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TURBINE LUBRICATION

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16 Claims. (Cl. 87—9)

This invention relates to improvements in turbine lubrication, and it comprises improved methods of lubricating turbines and the like with mineral oils and mineral oil compositions, known as turbine oils, wherein a small amount of a nitrophenyl alkyl thioether is maintained in the circulating turbine oil to mitigate or substantially retard the normal deterioration of the turbine oil occasioned by the operating conditions under which lubrication is effected, such as heat, moisture, aeration, etc.; and it also comprises improved turbine oils containing small amounts of an alkyl thioether of a nitrobenzene, the improved turbine oil being directly useful in lubricating turbines and the like, and useful as make-up oil in the lubricating systems of such machines; all as more fully hereinafter set forth and as claimed.

In lubricating turbines and the like, the requirements for satisfactory and safe lubrication are rather exacting. The modern steam turbines and the like are relatively large and complicated machines which operate at high speeds, and in which the rotating mechanism is delicately balanced. In commercial plants, these turbines are used for the continuous development of large amounts of power, and it is essential that the lubrication system be entirely safe; that is, continually remain operative, as well as be satisfactory from the standpoint of preventing undue wear upon the bearings and other moving parts.

In the usual lubricating system of such machines, the turbine oil is circulated under pressure from an oil reservoir through the various parts of the machine, such as bearings, gears, etc. Pressure is used to insure a positive feed or circulation of the oil. After passing through the parts of the turbine being lubricated, the oil is then cooled and collected in a separating reservoir or sump. In lubricating turbines, the oil is repeatedly re-cycled, and it is more or less purified before being returned to the oil reservoir containing the feed oil.

In the sump, the cooled oil is maintained more or less at rest to permit the separation or settling of the oil from other contaminating bodies; that is, the various impurities picked up by the oil during its passage through the turbine parts being lubricated. Also the oil is frequently filtered, centrifuged, or treated in other ways to separate such impurities. Many and various purifying methods or procedures have been suggested and used. But in all of them there is a substantial loss of oil in separating the water, sediment and sludge. For instance, in effecting the separation in the sump, the practice is to draw off from the bottom of the sump all the settled sediment or sludge, together with the overlying "lace", the withdrawal being continued until clear oil flushes the bottom of the sump. The "lace" is a water-oil emulsion and contains a substantial amount of oil. In this separation, which is standard in turbine lubricating systems, there is a substantial loss of undeteriorated oil. Thus substantial quantities of make-up oil are necessary in recycling, in addition to that required to replace the deteriorated oil. Therefore, the consumption of oil is substantial, although the bulk of it is recycled.

Generally, the solid impurities such as dirt, metal particles, other hard matter, etc., are present in the cooled oil in only relatively small amounts; and they may be termed foreign impurities, as distinguished from the contaminating bodies which are more or less inherent in the used lubricant, such as oil deterioration products and water. If the cooled oil were dry, the foreign solid impurities might be readily and completely separated by straining, settling, filtering, etc. But the presence of the water and other liquid or soft impurities, render it difficult to obtain quick and complete separation of the good oil from the various impurities.

In circulating through the turbine, the oil becomes more or less wetted. During the passage of the oil through the entire circulating system, it picks up more or less water, air, solid particles and other impurities. In passing through the main bearings, the oil becomes intimately churned together with the water and these foreign matters. Owing to the higher temperature and the great surface speed of the revolving shaft, the foreign matter and part of the oil form emulsions, and the oil gradually breaks down. The other impurities, whether in solution or in suspension, increase the emulsifying effect of the water on the oil. Sludge dissolved in the oil tends to promote such emulsification. The formation and presence of oil deterioration products is indicated by an increase in the acidity of the oil

and the appearance of sludge. When the deterioration has proceeded to a dangerous point, appreciable amounts of insoluble sludge separate from the oil. Prior to that time, intermediate deterioration products may remain dissolved or colloidally suspended in the oil. Such intermediate products tend to increase and stabilize the water-oil emulsion or "lace" and render it difficult to obtain a quick, clean stratification either in the sump or during a later centrifuging to obtain an oil free of dispersed water. After centrifuging, the separated oil might be heated to evaporate off any residual water, and this is sometimes done. But this is not always advantageous or satisfactory. For one thing the heated oil has to be again cooled before it can be fed into the turbine. This increases the expense. Second, although the water might be evaporated, the soluble oil deterioration products remain in solution; and they, by gradual accumulation, render the oil more susceptible to absorb water and to emulsification.

Thus in lubricating turbines, something more is required than to simply supply the turbine with an oil which has the necessary lubricating qualities. A prime requisite of safe turbine oil is that it be capable of relatively sharp stratification or separation from the moisture, etc., in the sump and centrifuge. Thus the emulsibility of turbine oils with water, aqueous solutions and steam are important factors with this type of lubricant.

Further, a satisfactory turbine oil must be substantially free of ingredients which readily deteriorate to form acids or emulsion-promoting products. Turbine oils must comply with a rather strict set of specifications. Generally turbine oils are low-viscosity neutral oils. The following table indicates the general range of their primary physical characteristics:

Gravity: °API	24.5– 33.0
Viscosity, SUV: 100° F	150 –650
Flash, OC: °F	390 –500
Color, NPA	1.0– 3.0

Turbine oils are obtained by thoroughly refining carefully selected stocks to remove deleterious and unstable components. The refining is so controlled as to remove unsaturated compounds, organic acids and other substances which might induce emulsification or sludge. The low-viscosity neutral oil so obtained must comply, within certain limits, with certain standard emulsion tests. One of these tests is the "Steam emulsion test" (ASTM D 157–36), wherein the time required for the separation of a definite volume of oil from a definite volume of condensed steam, measured in seconds, is known as the "SE number". An acceptable turbine oil should have an SE number not greater than 75. When the oil being recycled in the turbine shows an SE number greater than 400, the circulating oil contains such amount of deterioration products that it should be thoroughly purified and revitalized by the addition of substantial amounts of make-up oil, if the entire amount is not withdrawn and replenished.

Another important test is the test for acidity, commonly reported as the neutralization number. Initially, the oil should have practically no free organic acid present, and when the organic acidity of the oil accumulates to a point where the neutralization number is above 1.0, the oil should be discarded or reworked.

We have now found that by incorporating a moderate amount of nitro-phenyl alkyl thioethers into the turbine oil, we obtain better lubrication and a greater stabilization of the oil. The nitro-phenyl alkyl thioethers may be introduced into the circulating turbine oil, either as it is being fed to the turbine, or during the collecting and purifying of the oil; for instance, added in the sump. However, it is advantageous to incorporate this improvement agent with the turbine oil prior to introducing it into the supply reservoir. The turbine oils containing 0.1 to 1.0 percent of an ortho-nitro-phenyl alkyl thioether dissolved therein are superior lubricants for the modern turbine, and they may be recycled repeatedly, with intermediate separation of water and other impurities, for longer periods of time; the life of the lubricant being markedly increased by the presence of the said thioethers. That is, in the present methods of improving the lubrication of turbines, we maintain in the circulating oil a sufficient amount of the said nitro ethers to stabilize the oil and to facilitate the stratification from water and other impurities during the purification.

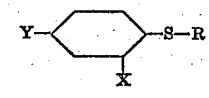
The nitro-phenyl alkyl thioether compounds here useful for improving turbine oils may be represented by the following formula:

$$O_2N—R_1—S—R_2$$

wherein R_1 represents a phenyl group, and R_2 represents an alkyl group. These alkyl thioethers of nitrobenzenes as a class are advantageous and the para-nitro and ortho-nitro compounds are ordinarily employed in the present invention. However, in some instances, we employ the 2:4-dinitro-phenyl alkyl thioethers. All of these nitro-phenyl thioethers are soluble in mineral oils and various organic solvents. They are insoluble and immiscible with water and aqueous liquids. They are substantially non-acid and do not readily develop acidity in contact with oil or water. They are excellent improvement agents for turbine oils.

These nitro-phenyl alkyl thioethers may be obtained by condensing a nitro-chlorobenzene in alcoholic solution with various metal mercaptans, such as alkali metal alkyl mercaptans, etc. In our co-pending application Serial No. 134,460, filed April 1, 1937, we describe and claim various methods of producing para-nitro-phenyl thioethers and the thioethers so obtained. In our co-pending application Serial No. 98,828, filed August 31, 1936, we also describe methods of producing nitro-phenyl thioethers and claim ortho-nitro-phenyl alkyl thioethers; the present application being a continuation-in-part of said prior application Ser. No. 98,828.

Any of the nitro-phenyl alkyl thioethers described in said applications may be employed in the practice of the present invention. That is, in improving turbine oils by the present invention, we may employ thio-ethers having the following formula:



wherein X and Y represent hydrogen or a nitro group, at least one nitro group being present, and R represents an alkyl group.

Of this class of thioethers, the following specific thioethers may be used to advantage in

improving turbine oils in accordance with this invention:

Methyl thioethers of para-nitrobenzene.
Ethyl thioethers of para-nitrobenzene.
Propyl thioethers of para-nitrobenzene.
n-Butyl thioethers of para-nitrobenzene.
n-Amyl thioethers of para-nitrobenzene.
Iso-amyl thioethers of para-nitrobenzene.
Hexyl thioethers of para-nitrobenzene.
Heptyl thioethers of para-nitrobenzene.
Octyl thioethers of para-nitrobenzene.
Nonyl thioethers of para-nitrobenzene.
Decyl thioethers of para-nitrobenzene.
Undecyl thioethers of para-nitrobenzene.
Dodecyl thioethers of para-nitrobenzene.
Cetyl thioethers of para-nitrobenzene.
Methyl thioethers of ortho-nitrobenzene.
Ethyl thioethers of ortho-nitrobenzene.
Propyl thioethers of ortho-nitrobenzene.
n-butyl thioethers of ortho-nitrobenzene.
n-amyl thioethers of ortho-nitrobenzene.
Iso-amyl thioethers of ortho-nitrobenzene.
Hexyl thioethers of ortho-nitrobenzene.
Heptyl thioethers of ortho-nitrobenzene.
Octyl thioethers of ortho-nitrobenzene.
Nonyl thioethers of ortho-nitrobenzene.
Decyl thioethers of ortho-nitrobenzene.
Undecyl thioethers of ortho-nitrobenzene.
Dodecyl thioethers of ortho-nitrobenzene.
Cetyl thioethers of ortho-nitrobenzene.
The butyl thioethers of 2:4-dinitro-benzene.
The amyl thioethers of 2:4-dinitro-benzene.

Also mixtures of these alkyl ethers may be employed in the practice of the present invention; for instance the mixed amyl thioethers derived from technical amyl mercaptans by methods described in the copending applications acknowledged ante. The para-nitro-phenyl alkyl thioethers yield turbine oils which may be re-cycled in the turbine for relatively long times without the neutralization number and SE number increasing beyond the values specified as safe for turbine lubrication. The ortho-nitro-phenyl alkyl thioethers effect a like improvement in the turbine oil, and in addition to this they impart extreme pressure characteristics to the turbine oil.

As stated, this invention may be practiced by introducing small amounts of these thioethers into the turbine oil while it is being re-cycled in the ordinary manner. Also we may prepare improved turbine oils which are relatively stable in storage, and which may be employed as make-up oil for the turbine lubrication system.

In making such improved turbine oils, ordinarily 0.1 to 1.0 per cent by weight on the oil of these thioethers is sufficient to produce the desired improvement of the turbine oil. However in some cases larger amounts may be employed; this being particularly so when the ortho nitro-phenyl alkyl thioethers are employed and it is desired also to impart extreme pressure characteristics to the turbine oil. The particular proportions employed depend upon the particular thioethers and the turbine oil being compounded together and the particular type of turbine lubricant desired. In the practice of the present invention, any suitable turbine oil may be employed as the starting material. Into such oils we incorporate these thioethers in any suitable manner. The thioether may be dissolved in the oil by simply mixing the thioether with the oil and agitating the mixture until a uniform solution is obtained. In the amounts here employed, the thioethers are readily and completely soluble in turbine oils. In forming the improved lubricant, a slight warming of the oil mixture during the agitation facilitates obtaining uniform lubricants. Warming to temperatures between 100° F. and 180° F. is usually sufficient. Also the thioethers may be first dissolved in a part of the turbine oil to form a master batch, which is subsequently blended with additional turbine oil to give the concentration of thioether desired in a particular turbine lubricating system. These master batches are particularly useful in improving the lubricant of a turbine, which has previously been operated with ordinary turbine oil. That is, these master batches are excellent as make-up oil.

These improved turbine oils, when subjected to any of the usual tests for turbine oils, readily show the improvements obtained as compared with the original turbine oil. In the inspection and examination of turbine oils, in addition to the tests which are commonly applied to all lubricating oils, turbine oils are subjected to other tests. In certain of the standard tests of that oil, the emulsifying properties of the turbine oils are determined under various conditions. One of these tests is the steam emulsion test (ASTM D 157–36). In that test the time in seconds required for the oil to separate from an equal volume of condensed steam is known as the SE number; a current of steam being passed into the turbine oil to form the oil and condensed steam emulsion. This test is an important one. It being important that the turbine oil retain its initial properties as long as possible in use, the turbine oil is frequently subjected to special accelerated tests to determine its resistance to deterioration. One such test is the special oxidation test. In this test, 500 cc. of turbine oil is air blown at 212° F. for many hours; air being passed through the warm oil at the rate of 10,000 cc. per hour. The oxidized oil is then subjected to the steam emulsion and other tests, to ascertain its stability with respect to certain properties. When so tested, our improved turbine oils are superior to the turbine oil from which they are prepared. By varying the particular nitro-phenyl alkyl thioether used and the amount thereof, we can controllably improve one or more properties of the turbine oil. In this way, turbine oils having a specified set of properties can be readily prepared by means of the present invention. In the illustrative examples given post, we set forth certain typical embodiments of the present invention. These examples are merely illustrative, and in the commercial practice of this invention, other and quite different practical embodiments may be employed. For instance, we may employ various mixtures of thioethers. In some cases, mixtures of ortho-nitro-phenyl and para-nitro-phenyl thioethers may be employed. In this way we can impart both marked extreme pressure characteristics and maximum stability to the turbine oils. Also mixed thioethers such as those derived from the natural mercaptans obtained from mineral oil, may be employed to improve turbine oils. In certain methods of refining mineral oils, particularly the lighter fractions thereof, such mercaptans are isolated from the oil. The so recovered mercaptans are complex mixtures, containing aliphatic, aromatic and cyclic compounds. These mercaptans, when converted into nitro-phenyl thioethers, yield mixed thioethers containing such compounds.

In the general practice of this invention, we

find it advantageous to employ thioethers or mixtures of thioethers which are liquid or easily liquefiable and which have the following properties:

TABLE A

Gravity: °Bé	12.0 to 25.0
Viscosity, SUV: 100° F	39.0 to 100
Pour: °F	Below −55 to +32
Color: NPA	5.5 to Dark
Sulfur: Percent	18 to 8
Neutralization No	0 to 0.1

For instance, the ethyl and amyl thioethers of ortho-nitrobenzene are liquids having the properties set forth in Table B; the amyl thioethers being the mixture of thioethers obtained from commercial amyl mercaptan.

TABLE B

	Ortho-nitro-phenyl ethyl	Alkyl thio-ether amyl
Gravity: °Bé	21.0	15.1
Specific gravity: 60°/60° F	1.1694	1.1162
Pounds per gallon	9.74	9.32
Viscosity, SUV: 100° F	40.1	43.6
Pour: °F	Below −55	Below −55
Color: NPA	5.5	6.0
Sulfur: Percent	17.4	14.2
Neutralization No	Nil	Nil

However, we may also employ the solid thioethers. In using these thioethers, it is advantageous to first dissolve them in a part of the turbine oil to obtain a master batch which may be further diluted with more oil to produce turbine oils having adjusted properties as desired.

The specific examples and tests given post are illustrative of detail embodiments of the present invention.

Example 1

Into a suitable vessel there are introduced 1000 gallons (approximately 7341 pounds) of a commercial turbine oil and the oil is warmed to 160° F. Then 18.35 pounds of the amyl thioether of ortho-nitrobenzene, (0.25% by weight on the oil) is gradually added and the mixture agitated until a uniform blend is obtained; about one hour being required. 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 amyl thioether used in this example had the properties given in Table A ante, and was a mixture of isomeric amyl compounds, it being prepared from a commercial amyl mercaptan and from commercial ortho-nitrochlorobenzene, both of which are widely marketed in the chemical industries under those names. The mixture so obtained is a superior turbine oil.

Example 2

By the method of Example 1, a like amount of the amyl thioethers of para-nitrobenzene is dissolved in the turbine oil. The turbine oil so obtained is even superior to that produced in Example 1; the para-nitro substituted thioether being an even better improvement agent for the turbine oil. The amyl thioether used in this example was also prepared for commercial mercaptan, and likewise is a mixture of isomeric amyl thioethers.

Example 3

Another improved turbine oil is produced by the method of Example 1 by employing the ethyl thioether of either ortho or para-nitro benzene. In this embodiment, the ethyl thioether given in Table A may be employed.

The properties of the improved oils obtained in Exampes 1 and 2, as compared with those of the original turbine oil, are as follows:

TABLE C

	Original oil	Improved oil	
		Example 1	Example 2
Gravity: API	29.8	29.8	29.8
Sp. gr., 60°/60° F	0.8772	0.8772	0.8772
Viscosity, SUV:			
100° F	158	156	156
210° F	43.4	43.4	43.4
Viscosity index	90	90	90
V-G constant	0.826	0.826	0.826
Flash, OC: °F	390	390	390
Fire, OC: °F	460	450	450
Pour: °F	+5	0	0
Color: NPA	1.25	1.75	1.75
Carbon residue: Percent	Trace	Trace	0.01
Neutralization No	Nil	Nil	Nil
Steam emulsion test: ASTM D 157—36, SE No. sec	10	12	11

From the above table it is clear that the addition of the thioether does not materially change the general character of the turbine oil; but the utility of the oil as a lubricant for turbines has been markedly improved. This improvement is demonstrated when the original oil and the two improved oils are subjected to the special oxidation test.

In the following Table D, tests made, after varying times of air blowing, with respect to neutralization number, SE number and colors are given. The effect of the nitro-phenyl alkyl thioethers in improving such characteristics of the turbine oil are clear.

TABLE D

Special oxidation test

Time hours	Original oil	Improved oils	
		Example 1	Example 2
Neutralization number			
0	Nil	Nil	Nil
406	0.11	0.07	0.07
796	0.15	0.07	0.08
1800	0.22	0.11	0.06
Steam emulsion number (sec.)			
0	10	12	11
406	308	238	138
796	358	345	179
1800	448	461	254
Color, NPA			
0	+5	0	0
406	4.75	3.75	2.75
796	6.00	4.25	2.25
1800	*3.50	5.5	4.5

*Diluted.

From the above table, it is evident that the compositions containing the para-nitro-phenyl alkyl thioether have a very satisfactory neutralization number and SE number, even after 1800 hours in the special oxidation test.

After the original oil and improved oils had been subjected to the special oxidation test for 1800 hours, the properties set forth in Table C were again determined. In the following table,

the results of such determinations are set forth.

TABLE E

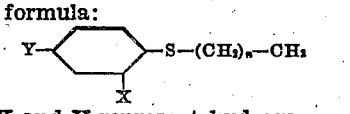
	Original oil	Improved oils	
		Example 1	Example 2
Gravity: API	29.7	29.7	29.6
Viscosity, SUV: 100° F.	163	157	161
V-G constant	0.825	0.826	0.827
Flash, OC: °F.	395	400	395
Fire, OC: °F.	455	460	455
Pour: °F.	+5	+5	+5
Color: NPA	3.5 dil.	5.5	4.5
Carbon residue: Percent	0.05	0.02	0.03
Nature	Med. hard	Med. hard	Med. hard
Neutralization No.	0.22	0.11	0.06
Steam emulsion test: ASTM D 157—36, SE No. (SEC)	448	461	254

From the above table, it is apparent that the nitro-phenyl alkyl thioethers not only improve certain characteristics of the oil but also do not deleteriously affect other properties of the oil which were initially satisfactory.

In the above examples, other commercial turbine oils may be employed and likewise improved. Also in lieu of the specific alkyl thioethers employed, other thioethers may be used. Likewise the proportion of thioethers employed might be varied as indicated ante in this specification. While we have illustrated our invention with reference to specific examples, it will be understood that our invention is not limited to the examples but may be practiced within the scope of the claims hereinafter presented. Moreover while we have in certain instances given certain preferred ranges and proportions, it will be understood that our invention is not limited thereto, and that such preferred ranges and proportions are in general selected for particular products and particular purposes; variations in proportions and in the methods of preparation result in products of different characteristics, such products having individual advantages and utilities.

What we claim is:

1. As an improvement in lubricating steam turbines with mineral lubricating oils by positively circulating such turbine oils under pressure through the moving parts of the turbine to be lubricated, collecting the oil, segregating the sediment, sludge and lace from the oil, separating the thus segregated oil from said materials and recycling the so separated oil, fresh oil being added during recycling as make-up oil to compensate for the oil contained in the separated sludge and lace, the improvement which comprises introducing into said mineral lubricating oil a minor amount of an alkyl thioether of nitrobenzene, and maintaining in said turbine oil during such recycling an amount of said thioether sufficient to substantially improve the lubrication of the turbine and the segregation of the oil from the sludge, sediment and lace, the said alkyl thioether of nitrobenzene being introduced at one stage in said cycle and having the following formula:



wherein X and Y represent hydrogen or a nitro group, at least one nitro group being present, and n is 0 to 15.

2. The improved method of claim 1 wherein the amount of said alkyl thioether so introduced is sufficient to maintain between 0.1 and 1.0 per cent by weight of said thioether dissolved in said turbine oil.

3. The improved method of claim 1 wherein said thioether is an amyl thioether of ortho-nitrobenzene.

4. The improved method of claim 1 wherein said thioether is an amyl thioether of para-nitrobenzene.

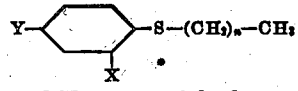
5. The improved method of claim 1 wherein said thioether is an amyl thioether of 2:4-dinitrobenzene.

6. The improved method of claim 1 wherein said thioether is introduced into the oil as it is being fed to the turbine.

7. The improved method of claim 1 wherein the said thioether is introduced during the collecting of the turbine oil subsequent to its passage through the turbine.

8. The improved method of claim 1 wherein the said thioether is added with the make-up oil in the form of a concentrated solution of said thioether in the said make-up oil.

9. As an improved lubricant suitable for and capable of lubricating steam turbines, an improved turbine oil comprising a solution of a minor amount of an alkyl thioether of nitrobenzene dissolved in a major amount of a mineral lubricating oil capable of lubricating said turbines, the said alkyl thioether being present in an amount sufficient to substantially improve the lubricating qualities, the stability and the resistance to emulsification of said oil and having the following formula:



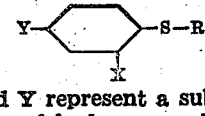
wherein X and Y represent hydrogen or a nitro group, at least one nitro group being present, and n is 0 to 15.

10. The improved turbine oil of claim 9, wherein 0.1 to 1.0 per cent by weight on the oil of an amyl thioether of ortho-nitrobenzene is dissolved in said mineral lubricating oil.

11. The improved turbine oil of claim 9, wherein 0.1 to 1.0 per cent by weight on the oil of an amyl thioether of para-nitrobenzene is dissolved in said mineral lubricating oil.

12. The improved turbine oil of claim 9, wherein 0.1 to 1.0 per cent by weight on the oil of an amyl thioether of 2:4-dinitrobenzene is dissolved in said mineral lubricating oil.

13. As an improved composition for lubricating turbines, the improved lubricant comprising a major proportion of a mineral lubricating oil capable of lubricating turbines and a minor proportion of an alkyl thioether of nitrobenzene having the formula



wherein X and Y represent a substituent of the class consisting of hydrogen and a nitro group, at least one nitro group being present, and R represents an alkyl group.

14. The improved lubricant of claim 13 wherein said turbine oil contains between 0.1 to 1.0 per cent by weight on the oil of said alkyl thioether.

15. The composition of claim 13 wherein said thioether is an alkyl thioether of para nitrobenzene.

16. The composition of claim 13 wherein said thioether is an alkyl thioether of 2:4-dinitrobenzene.

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