This invention relates to certain of the para alkyl phenyl trithiones having utility in lubricating oil compositions and the invention is more particularly directed to a new and outstandingly superior compound, namely 2-para-butyl phenyl trithione.

I have discovered, as disclosed in my application SN 433,788 filed June 1, 1954, that aryI trithiones can be readily prepared from certain ring substituted aliphatic hydrocarbons having a structure analogous to cumene or a substituted cumene by reaction with sulfur. A temperature of about 140°-230° C. is employed and the reaction is conducted in the presence of a small amount of a stable, soluble, strong organic base, such as an alkali guanidine, as a catalyst. I have further discovered, as disclosed in my application SN 433,789 filed June 1, 1954, that the aryI trithiones are effective as bearing corrosion inhibitors when incorporated in lubricating oils. I have found, however, that of the aryI trithiones, the 2-para-butyl phenyl trithione has special advantages for use in lubricating oil blends. The 2-para-butyl phenyl trithione has a very high degree of effectiveness in inhibiting bearing corrosion, combined with a satisfactory level of solubility in mineral oils of the lubricating oil range, i.e., about 2% by weight. By contrast, 2-phenyl trithione itself, although it imparts protection against bearing corrosion, is soluble in lubricating oil to the extent of less than 0.1% by weight, and requires the use of a solubilizing detergent for its incorporation to a practical concentration level.

The 2-para-alkyl phenyl trithiones are characterized by the following formula:

\[
\begin{align*}
\text{R} & \quad \begin{array}{c}
\text{H} \\
\text{S} \\
\text{S}
\end{array} \\
\text{C} & \quad \text{N}
\end{align*}
\]

where \( \text{R} \) is an alkyl group such as methyl, ethyl, propyl and the like. The ring junction is believed to be as indicated although that is probably not significant with respect to the usefulness of the new products. In general, the trithiones are crystalline solids which are usually of golden to deep red in color. The trithiones have relatively high melting point, 120° C. and higher. They are remarkably stable; for example, they are not appreciably decomposed by heating for 12 hours at 180° C. Hence they are well adapted for use in engine lubricating oil blends. As noted above, the trithiones have satisfactory solubility in mineral oils which improves from about 0.75% by weight for 2-p-tolyI trithione to about 2% by weight for 2-p-butyl phenyl trithione. If desired in use, relative solubility can be further increased by the use of solubilizing detergents such as an alkali metal or alkaline earth metal salt of a phosphorous pentasulfide-butylene polymer reaction product, for example.

The products also show fungicidal activity. Of these 2-para-alkyl phenyl trithiones the 2-para-butyl phenyl trithione is new and outstandingly superior as shown by the data hereinafter set forth and set forth in my copending application 433,789 hereinafore noted.

The p-alkyl phenyl trithiones may be prepared by refluxing the starting alkyl cumene, e.g., p-cymene, with sulfur in the presence of a small amount of a soluble organic base such as di-orthotolylguanidine as a catalyst.

A temperature in the range of 140°-230° C. is effective but a temperature of about 180°-190° C. is usually advantageous. An excess of the starting alkyl cumene is advantageous for ease of operation, separation of product and purity of product. About 5 to 50% by weight of sulfur is suitable. The catalyst may be employed in the concentration of about 0.01 to 2 weight percent, and about 0.2% by weight is practical.

The preparation and properties of certain of the 2-p-alkyl phenyl trithiones will be illustrated by way of specific example.

The trithiones listed in the table below were prepared by heating a mixture of 1 mol of the cumene hydrocarbon, 1.5 mol sulfur and 0.165 mol percent di-o-tolylguanidine at reflux (cumene, p-cymene) or at 185°-200° C. until no free sulfur remained. Free sulfur can be detected by heating a 1% test sample in an inert hydrocarbon (high-boiling ligroin or refined oil) with a polished copper strip at 100° C. for 1 hour. Free sulfur will blacken the strip. After chilling the reaction mixture at 0°-10° for several hours, the crystals were filtered and recrystallized from benzene alone or diluted with hexane. The analyses of the materials prepared are given in the table. The methiodide derivatives were prepared in nearly quantitative yields from the trithiones and excess methyl iodide in n-butyl acetate at reflux for 2 hours.

In a typical preparation, a mixture of 1106 g. (8.25 moles) p-cymene, 400 g. (12.5 moles) sulfur and 8.2 g. di-tolylguanidine was refluxed at 185° C. for 21 hours. Hydrogen sulfide evolved steadily. The mixture was then kept at 5° C. for 2 hours to allow the trithione to crystallize. The red crystals were collected on a filter, washed with 400 ml. of 1:3 benzene:hexane, and sucked dry. There was obtained 355 g. (77%) 2-p-tolyI-trithione, M. P. 119-120° C. After one crystallization from benzene it melted at 122.5-123° C.

Vacuum distillation of the filtrate from the trithione crystals gave 575 g. p-cymene (Bp 54-59° C.).

**TABLE**

**Examination of 2-aryI trithiones**

<table>
<thead>
<tr>
<th>Trithione</th>
<th>M. P., °C.</th>
<th>Analysis</th>
<th>Methiodide Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Carbon</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>2-p-tolyI</td>
<td>122.5-5</td>
<td>224-226</td>
<td>53.60</td>
</tr>
<tr>
<td>2-p-ethylphenyl</td>
<td>123-129</td>
<td>228-229</td>
<td>53.43</td>
</tr>
<tr>
<td>2-p-butyIphenyl</td>
<td>146-151</td>
<td>269-272</td>
<td>56.81</td>
</tr>
<tr>
<td>2-p-amylphenyl</td>
<td>112-114</td>
<td>280-283</td>
<td>56.00</td>
</tr>
<tr>
<td>2-p-tert-amylphenyl</td>
<td>120-122.5</td>
<td>283-285</td>
<td>56.05</td>
</tr>
</tbody>
</table>

**Notes:**

- Table includes analysis results for various trithiones with specific M. P. values and analysis data (carbon, hydrogen, sulfur, and methiodide analysis).
- The table provides a comparison of the calculated and found values for each element, indicating the accuracy of the analysis.
- The methiodide analysis includes the calculated and found values for iodine content.

**References:**

- Ellis K. Fields, Chicago, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana
- Application June 1, 1954, Serial No. 433,789
- Claim (Cl. 260-327)

**Patented Dec. 10, 1957**
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I claim:
2-para-t-butyl phenyl trithione.

References Cited in the file of this patent

UNITED STATES PATENTS
2,688,620 Gaudin Sept. 7, 1954

2,816,116

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OTHER REFERENCES