This invention relates to superior mixed inhibitors which are especially adapted to reduce deterioration of lubricating engine oils, the presence of air at high temperatures, such as those employed for lubricating internal combustion engines. More specifically, it deals with the production of lubricating oil inhibitors comprising a mixture of an organic high temperature oxidation inhibition inhibitor and a metallo organic compound of a metal of the class of bismuth, antimony and tin, as well as compositions containing such mixtures.

Recent systematic research has disclosed that at least two classes of inhibitors are effective in retarding or suppressing the deterioration of mineral lubricating oils in presence of air, moisture, metals, and the like. One type, exemplified by alpha naphthol, is active at ordinary temperatures up to about 200-300° F. Above this temperature it loses its activity and the oil behaves in the same manner as an uninhibited oil. Hence, although an inhibitor of this type may be satisfactory for turbine lubrication in which the temperature rarely exceeds 250° F., it is valueless for lubricating automotive internal combustion engines in which the oil is subjected to a temperature of 450-500° F. or higher in the proximity of the combustion zone.

The other type of inhibitors is the class of compounds which are very effective at elevated temperatures, especially in the neighborhood of 400-500° F., although the members of this group may or may not have some activity at lower temperatures. These materials are particularly useful in suppressing or retarding the deterioration of lubricating oils for internal combustion engines, and especially for aviation engines which operate at excessively high temperatures.

Of the numerous tests employed for judging the ability of an oil to resist deterioration at high temperature in an engine, the cone test has been found to give data which most closely approach results obtained in the C. F. R. (Cooperative Fuel Research) test engine. In the cone test a determined volume of a given oil is allowed to flow slowly over an open heated metal (generally steel) cone having a circumferential groove milled out in screw fashion on the periphery so as to allow a time of contact of about one minute between the heated steel surface and the oil. A total volume of 60 cc. of oil is allowed to flow over this cone during a period of 2 hours to obtain this rate. The temperature of the cone is generally kept at 250° C. (482° F.), this temperature having been found to give most concordant data with engine results. The cone is weighed before the test. After all of the oil is run over the metal surface, the cone is washed with naphtha to remove adhering oil and the total deposit is obtained by the difference in weight. This value is generally reported in grams, the higher value showing a poorer oil. The same oil may be passed over the cone two, three or more times to give a better indication as to its resistance after each exposure. This test will be referred to further in the discussion.

The stabilizing process employed in this invention, therefore, involves the use of a mixture of two organic compounds, namely: (1) A soluble aromatic high temperature oxidation inhibitor and (2) soluble metallo organic compound of bismuth, tin and/or antimony. The former is preferably used in excess of the latter. These may be added to the lubricating oil in small proportions neighboring the values of 0.1 to 0.3 or 0.2 or even 0.5 or 1% of the individual compounds.

The first mentioned materials, i.e., the high temperature inhibitors consist broadly of high boiling organic compounds soluble in mineral oils and having the structure:

\[
R - X - R'
\]

where \( R \) and \( R' \) may be aliphatic, cyclic (e.g., aromatic, heterocyclic, naphthenic, etc.), or mixed groups. Either \( R \) or \( R' \) may even be or contain an inorganic group. \( X \) is a negative element of Group VI of the periodic table, such as sulfur, oxygen, selenium and tellurium, and covers structural groups such as

\[
\begin{align*}
&-\text{S-}, -\text{S-S-}, -\text{S-S-S-}, -\text{S-S-S-S-}, -\text{S-}, -\text{S-} \\
&-\text{S-}, -\text{S-}, -\text{S-} \\
&-\text{O-}, -\text{O-} \\
&-\text{O-}, -\text{O-}
\end{align*}
\]

and the like; \( n \) is an integer of one or more, usually 1, 2, 3 or 4.

Examples of such compounds are dialyl trisulfide \((\text{C}_4\text{H}_8\text{O})_2 \cdot \text{S-S-S-C}_8\text{H}_8\text{O})\), amyl alpha xanthogenoacetic ethyl ester

\[
\begin{align*}
\text{O}_8\text{C}-\text{CH}_3\text{R}_{\text{(C}_8\text{H}_8\text{O})_2}\text{O}_8\text{C}-\text{CH}_3\text{R}_{\text{(C}_8\text{H}_8\text{O})_2}
\end{align*}
\]

or compounds of the type of

\[
\begin{align*}
\text{O}_8\text{C}-\text{C}_8\text{H}_8\text{S}_2\text{C}_8\text{H}_8\text{O}_8\text{C}-\text{CH}_3\text{R}_{\text{(C}_8\text{H}_8\text{O})_2}
\end{align*}
\]

and similar materials preferably those boiling above 200° C. at atmospheric pressure.
In my copending application Ser. No. 704,131, filed on December 27, 1933, I have disclosed certain soluble aromatic inhibitors which are very effective in retarding or suppressing deterioration of mineral lubricating oils at high temperatures. These compounds comprise an aromatic group containing an oxidation inhibiting group (OH, NH, or SH) and another organic group (either alkyl, aryl or aralkyl) attached to the aromatic nucleus by at least one member of the negative elements of Group VI of the periodic table, as for example sulfur, oxygen, selenium or tellurium atom. An example of such a material is the following:

\[
\begin{array}{c}
\text{S} \\
\text{R}
\end{array}
\]

Where R is a substituent, preferably one which will increase solubility in lubricating oils (e.g., halogen, alkyl and similar groups), R' is an alkyl, aryl or aralkyl group, while n is an integer of one or more, usually 1, 2, 3, or 4. The sulfur or oxygen may be in the following structural group:

\[
\begin{array}{c}
\text{S} \\
\text{S}
\end{array}
\]

and the like. Specific examples of such compounds are tri-tertiary butyl phenol thio ether, tertiary amyl phenol dimethox, 4 butoxy-2-amino naphthalene, their polymers, and the like.

Such inhibitors, as shown by cone data, are very effective in initially reducing the deterioration rate of mineral lubricating oils. However, this effect is lost to a certain degree over an extended period of time, as shown by the fact that the cone residue is increased when the oxidized oil is again repeatedly passed over the cone.

According to the present invention, the increase in rate of deterioration of the oil thus inhibited can be reduced to a considerable extent by the addition thereto of the second mentioned material, i.e., a soluble organo metallic compound of bismuth, tin, or antimony. Examples of such compounds are triphenyl bismuth, triphenyl tin iodide, dimethyl triphenyl bismuth, tetra propyl tin, tetra isobutyl tin, triphenyl stibine, and the like. Apparently this class or organo metallic compounds, though often not as effective by itself in reducing the cone deposit as the high temperature inhibitors, exerts some stabilizing effect upon the latter to produce a much more resistant blend.

The effect will be more clearly understood from an examination of the following test results:

**Example 1**

An SAE 50 grade lubricating oil (oil A) of about 100 viscosity index prepared by hydrogenation of a Colombian crude oil fraction was subjected to the cone test with and without the following blending agents: 0.4% tertiary butyl phenol sulfide (blend B), 0.2% triphenyl bismuth (blend C), 0.4% tertiary butyl phenol sulfide and 0.2% triphenyl bismuth (blend D), 0.2% triphenyl tin iodide (blend E), and 0.4% tertiary butyl phenol sulfide and 0.2% triphenyl tin iodide (blend F).

The oils were passed three times over the cone according to the test procedure described previously, and the residue was weighed after each pass. The results are as follows:

<table>
<thead>
<tr>
<th>Blend</th>
<th>First pass</th>
<th>Second pass</th>
<th>Third pass</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.20</td>
<td>0.23</td>
<td>0.27</td>
</tr>
<tr>
<td>B</td>
<td>0.20</td>
<td>0.22</td>
<td>0.23</td>
</tr>
<tr>
<td>C</td>
<td>0.20</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>D</td>
<td>0.15</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>E</td>
<td>0.10</td>
<td>0.17</td>
<td>0.25</td>
</tr>
<tr>
<td>F</td>
<td>0.08</td>
<td>0.17</td>
<td>0.25</td>
</tr>
</tbody>
</table>

As shown by the above data, blends D and F, containing the mixed inhibitors, give the best results after the third pass when compared with the non-inhibited oil or the blends having only one inhibitor.

**Example 2**

A phenol treated lubricating oil of SAE 50 grade (oil G) having a viscosity index of about 90 subjected to a light clay treat was tested in a cone in the same manner as in Example 1 with and without the following blending agents: 0.4% di-tertiary butyl phenol thio ether (blend H), 0.2% tri-phenyl bismuth (blend J), and 0.4% di-tertiary butyl phenol thio ether with 0.2% triphenyl bismuth (blend K).

The data are as follows:

<table>
<thead>
<tr>
<th>Blend</th>
<th>1st pass</th>
<th>2nd pass</th>
<th>3rd pass</th>
<th>4th pass</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>0.20</td>
<td>0.23</td>
<td>0.23</td>
<td>0.25</td>
</tr>
<tr>
<td>H</td>
<td>0.20</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>J</td>
<td>0.20</td>
<td>0.23</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>K</td>
<td>0.20</td>
<td>0.23</td>
<td>0.22</td>
<td>0.22</td>
</tr>
</tbody>
</table>

As seen from the above data, the mixed inhibitor blend (blend K) is much more superior after the fourth pass to any of the blends containing the individual compounds.

The lubricating oils used for the purposes of this invention are mineral oils such as Pennsyl- vania, Coastal, Mid-Continent, Venezuelan, Colombian, etc., suitable for use in internal combustion engines, say as low as 30–45 viscosity at 210° F. to viscosities neighboring those of bright stocks, as 70 to 150 seconds at 210° F. Such oils may be of SAE grades 10, 20, 30, 40, 50 or higher. Synthetic hydrocarbon oils are not excluded. These lubricating oils may be in the crude form or partially or highly refined by distillation, treatment with selective solvents, chemical reagents, hydrogenation, volatilization, absorptive agents, dewaxing processes, and the like.

Especially preferred are those mineral oilshaving high viscosity indices, i.e., viscosity indices in the neighborhood of 70, 80, or 90 to 100 and sometimes up to 120. Such oils tend to deteriorate more rapidly in high temperature internal combustion engines than other mineral oils, and hence are much more improved in value by this invention. Furthermore, a flat viscosity temperature curve inherent in such oils is generally desirable for engine operation.

The above inhibited blends may be used in conjunction with other lubricating oil blending agents, such as pour inhibitors, thickeners, V. I. improvers, dyes, sludge dispersing agents, extreme pressure lubricants, metallic soaps, co- loidal solids, volatilized mineral or fatty oils or waxes, and the like.

Although there have been shown and described specific embodiments of this invention, many modifications thereof are possible. The invention, therefore, is not to be restricted except insofar as is necessitated by the prior art and by the spirit of the appended claims.
I claim:

1. Composition of matter comprising a viscous mineral lubricating oil containing a small proportion of a soluble organic oxidation inhibitor having a boiling point above 200° C. at atmospheric pressure and possessing the structure

\[ R - X_n - R' \]

where \( R \) and \( R' \) are organic groups, \( X \) is a negative element of Group VI of the periodic system, and \( n \) is an integer from 1 to 4, and a small proportion of a soluble metallo-organic compound of a metal of the class consisting of bismuth, antimony and tin, said metallo-organic compound containing a carbon-metal linkage.

2. Composition of matter according to claim 1 in which the viscous mineral oil has a viscosity index above 70.

3. Composition of matter according to claim 1 in which the proportion of organic oxidation inhibitor is greater than the proportion of metallo-organic compound.

4. Composition of matter according to claim 1 in which the proportion of organic oxidation inhibitor is from 0.01% to 1%.

5. Composition of matter according to claim 1 in which the proportion of metallo-organic compound is from 0.01% to 1%.

6. Composition of matter comprising a mineral lubricating oil containing 0.4% of an alkylated phenol thio-ether, and 0.2% of triphenyl bismuth.

7. Composition of matter according to claim 1 in which the oxidation inhibitor possesses the structure

\[ R - X_n - R' \]

where \( R \) is an aromatic group having an oxidation inhibiting group, \( R' \) is an organic group, \( X \) is an element selected from the group consisting of oxygen and sulphur, and \( n \) is an integer from 1 to 4.

8. Composition of matter according to claim 1 in which the proportion of organic oxidation inhibitor is from 0.01% to 1%, and in which the proportion of metallo-organic compound is from 0.01% to 1%.

9. Composition of matter comprising a mineral lubricating oil containing 0.4% of an alkylated phenol thio-ether, and 0.2% of a metallo-organic compound of a metal of the class consisting of bismuth, antimony and tin, said metallo-organic compound containing a carbon-metal linkage.

10. Composition of matter comprising a mineral lubricating oil containing 0.4% of an alkylated phenol thio-ether, and 0.2% of triphenyl tin iodide.

Raphael Rosen.