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PREPARATION OF BARIUM SALTS OF ALKYL PHENOL SULPHIDES

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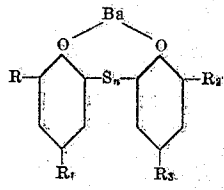
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7 Claims. (Cl. 260—609)

This invention relates to a new and improved method of preparing barium salts of alkyl phenol sulphides.

In U. S. Patent No. 2,270,183, issued January 13, 1942, to E. W. Cook and W. D. Thomas, Jr., the said E. W. Cook being one of the inventors of the present invention, it is disclosed that the 2,4-dialkyl phenol sulphides and metal salts thereof, particularly the barium salts, are highly effective when added to hydrocarbon lubricating oils in the prevention of sludge formation in the oil, varnish formation on the pistons and other metallic parts of the engine and in preventing corrosion of alloy bearings. Other alkyl phenol sulphides, including the polysulphides as well as the monoalkyl substituted phenol sulphides, particularly the barium salts thereof, are also effective when added to lubricating oils in the prevention of sludge formation and as corrosion inhibitors.

The various barium alkyl phenolate sulphides of value as lubricating oil additives as sludge dispersants and corrosion inhibitors whose preparation is contemplated by the present invention may be represented by the following general formula



in which R and R_2 are members of the group consisting of hydrogen and alkyl radicals, R_1 and R_3 are alkyl radicals and n is a small whole number.

So far as we are aware the barium salts of the alkyl phenol sulphides have been prepared only by the neutralization of the alkyl phenol sulphides with barium oxide or barium hydroxide. Although the preparation of these barium salts is conveniently carried out with either barium oxide or barium hydroxide, the use of the oxide or hydroxide presents a number of disadvantages. Chemically the reaction involves the formation of one mole of water, which requires removal from the product before it can be added to a lubricating oil as a corrosion inhibitor and sludge dispersant. Economically, barium oxide and hydroxide are relatively expensive chemicals and, at the present time, not available in sufficient quantities to prepare the barium salts of alkyl phenol sulphides in commercial quantities.

The high cost of barium oxide and barium hydroxide is based in part upon the difficulty of preparing the compounds from available raw materials. Commercial methods of preparation involve igniting native sulphate or heavy spar with coal, or charcoal, whereby an impure barium sulphide is obtained. This is converted into barium carbonate by heating in a current of moist carbon dioxide. Super-heated steam is then passed over the heated carbonate, resulting in the formation of $Ba(OH)_2$ and CO_2. BaO may be prepared by heating witherite ($BaCO_3$) in admixture with coal to 1100 to 1200° C. in a reducing atmosphere. Unfortunately, however, witherite is not available at a reasonable cost, and it is necessary to start with barytes ($BaSO_4$) and prepare the barium hydroxide as outlined above.

We have now discovered that the barium salts of alkyl phenol sulphides may be prepared in good yields and of satisfactory purity suitable for use in the preparation of heavy duty, anti-sludge forming, anti-corrosion lubricating oils by the use of barium sulphide as will hereinafter be described. The fact that barium sulphide can be employed for neutralization purposes in the preparation of these alkyl phenol sulphides is very surprising since hydrogen sulphide is a stronger acid than phenol and one would ordinarily predict that a phenol could not be neutralized with barium sulphide. This surprising effect is further accentuated by the fact that the alkyl substituents on the phenol radicals would ordinarily tend to further decrease the reactivity of the phenol.

The reaction is carried out by simply mixing finely ground BaS with a selected alkyl phenol sulphide dissolved in a suitable solvent such as alcohol, mineral spirits or the like and heating the mixture under a reflux condenser with agitation in the presence of a small amount of water until the desired stage of reaction has been attained. This may be determined by the evolution of hydrogen sulphide which is formed as a result of the reaction. When hydrogen sulphide ceases to come off from the reaction mixture it may be assumed that the reaction is complete. Since hydrogen sulphide is formed and is an obnoxious gas, provision for its disposal should be made. The water remaining in the reaction product may then be removed by means of a water trap fitted to the reflux condenser and the product filtered to remove excess barium sul-

phide and contaminating salts which may have been added therewith. The solvents may then be removed and the product blended with lubricating oils for sale and use as a lubricating oil additive.

Although we may use chemically pure barium sulphide, it is not necessary to do so. For economic reasons, we prefer to use a crude barium sulphide product, known in the trade as black ash. This crude product is prepared by reducing barium sulphate with coal, the following method having been found suitable: A sample of the mineral barytes was crushed in a jaw crusher and stage-crushed on rolls to pass a 30-mesh screen. A sample of low ash anthracite coal was also crushed and passed through a 30-mesh screen. 100 parts of barytes and 19 parts of coal were then mixed and passed through a rotary kiln heated to a temperature of 1100° C. The crude product was found to contain 78% water-soluble BaS or acid-soluble material equivalent to about 90% BaS. The insoluble materials other than BaS are for the most part inert and are removed from the barium salt of the alkyl phenol sulphide by filtration at the completion of the neutralization reaction.

Of the various alkyl phenol sulphides we prefer to employ the dialkyl phenol monosulphides in our process since the barium salts of these compounds have greater oil-solubility and better sludge-dispersing and anti-corrosion inhibiting characteristics than other alkyl phenol sulphides. The dialkyl phenol polysulphides, in which n in the formula set forth hereinbefore is the small whole number 2 or 3, are easily oil-soluble but tend to be unstable at the sulphur linkage. The monoalkyl phenol sulphides have a decreased oil solubility since they contain but one alkyl group attached to each phenol radical. However, if the alkyl radical is of sufficient length, i. e. R_1 and R_3 are alkyl radicals of about 8 carbon atoms or more the compounds are readily oil-soluble and may be employed without difficulty in the preparation of improved lubricating oils.

Among the various alkyl phenol sulphides which may be reacted with barium monosulphide in accordance with our invention may be mentioned 2,4-diamyl phenol monosulphide, 2,4-diamyl phenol disulphide, 2-methyl-4-tert. butyl phenol monosulphide, p-tert. butyl orthocresol monosulphide, 2-dodecyl-4-tert. amyl phenol monosulphide, 4-lauryl phenol monosulphide, 4-lauryl phenol disulphide, 4-n-octyl phenol monosulphide, 2,4-dioctyl phenol monosulphide, 2,4-dibutyl phenol monosulphide and others of similar character.

The preparation of a typical barium salt of an alkyl phenol sulphide will now be illustrated by the following example which is given, however, by way of illustration, since our invention in its broader aspects is to be limited only by the scope of the appended claims.

50 parts by weight of 2,4-diamyl phenol monosulphide was dissolved in approximately 40 parts by weight of aromatic mineral spirits and was heated at refluxing temperatures under a reflux condenser with stirring with 10 parts by weight of water and 21 parts by weight of finely ground black ash (barium sulphide 80%) for 2 hours. At this point it was found that 56% of the 2,4-diamyl phenol monosulphide was neutralized to the corresponding barium salt. As H_2S was still being evolved heating of the reaction mixture was continued. After about 5 hours heating the water in the reaction mixture was removed by means of a water trap fitted to the reflux condenser, 40 parts by weight of mineral spirits was then added and the product filtered to remove unreacted barium sulphide and insoluble impurities contained in the black ash. The solvent was then removed by evaporation with stirring under a vacuum. When about ⅔ of the solvent was removed a 10–W grade lubricating oil was blended with the reaction product to bring the final mixture to a content of 50% of the barium salt of 2,4-diamyl phenol monosulphide. The remainder of the solvent was then removed by evaporation and the product was ready for use.

What we claim is:

1. A method of preparing barium salts of alkyl phenol sulphides which comprises mixing and heating an alkyl phenol sulphide with barium sulphide in amounts sufficient to substantially neutralize said alkyl phenol sulphide.

2. A method of preparing barium salts of dialkyl phenol sulphides which comprises mixing a dialkyl phenol sulphide with barium sulphide in amounts sufficient to substantially neutralize said dialkyl phenol sulphide and heating the reaction mixture until the evolution of hydrogen sulphide has substantially ceased.

3. A method of preparing barium salts of 2,4-diamyl phenol monosulphide which comprises mixing 2,4-diamyl phenol monosulphide with barium sulphide in amounts sufficient to substantially neutralize said 2,4-diamyl phenol monosulphide and heating the reaction mixture until the evolution of hydrogen sulphide has substantially ceased.

4. A method of preparing barium salts of 2,4-dibutyl phenol monosulphide which comprises mixing 2,4-dibutyl phenol monosulphide with barium sulphide in amounts sufficient to substantially neutralize said 2,4-dibutyl phenol monosulphide and heating the reaction mixture until the evolution of hydrogen sulphide has substantially ceased.

5. A method of preparing barium salts of 4-alkyl phenol monosulphide which comprises mixing 4-alkyl phenol monosulphide with barium sulphide in amounts sufficient to substantially neutralize said 4-alkyl phenol monosulphide and heating the reaction mixture until the evolution of hydrogen sulphide has substantially ceased.

6. A method of preparing barium salts of 4-octyl phenol monosulphide which comprises mixing 4-octyl phenol monosulphide with barium sulphide in amounts sufficient to substantially neutralize said 4-octyl phenol monosulphide and heating the reaction mixture until the evolution of hydrogen sulphide has substantially ceased.

7. A method of preparing barium salts of alkyl phenol sulphides which comprises mixing barium mono-sulphide, water and an alkyl phenol sulphide dissolved in a solvent and heating the reaction mixture at the refluxing temperature of the mixture until evolution of H_2S has substantially ceased, separating insoluble material from the reaction mixture, and evaporating the solvent while concurrently adding thereto hydrocarbon lubricating oil.

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