lubricants. A number of materials have been developed which, when added to hydrocarbon oil, materially increase the extreme-pressure properties of the oil; the resultant compositions give more acceptable service under higher pressures between bearing surfaces than is true of the untreated oil. Some of these agents are extremely effective but too expensive for general use, and others, while contributing satisfactory extreme-pressure properties to the oil, are unsatisfactory for other reasons. A primary requisite of any improvement agent is good oil-solubility under service and marketing conditions; such agents when added to hydrocarbon oils in small amounts should not impart to the resulting compositions a hazy or cloudy appearance, should not deposit out when the compositions are stored and packaged prior to sale, and should not attack metal surfaces of containers used for packaging and storing them. The improvement agent should also be highly effective per unit concentration in the lubricating oil compositions; otherwise it would be necessary to add such an amount of the improvement agent as to substantially modify many of the desirable physical properties of the lubricating oil itself. Such oils have been carefully refined to meet exacting specifications, and if it is necessary to incorporate therein relatively large amounts of some agent or agents differing in physical properties from the oil itself, the resulting compositions may prove unsatisfactory for the purposes for which the lubricating oils were prepared. In general it is desirable that any improvement agent should be effective at concentrations not exceeding 1 or 2 per cent, or at the most 5 per cent, by weight of the lubricating oil.

For many purposes it is not necessary to increase the load-carrying properties of lubricating oils to several times the load-carrying properties of the original oils. For example, in the

lubrication of automotive engines, difficulty frequently encountered at points where the pressures between bearing surfaces are thus frequently extremely high. Difficulties are thus encountered in maintaining effective lubrication between piston rings and the side walls of the cylinders, due to the fact that the temperatures of the surfaces may run very high. With ordinary lubricating oils it may be impossible or at least difficult to provide safe and effective lubrication for mechanically efficient engines having a tendency to develop high temperatures at this point. While this difficulty is due primarily to the fact that lubricating oils have been variously explained but are probably due to the fact that such extreme-pressure agents adheres to the metal and the oil wet or adhere to the extreme pressure agent. herefore, an object of our invention to improvement agent or agents of the dicated herein, having the property desirable extreme-pressure characdrocarbon oils when incorporated rent or agents shall be free from disadvantages of agents pre- the same general purpose, to produce. our invention is to pro- compositions comprisils having advantaorated therein. cts such advements

2-Nitro-4-Alkyl Ethers of 2:4-Dinitrobenzene.

2-Nitro-4-alkyl ethers of 2:4-dinitrobenzene.

wherein R represents a phenylene residue and R5 represents an alkyl group having three or more carbon atoms. The secondary and tertiary alkyl-phenyl ethers of 2:4-dinitrobenzene.

wherein R represents a phenylene residue and R5 represents an alkyl group having a branched chain.

In general these substituted diaryl ethers are insoluble in water and in aqueous caustic solutions, but are soluble in alcohol and other organic solvents. They are soluble in mineral lubricating oil and other petroleum products. They are dissolved in mineral lubricating oils, the resulting oil and other petroleum products. They are stable lubricants which produce films having extreme-pressure characteristics.

In making improved lubricants by the invention, between 0.1 to 5 per cent of these diaryl ethers are dissolved in the oil. The exact amount desired on the oil of lubricant and of solved in the type of the initial oil and upon the type of lubricant desired. acter of the oil. The exact amount ether employed. Likewise, in the lubrication of Likewise, in the lubrication chines wherein the lubricant is subjected to ativelv high pressures, specially high pressures, it is advantageous to use it is advantageous to use of these diaryl ethers in of these diaryl ethers improving the lubricating improving the lubricating substituted diaryl ethers substituted diaryl ethers e. together with together with

pending application, Serial No. 99,488, there is disclosed a process of manufacturing an anti-oxidant wherein a phenol is mixed with from 1 to 10 per cent of sulfuric acid having a strength of 60 to 100 per cent, or even fuming sulfuric acid, and an olefin or a mixture of olefins is passed, preferably in the vaporous or gaseous phase, through the liquid mixture until the phenol undergoing reaction has gained in weight from 100 to 200 per cent, or thereabouts, followed by washing the product so obtained with water and with caustic soda solution, the concentration of which does not exceed 15 per cent. Various phenols may be employed, for example, phenol (C_6H_5OH) itself, the three cresols

$$(H_3C—C_6H_4—OH),$$

and certain xylenols [$(H_3C)_2—C_6H_3—OH$] and crude cresylic acids may be employed. Pyridines, if present, should be removed by conventional methods, such as washing with acid or by distillation.

As olefinic starting materials, there may be employed individual olefins themselves, mixtures of olefins, or mixtures of olefinic and non-olefinic material. By way of example, the olefinic starting material may be butylenes, amylenes, refinery gases containing normally gaseous olefins (propylene, butylene) in varying amounts, and cracked distillates or other relatively low-boiling hydrocarbon mixtures containing normally liquid olefins and in some instances also containing substantial amounts of dissolved normally gaseous olefins.

When the reaction is conducted with the olefin in the gaseous phase, the product is relatively highly concentrated with respect to the effective anti-oxidant material (alkyl-phenols) and may not require distillation or concentration for the purpose of isolating the latter. On the other hand, when the reaction is conducted with the olefinic material in liquid phase, and especially when the concentration of olefins in the starting material is comparatively low, the product may be relatively dilute with respect to the effective anti-oxidant material, comprising for example a solution of such anti-oxidant in gasoline-like polymers or unreacted liquid hydrocarbons. In such case, the anti-oxidant material may be concentrated by distillation or otherwise as set forth in the above-mentioned co-pending applications, prior to being converted into diaryl ethers by the method described herein.

The exact chemical and structural natures of the anti-oxidant materials, as thus prepared and employed as a starting material in the manufacture of our improved addition agents, is largely obscure. Although we have been able to identify certain types of compounds in these anti-oxidant materials, it will be realized that, especially since mixtures of various phenols and mixtures of various olefins are frequently employed in the manufacture of these anti-oxidants, the number of possible chemical compounds is large and varied. In general, they differ from the simple alkylated phenols in that they are insoluble in dilute caustic soda solution (15% solutions), and also in that they are good anti-oxidants and gum-inhibitors, whereas simple alkylated phenols (such as cresol and xylenol) are not. In general, also, the alkylations, in such instances as they occur, are of secondary and tertiary types; the methods set forth in the above co-pending applications of Stevens and Gruse and of Troy Lee Cantrell, do not produce normal or primary alkylated linkages. The alkylated phenols, obtained by the methods of those applications and which contain secondary and tertiary alkyl groups, are converted by the methods of our co-pending application Ser. No. 138,858 into substituted diaryl ethers which are advantageous in the present invention for improving mineral lubricating oils or like lubricants.

However, diaryl ethers useful in the present invention may also be obtained by the methods of our application Ser. No. 138,858 from alkylated phenols with normal or primary linkages. While those alkylated phenols are not themselves good antioxidants or gum inhibitors in cracked gasolines and themselves are undesirable for addition to mineral oils, due to the fact that both such materials (alkylated phenols of both primary and normal linkages) tend to be insoluble in the high-gravity lubricating oils, the alkylated phenyl ethers of 2:4-dinitrobenzene obtained from them are readily soluble in mineral lubricating oils and improve the lubricating properties of such oils.

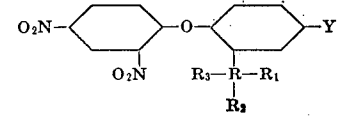
Further, it is possible that certain alkylated phenols of normal or primary linkage might be satisfactory for addition to high-gravity lubricating oils, provided the alkyl chains were long enough, say chains of four carbon atoms or more, on account of the closer resemblance in structure of such compounds to paraffinic lubricating oil constituents. As disclosed in our co-pending application Ser. No. 138,858, such long chain alkylated phenols may be converted into useful diaryl ethers by the methods described therein. Those diaryl ethers are also useful in the present invention. However, the diaryl ethers obtained from the alkylated phenols which are insoluble in dilute caustic soda solution and which are good antioxidants or gum inhibitors, are very effective improvement agents for mineral lubricating oils and we find such alkylated phenols to be advantageous for preparing the diaryl ethers used in the practice of the present invention.

We have identified constituents in the various anti-oxidant materials prepared as set forth hereinbefore, such compounds as follows:

Ortho-isopropyl phenol
Ortho-tertiary butyl phenol
2:4-di-tertiary butyl phenol
Ortho-isoamyl phenol
Ortho-tertiary amyl phenol

In addition to the above listed compounds, similar derivatives of various homologues of mono-, di-, and poly-hydroxy phenols may be present.

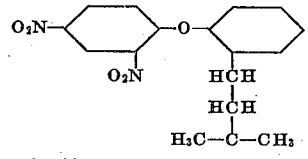
We have now found that the substituted diaryl ethers obtained from such alkyl-phenols or mixtures thereof, by the methods of our co-pending application Serial No. 138,858, have the property of improving mineral oils when dissolved therein in small amounts. Thus in the practice of the present invention, it is advantageous to employ diaryl ethers having the following formula:



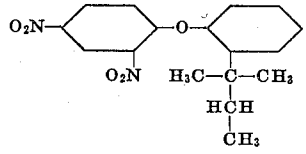
wherein Y represents hydrogen or an alkyl group, R is an aliphatic radical and R_1, R_2 and R_3 represent hydrogen or an alkyl group. Such substituted diaryl ethers may be readily obtained from the correspondingly substituted alkyl-phenols and 2:4-dinitrochlorobenzene.

As illustrative of the above advantageous class of substituted diaryl ethers, we may mention the following ethers which have the representative structural formulae:

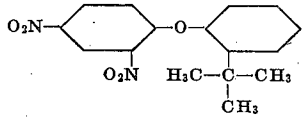
The ortho-isoamyl-phenyl ether of 2:4-dinitrobenzene,



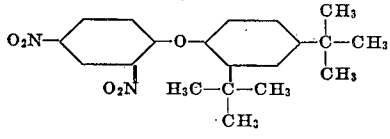
The ortho-tertiary amyl-phenyl ethers of 2:4-dinitrobenzene,



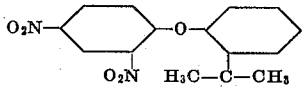
The ortho-tertiary butyl-phenyl ether of 2:4-dinitrobenzene,



The 2:4-tertiary butyl phenyl ether of 2:4-dinitrobenzene,



The ortho-isopropyl-phenyl ethers of 2:4-dinitrobenzene,



As stated ante, mixtures of the above diaryl ethers may be employed. Also, various mixed ethers containing the above compounds may be used to advantage. In general, we have found that substituted diaryl ethers or mixtures of them, having the following properties, yield valuable improved lubricants according to this invention.

Gravity: API	15 to 25
Viscosity, SUV: 100° F.	150 to solid
Color	water white to 7 NPA
Pour: °F. (liquid only)	0 to 30
Melting point: °F. (solid only)	80 to 265

Generally, the diaryl ethers here employed are readily miscible and compatible with petroleum oils in the percentages necessary for the present purposes. They may be incorporated with the mineral oil or lubricating base in any suitable manner. They may be dissolved in the oil by simply mixing the diaryl ether with the oil and slightly warming with agitation to obtain uniform lubricants. Warming to temperatures between 100° F. and 180° F. is usually sufficient; the ethers being readily soluble. With the heavier and more viscous lubricating oils this warming is advantageous since the heating lowers the viscosity of the oil facilitating the blending. In some cases, the ethers may be dissolved in suitable volatile solvents and the solution added to the oil, the solvent being subsequently distilled off. This solvent method is particularly effective with the solid diaryl ethers. Also, the diaryl ethers may be first dissolved in a suitable lubricating oil to form a master batch which is subsequently blended with more lubricating oil to give a range of lubricating compositions as desired. Likewise, the compounded lubricant may be converted into thickened compositions or greases in any of the usual ways. Sometimes the diaryl ether may be directly added to metal soap greases or other compounded lubricants in which a petroleum oil is the lubricating base.

In the practice of the present invention any suitable lubricating oil base may be employed. Ordinarily it is best to select a good grade of lubricating oil which has suitable initial properties for the lubrication required. Then the addition of the substituted diaryl ethers produces the additional characteristics desired, such as the necessary extreme pressure qualities, etc. That is, petroleum oils and lubricants of the usual grades may be employed in this invention. The oils falling within the well known SAE classes are among those which can be advantageously improved by our invention. Likewise, special lubricants such as obtained by blending certain non-petroleum oils with mineral oil may be improved by the addition of these substituted diaryl ethers.

In evaluating the improvement in extreme pressure characteristics obtained by the addition of these substituted diaryl ethers to various lubricants, they may be tested by any of the usual methods for determining the extreme pressure characteristics of a lubricant. For instance, the improved lubricants may be subjected to the Almen test and by comparison with the original oil in a like test, the necessary addition of diaryl ethers to obtain the desired low bearing qualities can be readily determined for a given lubricant.

The following examples are illustrative of certain typical embodiments of this invention:

Example 1

Into a suitable vessel there are introduced 1000 gallons (7341 lbs.) of Pennsylvania motor oil SAE 60 grade and the oil warmed to 160° F. Then 73 pounds of a mixture of substituted diaryl ethers having the following properties:

Gravity: Bé. 60° F.	14.4
Viscosity, SUV 100° F. (seconds)	143.0
Pour: °F.	−10

are gradually added and the mixture agitated until a uniform blend is obtained; about 1 hour usually being required. The improved motor oil is then cooled and is a finished product.

In agitating the mixture, ordinary mechanical agitators may be employed or a current of air may be passed through the warm mixture, to produce uniform blending.

The properties of the original and improved motor oil are as follows:

Table A

	Original oil	Improved lubricant
Gravity: °API	29.0	28.8
Viscosity, SUV:		
100° F.	1580	1450
210° F.	616	593
Flash, O. C.: °F.	530	530
Fire, O. C.: °F.	605	610
Pour: °F.	0	0
Color: NPA	3.0	3.25
Carbon residue: Percent	0.30	0.35
Copper strip test	Passes	Passes

From the above table, clearly the addition of the substituted diaryl ether does not substantially change the ordinary properties of the oil. However, the improved lubricant obtained is a satisfactory extreme pressure lubricant.

When tested by the Almen test, the following results were obtained:

Journal speed: RPM	600
Rubbing speed: Ft. per min.	40
Lever load: Lb.	20
Torque: Lb. ft. x 10	24
Unit Load: Lb. sq. in.	10,000
Lubricant temperature: °F.	
Initial	76
Final	175

From the above results, the beneficial effect of the mixture of substituted diaryl ethers as an improvement agent for the oil is quite apparent.

The mixture of substituted diaryl ethers employed in the above example was prepared according to Example 4 of Serial No. 138,858.

By employing the same blending procedure as in the above example but substituting other motor oils, those motor oils may be likewise improved. Also, in the above examples, other mixtures of substituted diaryl ethers may be used in lieu of the particular mixture given and the same improvements obtained. Again, any one of the particular substituted diaryl ethers mentioned ante may be employed instead of a mixture of such ethers.

The above example and specific compounds mentioned herein are illustrative embodiments of the present invention. That is, the percentage of diaryl ethers employed may be varied as indicated, according to the particular properties desired in the final lubricant. Likewise, the lubricating base desired may be selected according to the lubricant to be produced. For instance, any of the usual greases or mixtures of mineral oils and non-mineral oils, may be used in making lubricants of our improved type. In making these improved lubricants, various diaryl ethers may be used to particular advantage. These subclasses of diaryl ethers have been pointed out ante. For instance, those containing an alkyl group having one or more branched chains, such as iso-propyl, tertiary-butyl, isoamyl, etc., may be advantageously employed in the present invention because of their effectiveness and marked solubility in mineral lubricating oils. Also, the polyalkylated diaryl ethers have advantage. In these, the multiplicity of alkyl groups likewise improves the oil solubility of the diaryl ethers. Further, with one or more alkyl groups in the ortho position, the aryl ethers seemingly are sensitized with respect to their ability to impart extreme pressure characteristics to these lubricants.

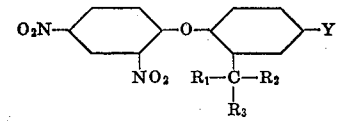
What we claim is:

1. As a composition of matter, an improved lubricant containing a major proportion of mineral lubricating oil and minor proportion of an alkyl-phenyl oxy-ether of 2:4-dinitro benzene.

2. The composition of claim 1 wherein said ether is an ortho-alkyl-phenyl ether.

3. The composition of claim 1 wherein said ether is a polyalkyl-phenyl ether.

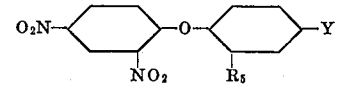
4. As a composition of matter, an improved lubricant comprising mineral lubricating oil and a minor proportion of a substituted di-aryl ether having the following formula:



wherein Y represents a substituent of the class consisting of hydrogen and an alkyl group, and R_1, R_2 and R_4 represent a substituent of the class consisting of hydrogen and an alkyl group, at least one of the substituents represented by R_1, R_2 and R_3 being an alkyl group, sufficient of diaryl ether being present to impart extreme pressure characteristics to said mineral oil.

5. The improved lubricant of claim 1 wherein said alkyl-phenyl ether contains at least one branched chain alkyl group attached to said phenyl group.

6. As a composition of matter, an improved lubricant comprising a major proportion of mineral lubricating oil and a minor proportion of an alkyl-phenyl oxy-ether having the following formula:



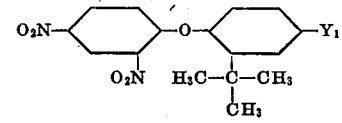
wherein Y represents a substituent of a class consisting of hydrogen and an alkyl group and R_5 represents an alkyl group containing a branched chain.

7. The composition of claim 4 wherein said substituted diaryl ether is the 2-isoamyl-phenyl oxy-ether of 2':4'-dinitrobenzene.

8. The composition of claim 4 wherein said substituted diaryl ether is a 2:4-dialkyl-phenyl oxy-ether of 2':4'-dinitrobenzene.

9. The composition of claim 6 wherein said alkyl-phenyl ether is the 2:4-di-tertiary-butyl-phenyl oxy-ether of 2':4'-dinitrobenzene.

10. The composition of claim 6 wherein the said alkyl-phenyl ether is a substituted diaryl-ether having the formula

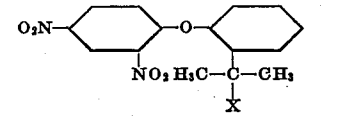


wherein Y_1 represents a substituent of the class consisting of hydrogen and a butyl group.

11. The composition of claim 6 wherein said alkyl-phenyl ether is the 2-tertiary-butyl-phenyl oxy-ether of 2':4'-dinitrobenzene.

12. The composition of claim 6 wherein said alkyl-phenyl ether is the 2-isopropyl-phenyl oxy-ether of 2':4'-dinitrobenzene.

13. The composition of claim 6 wherein said alkyl-phenyl ether is a di-substituted diaryl ether having the formula:



wherein X is a substituent of the class consisting of hydrogen, CH_3 and C_2H_5.

14. The composition of claim 6 wherein said alkyl-phenyl ether is the 2-tertiary-amyl-phenyl oxy-ether of 2':4'-dinitrobenzene.

TROY LEE CANTRELL.
JAMES OTHO TURNER.