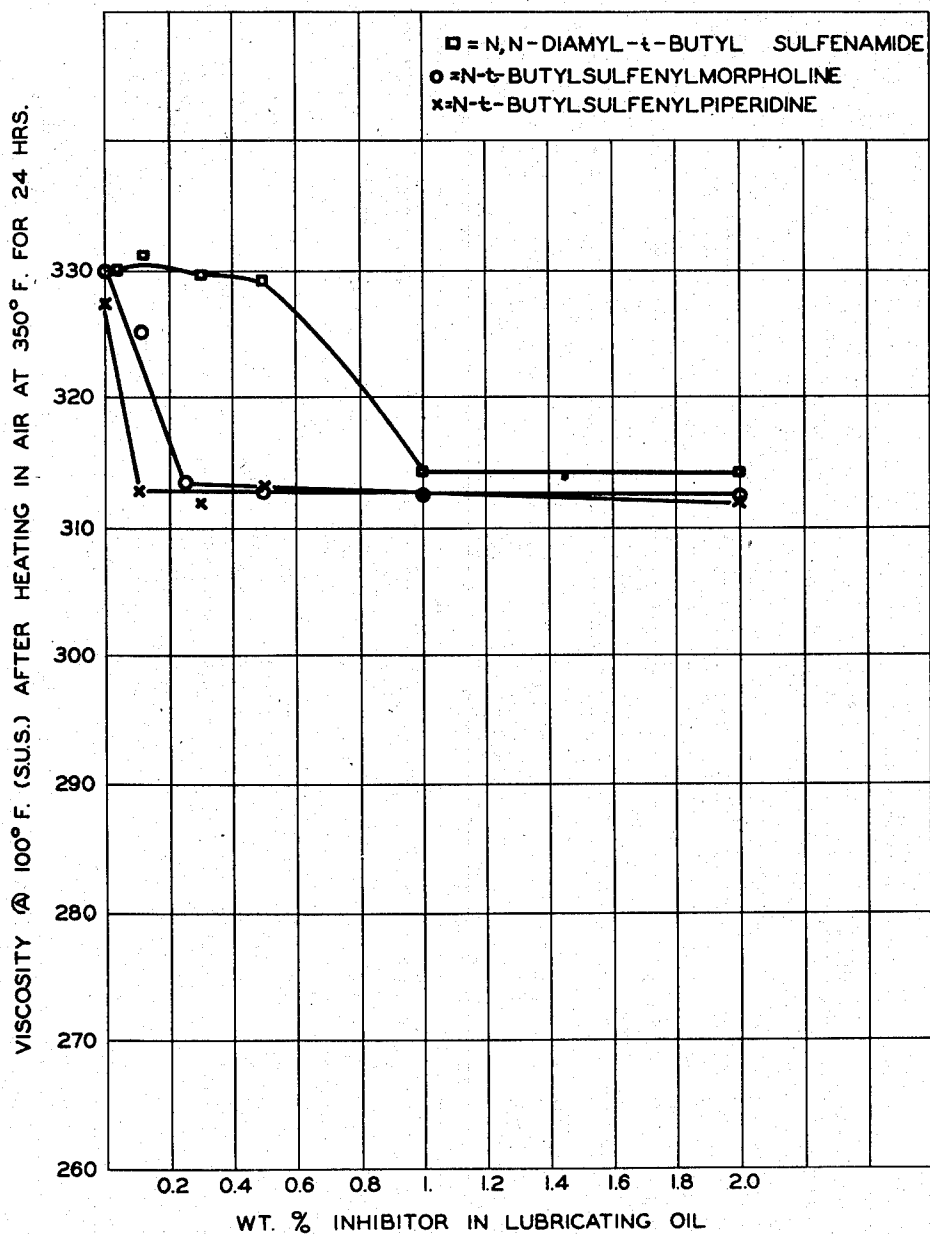


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LUBRICATING OIL ADDITIVES

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LUBRICATING OIL ADDITIVES

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12 Claims. (Cl. 252—47)

1 This invention relates to lubricating oil additives which are particularly valuable in increasing the resistance of said oils toward oxidation. More specifically the invention relates to the use of sulfenamides as antioxidants for lubricating oils. The invention is further concerned with a method for inhibiting the oxidation of lubricating oils through the use of a class of compounds known as alkyl sulfenamides which may be synthesized by the interaction of aliphatic mercaptans with primary and secondary amines.

There are numerous factors involved in the deterioration of a lubricating oil. On account of the complex nature of lubricating oils and the variety of uses to which they are subjected, many problems arise which must be solved if these materials are to be satisfactory. One of the principal factors involved in the deterioration of an oil is the reaction with oxygen. It is obvious that any addition agent which will retard the rate of oxidation of a lubricating oil is highly desirable. Some agents of this type, however, may also influence the direction and character of other accompanying reactions such as polymerization, condensation and the like, with the result that many of the oxidation products may be affected. It is, therefore, important that any additive which is employed to reduce or substantially eliminate oxidation of the oil must not induce other reactions which will produce undesirable effects.

The principal object of the present invention is to provide improved lubricating oil additives and lubricating oil containing the same. Another object is to provide additives which increase the resistance of lubricating oils toward oxidation. Another object is to provide additives which give superior protection against oxidation at a very low cost per unit of finished oil. Another object is to provide additives which are unobjectionable both initially and upon prolonged use of the oil in an engine. Another object is to provide additives which can be made at low cost from relatively cheap and readily available raw materials. Many other objects will more fully hereinafter appear.

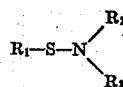
We have now found that alkyl sulfenamides have superior properties as lubricating oil additives and are particularly effective as antioxidants. These compounds when added in relatively small quantities to lubricating oils, exert an unexpected reduction in the tendency of the oils to oxidize and, at the same time, do not produce deleterious effects on other properties.

The alkyl sulfenamides employed in carrying

2 out this invention comprise a group of compounds containing the linkage



and may be represented by the formula



wherein R_1 is an alkyl group, either unsubstituted or substituted, and R_2 and R_3 are hydrogen or substituted or unsubstituted alkyl, aralkyl, aromatic or cycloalkyl groups and wherein R_2 and R_3 may be the same or different and wherein R_2 and R_3 may be part of a cyclic structure, for example, may have a bond directly connecting them or other linkage such that with the nitrogen atom a heterocyclic ring, usually six-membered, is formed. R_1 , R_2 and R_3 may be the same alkyl groups or may consist of any combination of the indicated groups.

Upon heating in the presence of oxygen, most uninhibited oils show marked increases in the values for neutralization number, carbon residue and viscosity. All three of these values may be considered as indications of the stability of a given oil toward oxidation. The effectiveness of an oxidation inhibitor may be measured by its ability to minimize the increases in these values which would normally occur upon heating. In general there is a direct correlation between antioxidant effect and the values for neutralization number, carbon residue and viscosity. In most oils an increase in viscosity occurs on heating in air and an antioxidant prevents this increase. The particular oils tested to obtain the data reported herein displayed this characteristic.

The oxidation stability of both the uninhibited and the inhibited oils was determined by the aluminum block method as follows. The apparatus consists essentially of an electrically heated and thermally insulated block of aluminum which has been bored out to receive beakers of about 400 ml. capacity in which the oil is heated. The temperature of the block is thermostatically controlled to give the desired oil temperature in the beakers. Samples of oil are heated in contact with air at a temperature of 350° F. for twenty-four hours and the changes in physical characteristics resulting from heating are determined.

The official Government designation for the above test method is: Federal Specification VV-1-791b, Method 345.2—Stability of Lubricating

Oils. It is a well-known and accepted method for determining lubricating oil stability.

Our invention is generally applied to mineral lubricating oils, that is oils of petroleum or hydrocarbon origin. However, it is equally applicable to mixtures of mineral lubricating oil and other oils such as oils of animal or vegetable origin. Application of our invention to non-mineral lubricating oils is not excluded. Likewise the invention is not limited to oils used for lubricating internal combustion engines, but may be applied to oils used for any lubricating service where resistance to oxidation is desired.

The synthesis of the compounds employed in accordance with the present invention may be effected by various means. In a copending application of one of us, Serial No. 617,871, filed September 21, 1945, a method for the preparation of alkyl sulfenamides from alkyl mercaptans and amines is described. The synthesis may be accomplished with both primary and secondary aliphatic or aromatic amines as well as with heterocyclic amines which are secondary such as morpholine, thiomorpholine, piperidine, etc. When cyclic amines such as morpholine are employed, the nitrogen atom in the resulting sulfenamide is a part of the morpholine ring.

For a detailed description of one method of making the sulfenamides used in practicing the present invention, attention is directed to said application Serial No. 617,871 which is hereby incorporated herein by reference. However it is to be understood that any other method of preparation of the sulfenamides which may be discovered in the future may be employed and that the present invention is not concerned with the preparation of the compounds but with their utilization as improved oil additives.

In practicing our invention we take lubricating oil of any suitable type and blend therewith in any suitable manner a minor proportion of the alkyl sulfenamide. The addition is usually accomplished by simple admixtures since the additives of the present invention are readily soluble in lubricating oil to an extent much more than sufficient to effect substantially complete inhibition of oxidation of the oil.

The amount of the alkyl sulfenamide employed will almost invariably be less than 8 per cent by weight based on the weight of the oil. Generally it will range between 0.01 and 5 per cent by weight. We have found that there is for every specific alkyl sulfenamide an upper limit beyond which increased amounts of the compound exert no additional antioxidant effect. This is illustrated in the accompanying drawing in which viscosity measured in Saybolt Universal seconds at 100° F. after heating in contact with air at a temperature of 350° F. for twenty-four hours is plotted against per cent by weight of three different alkyl sulfenamides used as antioxidants in accordance with this invention. The alkyl sulfenamides shown are N,N-diamyl-t-butyl sulfenamide, N-t-butylsulfenylmorpholine and N-t-butylsulfenylpiperidine. The oil used was a Mid-Continent neutral oil having a viscosity of approximately 290 Saybolt Universal seconds at 100° F. before heating. It will be observed that increases in amount of the sulfenamides above 1, 0.25 and 0.1 per cent, respectively for the three named sulfenamides, gave no further reduction in viscosity increase. However we often prefer to use amounts somewhat in excess of these critical amounts in order to provide a reserve of antioxidant in the oil during the life of the oil

to take care of possible loss by volatilization and decomposition especially while in the engine. The excess amount may vary from 20 to 300 per cent of the critical amount. An even greater excess may be employed. For example in the case of inhibitors such as the tertiary butyl sulfenamides of morpholine and piperidine of which only a few tenths of one per cent produce maximum inhibition, we may employ amounts ranging as high as 1 per cent or even 2 per cent.

Our invention is based on the discovery that the alkyl sulfenamides have the unique combination of properties which render them outstandingly valuable as lubricating oil antioxidants. They have the requisite degree of stability and anti-oxidant power as well as compatibility with a wide range of lubricating oils. They may be made from cheap and available raw materials such as petroleum mercaptans.

Examples of alkyl groups which may be attached to the sulfur atom are methyl, ethyl, n-propyl, isopropyl, and higher ranging as high as C₂₀ or even higher. Alkyl groups having 4 or more carbon atoms are preferred because they impart lower volatility to the resulting sulfenamide. Tertiary alkyl groups are preferred because of the greater availability and lower cost of tertiary mercaptans and the greater ease of preparation of the tertiary alkyl sulfenamides. Tertiary butyl and tertiary heptyl are examples of tertiary alkyl groups which are eminently satisfactory.

The alkyl group connected to sulfur in the sulfenamide is ordinarily unsubstituted. However it may be substituted. Examples of substituents which may be present on the alkyl group are halogens, namely fluorine, chlorine, bromine and iodine, nitro groups, sulfide groups (—SR), etc.

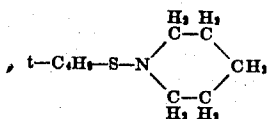
The amines employed in the preparation of the sulfenamides used in the present invention are preferably high-boiling, i. e. have a low vapor pressure, in order to produce an additive of low volatility so that it remains in the oil upon use. Other than this factor a very wide range of amines can be used to give inhibitors of varying anti-oxidant power. For instance, excellent results have been obtained with the sulfenamides prepared from tertiary butyl mercaptan and the following amines: diamylamine, morpholine and piperidine. In the case of these three amines the corresponding tertiary butyl sulfenamides gave essentially complete inhibition of oxidation of a selected Mid-Continent lubricating oil base, using concentrations of 1, 0.25 and 0.1 per cent respectively, as is illustrated in the accompanying drawing. Other amines which are useful include aniline, N-methyl aniline, N-ethyl aniline, N-propyl aniline, phenyl beta naphthylamine, carbazole, diphenylamine, dioctylamine, isobutylamine, dimethylamine, di-n-butylamine, piperazine, thiomorpholine, or any other primary or secondary amine including ammonia.

By using a higher-boiling mercaptan, such as tertiary amyl, tertiary hexyl, or tertiary heptyl, sulfenamides of lower volatility are produced. Similarly by using a higher-boiling amine, a decrease in volatility of the sulfenamide is attained. It is often preferred either to use a mercaptan containing more than 4 carbon atoms per molecule or to use an amine having a boiling point above 190° C., or to use both of these expedients if desired, to reduce evaporation losses during use of the lubricating oil prepared in accordance with the present invention. It will be understood that by using a higher mercaptan it is in

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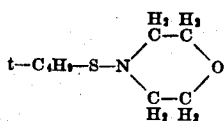
general possible to use a lower-boiling amine and vice versa, in order to obtain sulfenamides of like volatility.

The sulfenamide made from tertiary butyl mercaptan and piperidine was the most effective antioxidant of those tested. This compound has the formula

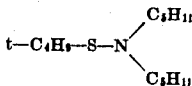


and may be designated N-t-butylsulfenylpiperidine.

Next in effectiveness was the sulfenamide made from tertiary butyl mercaptan and morpholine, denoted N-t-butylsulfenylmorpholine and having the formula



The next most effective antioxidant tested was the sulfenamide prepared from tertiary butyl mercaptan and diamylamine. This compound may be denoted N,N-diamyl-t-butyl sulfenamide and has the structural formula



Two antioxidants which are especially valuable for practicing the present invention, particularly in view of their low volatility, are the tertiary butyl sulfenamides prepared from N-methyl aniline and from phenyl beta-naphthylamine. These are designated N-phenyl-N-methyl-t-butyl sulfenamide and N-phenyl-N-β-naphthyl-t-butyl sulfenamide, respectively.

Most of the alkyl sulfenamides which we have prepared are normally liquid materials or low-melting solids and possess the advantageous property of relatively high solubility in mineral lubricating oil.

Any lubricating oil may be used in practicing the invention. While we have made particular reference herein to a mineral oil of Mid-Continent origin, oils or blends of oils from any source may be used so long as they have lubricating properties. While the resulting product is usually used as a lubricating oil, it is to be understood that it may be put to other uses where resistance to oxidation of the lubricating oil is desired. For example it may be employed in the manufacture of greases. The employment in the lubricating oil of other additives and materials compatible with the additives of the present invention is within the scope of our invention.

EXAMPLE I

A sample of a sulfenamide prepared from morpholine and tertiary butyl mercaptan was tested to determine its value as a lubricating oil antioxidant. The sulfenamide was mixed with a neutral oil and the blend heated by the aluminum block method after which certain properties or the resulting material were studied. In order to determine the effect of the additive, a control test was made on a sample of oil in which none of the sulfenamide had been introduced. Table I shows the effect of heating a neutral oil while Table II gives the results obtained by heating

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that same oil to which 0.25 weight per cent of the sulfenamide had been added.

TABLE I

Effect of heating on Mid-Continent neutral oil

	New Oil	Heated at 350° F.
Evaporation Loss.....		4.2
Naphtha Insoluble, per cent.....		0.09
Neutralization Number.....	0.07	0.47
Carbon Residue, Ramsbottom.....	0.03	0.19
Viscosity at 100° F., SUS.....	292.4	329.9
Viscosity (corrected for Evaporation Loss).....	313.6	
Viscosity Increase, per cent.....		5.20

TABLE II

Effect of heating on Mid-Continent neutral oil containing 0.25 weight per cent N-t-butylsulfenylmorpholine

	New Oil	Heated at 350° F.
Evaporation Loss.....		3.7
Naphtha Insoluble, per cent.....		0.03
Neutralization Number.....	0.06	0.18
Carbon Residue, Ramsbottom.....	0.06	0.06
Viscosity at 100° F., SUS.....	287.3	311.4
Viscosity (corrected for Evaporation Loss).....	308.9	
Viscosity Increase, per cent.....		0.81

EXAMPLE II

Three parallel tests were made on a sample of oil to determine the effect of the presence of an alkyl sulfenamide on the oxidizing properties of the oil. The sulfenamide employed was that synthesized from tertiary butyl mercaptan and morpholine. The procedure of Example I was followed. Table III gives the data obtained on a sample of the neutral oil without the additive and also shows the results of introducing the sulfenamide in amounts of 0.05 and 1.0 weight per cent, respectively.

TABLE III

Effect of N-t-butylsulfenylmorpholine on oxidizing properties of Mid-Continent neutral oil

	Control		Oil+0.05 per cent Sulfenamide		Oil+1.0 per cent Sulfenamide	
	New Oil	Heated at 350° F.	New Oil	Heated at 350° F.	New Oil	Heated at 350° F.
Evaporation Loss.....		4.2		3.8		3.9
Naphtha Insoluble, per cent.....		0.08		0.07		0.04
Neutralization Number.....	0.07	0.47	0.06	0.33	0.06	0.03
Carbon Residue, Ramsbottom.....	0.03	0.16	0.05	0.14	0.07	0.09
Viscosity at 100° F., SUS.....	292.4	326.3	291.2	321.8	276.9	309.1
Viscosity (corrected for Evaporation Loss).....	313.6		311.0		304.3	
Viscosity Increase, per cent.....		4.05		3.47		1.58

EXAMPLE III

A Mid-Continent neutral lubricating oil like that used in the foregoing examples was inhibited against oxidation with varying amounts of the sulfenamide prepared from tertiary butyl mercaptan and piperidine. The results are shown in Table IV. From a comparison of the properties of the blends with those of the blank after heating in air at 350° F. for twenty-four hours it will be seen that the inhibitor displayed substantially its full effectiveness when 0.10 per cent

was added and that increase up to 2.00 per cent brought about substantially no improvement.

2. An improved lubricant comprising a major proportion of a lubricating oil and as an oxida-

TABLE IV
N-t-butylsulfenylpiperidine as inhibitor

	Per Cent of Inhibitor	Evaporation Loss	Vis. @ 100° F. Saybolt Universal Seconds	Carbon Residue, Ramsbottom	Neutralization Number	Naphtha Insoluble Per Cent
Heated at 350° F.-----	0.00	3.86	327.4	0.15	0.46	0.08
Unheated.-----			290.3	0.02	0.00	0.03
Heated at 350° F.-----	0.10	3.29	313.0	0.20	0.14	0.02
Unheated.-----			290.4	0.00	0.11	
Heated at 350° F.-----	0.25	3.30	311.5	0.06	0.28	0.01
Unheated.-----			287.1	0.00	0.10	
Heated at 350° F.-----	0.50	3.44	313.0	0.08	0.33	0.02
Unheated.-----			282.8	0.04	0.16	
Heated at 350° F.-----	1.00	4.30	312.2	0.04	0.24	0.03
Unheated.-----			276.5	0.01	0.17	
Heated at 350° F.-----	2.00	4.82	311.8	0.08	0.27	0.05
Unheated.-----			281.9	0.07	0.22	

EXAMPLE IV

A Mid-Continent neutral lubricating oil like that used in the previous examples was inhibited with varying amounts of the sulfenamide prepared from diamylamine and tertiary butyl mercaptan. The results of tests on the resulting blends are set forth in Table V.

TABLE V
N,N-diamyl-t-butyl sulfenamide as inhibitor

	Per Cent of Inhibitor	Evaporation Loss	Vis. @ 100° F. Saybolt Universal Seconds	Carbon Residue, Ramsbottom	Neutralization Number	Naphtha Insoluble Per Cent
Heated at 350° F.-----	0.00	3.4	324.0	0.14	0.33	0.04
Unheated.-----			290.3	0.02	0.00	
Heated at 350° F.-----	0.10	3.8	326.5	0.20	0.35	0.06
Unheated.-----			289.4	0.04	0.00	
Heated at 350° F.-----	0.25	4.0	332.3	0.22	0.38	0.06
Unheated.-----			283.6	0.03	0.00	
Heated at 350° F.-----	0.50	4.3	329.4	0.24	0.42	0.19
Unheated.-----			283.8	0.04	0.00	
Heated at 350° F.-----	1.00	4.8	313.5	0.07	0.24	0.06
Unheated.-----			281.1	0.05	0.00	
Heated at 350° F.-----	2.00	4.8	313.0	0.07	0.15	0.01
Unheated.-----			270.8	0.05	0.00	

From Table V it will be noted that substantially no further reduction in the viscosity of the oil occurred when an amount greater than 1.00 per cent of the inhibitor was employed.

From the foregoing it will be apparent that use of the alkyl sulfenamides as lubricating oil additives is very advantageous. Among advantages effected by the present invention are that it provides a cheap and effective method of reducing the oxidation tendency of lubricating oil, the additives used are free from objection since they form no undesirable products in the oil and are not corrosive and are not injurious to the engine, and they are readily prepared from cheap and readily available raw materials. A very important advantage is that by means of the present invention the oil is inhibited against oxidation more effectively than with the antioxidants now commercially available and at a fraction of the cost of using present antioxidants. Numerous other advantages of our invention will be apparent to those skilled in the art.

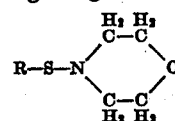
We claim:

1. An improved lubricant comprising a major proportion of a lubricating oil and as an oxidation inhibitor therefor an unsubstituted alkyl sulfenamide, said sulfenamide being present in an amount ranging from 0.01 to 5 per cent by weight of said oil.

tion inhibitor therefor a tertiary alkyl sulfenamide, said sulfenamide being present in an amount ranging from 0.01 to 5 per cent by weight of said oil.

3. An improved lubricant comprising a major proportion of a lubricating oil and as an oxida-

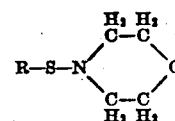
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wherein R is an alkyl group, said sulfenamide being present in an amount ranging from 0.01 to 5 per cent by weight of said oil.

4. An improved lubricant comprising a major proportion of a lubricating oil and as an oxidation inhibitor therefor a tertiary alkyl sulfenamide having the general formula

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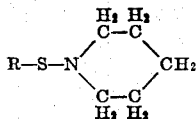
wherein R is a tertiary alkyl group, said sulfenamide being present in an amount ranging from 0.01 to 5 per cent by weight of said oil.

5. An improved lubricant comprising a major proportion of a lubricating oil and as an oxidation inhibitor therefor N-t-butylsulfenylmorpholine, said sulfenamide being present in an amount ranging from 0.01 to 5 per cent by weight of said oil.

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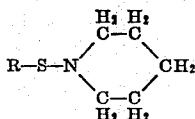
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6. An improved lubricant comprising a major proportion of a lubricating oil and as an oxidation inhibitor therefor an unsubstituted alkyl sulfenamide having the general formula



wherein R is an alkyl group, said sulfenamide being present in an amount ranging from 0.01 to 5 per cent by weight of said oil.

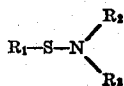
7. An improved lubricant comprising a major proportion of a lubricating oil and as an oxidation inhibitor therefor a tertiary alkyl sulfenamide having the general formula



wherein R is a tertiary alkyl group, said sulfenamide being present in an amount ranging from 0.01 to 5 per cent by weight of said oil.

8. An improved lubricant comprising a major proportion of a lubricating oil and as an oxidation inhibitor therefor N-t-butylsulfenylpiperidine, said sulfenamide being present in an amount ranging from 0.01 to 5 per cent by weight of said oil.

9. An improved lubricant comprising a major proportion of a lubricating oil and as an oxidation inhibitor therefor an unsubstituted alkyl sulfenamide having the general formula



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wherein R₁ is selected from the group consisting of unsubstituted alkyl groups and R₂ and R₃ are selected from the group consisting of hydrogen, substituted and unsubstituted alkyl, aralkyl, aromatic or cycloalkyl groups and wherein R₂ and R₃ may be the same or different and wherein R₂ and R₃ may be part of a cyclic structure, said sulfenamide being present in an amount ranging from 0.01 to 5 per cent by weight of said oil.

10. An improved lubricant comprising a major proportion of a lubricating oil and as an oxidation inhibitor therefor N-phenyl-N-methyl-t-butyl sulfenamide, said sulfenamide being present in an amount ranging from 0.01 to 5 per cent by weight of said oil.

11. A lubricant in accordance with claim 5 wherein said sulfenamide is employed in an amount substantially equal to 0.25 weight per cent based on the weight of said oil.

12. A lubricant in accordance with claim 8 wherein said sulfenamide is employed in an amount substantially equal to 0.1 weight per cent based on the weight of said oil.

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

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