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2,902,511

OIL ADDITIVE AND PROCESS FOR ITS PREPARATION

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7 Claims. (Cl. 260-504)

This invention relates to a method of making an oil additive and to the oil additive so produced.

Various oil additives have been proposed in the past containing alkaline reserve for neutralizing acids that may be present or that may be formed in the oil, particularly in lubricating oil, under the conditions of service. These oil additives are often made from petroleum sulfonates or mahogany sulfonates. One common type of oil additive is an alkaline earth metal petroleum sulfonate that is first formed from the alkali metal sulfonate and then loaded with alkaline reserve.

I have discovered that alkaline earth metal alkylaryl sulfonates, and particularly alkaline earth metal petroleum or mahogany sulfonates, may be prepared and loaded with extremely high alkaline reserve in essentially a single operation. In this method, an alkali metal petroleum sulfonate, otherwise known as a mahogany sulfonate, is heated with an aqueous solution of an alkaline earth metal halide and an aqueous solution of either an alkali metal carbonate or an alkali metal borate to simultaneously form the alkaline earth metal petroleum sulfonate and load it with increased alkalinity. In this method, the alkaline earth metal halide functions to provide the alkaline earth content of the sulfonate and the alkali metal salt, specifically the carbonate or the borate, is used to provide the alkaline reserve-bearing compound. The reaction between these reagents and the alkali metal sulfonate forms a connecting bridge of alkaline reserve radicals between the alkaline earth sulfonate groups that are formed.

In preparing the oil additive, the alkali metal sulfonate, such as the ordinary sodium mahogany sulfonate of commerce, is mixed preferably simultaneously with two separate portions of an aqueous solution of an alkaline earth metal halide, such as the halides of calcium, manganese, strontium, or barium, and an aqueous solution of either an alkali metal carbonate or an alkali metal borate. These two solutions are preferably added while the alkali metal petroleum sulfonate is maintained at an elevated temperature, preferably between about 180-210° F. The resulting mixture is then heated at a temperature above about 200° F. until substantially all of the water has been driven off. When this procedure is followed, the resulting product or complex has up to three times or more as much alkaline earth metal content as that of a neutral alkaline earth metal mahogany sulfonate. This value is expressed as having a loading value of 3-1, being three times that of the neutral sulfonate.

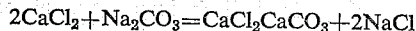
A suitable alkaline earth metal halide is calcium chloride because of its availability, inexpensiveness, and generally satisfactory results. The aqueous solution of the alkaline earth metal halide and the aqueous solution of

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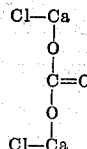
either alkali metal carbonate or borate are added preferably simultaneously in separate batches to the alkali metal petroleum sulfonate, preferably diluted with a neutral oil while agitating the sulfonate and while the sulfonate and oil mixture is at a temperature between about 180-210° F. After the addition has been completed, the heat is continued at a temperature that is above about 200° F. until substantially all of the water has been driven off. The heating temperature is preferably above about 240° F. up to a maximum of about 350-400° F.

The amounts of alkaline earth metal halide and alkali metal carbonate or borate used to react with the sodium sulfonate is preferably from 2-5 times the amount of the sulfonate on an equivalent weight basis.

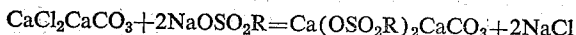
The mechanics of the various reactions involved are believed to be as follows with calcium chloride being used as an example of the alkaline earth metal halide, sodium carbonate as an example of the alkali metal carbonate, and sodium borate or borax as the alkali metal borate, and the sodium mahogany sulfonate being expressed as NaOSO₂R: If an excess of CaCl₂ is added to Na₂CO₃ in solution, momentarily an intermediate compound is apparently formed before the resolution to the end product CaCO₃—for instance:



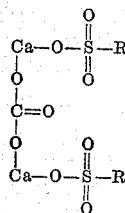
Structurally illustrated, this is as follows:



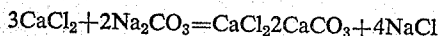
This in turn appears to react with sodium sulfonate in this manner:



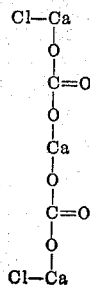
The structural formula is believed to be as follows:



The metal ratio is 2 to 1 and one mol of CaCO₃ as alkaline reserve is available. However, for a safety factor in heavy duty oils, it is preferred to use a 3 to 2 mol ratio:

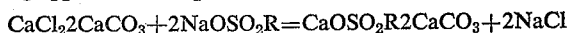


Structurally indicated as follows:

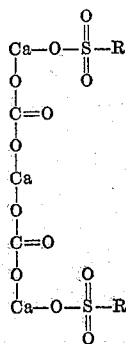


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On reaction with 2 mols of sodium sulfonate, the following appears to take place:



The structure of this compound is as follow:



This has a 3 to 1 metal ratio and has 2 mols of CaCO_3 available as alkaline reserve. Since this reserve is deemed satisfactory in general practice for an additive to be used in motor oil blending, this is one preferred form. It will be obvious that higher metal ratios may be secured by increasing the CaCl_2 and Na_2CO_3 quantities, limited only by the stability of the carbonate-calcium chain. Thus it is apparent that when the metal ratio is to be increased, a molar excess of the alkaline earth metal halide (A.E.M.H.) should be maintained over the other two ingredients; namely, the alkali metal carbonate or borate (AMC-B) and the alkali metal petroleum sulfonate (AMPS). Expressed as a formula where N equals the molar proportions, N similarly indicates as N the metal reserve, thus:

$$N(\text{AEMH}) + (N-1)(\text{AMC-B}) + (N-1)(\text{AMPS}) = N:1$$

Metal Reserve Ratio.

Example 1

1428 pounds of sodium sulfonate of about 3.5% sodium content are blended with 1428 pounds of a lubricating oil stock such as 100@100 neutral in a kettle of suitable size equipped with means of heating and stirring. The mixture is then heated.

When the temperature of the agitated mass has reached $180^\circ\text{--}190^\circ\text{ F.}$, 333 pounds of anhydrous CaCl_2 dissolved in 1,000 pounds of water, and 212 pounds of anhydrous Na_2CO_3 dissolved in 1,000 pounds of water are added simultaneously and at the same rate, taking care that the solutions do not come in contact before entering the oil sulfonate mixture, and that they enter the oil as near the middle of the vortex of the agitation as possible. As soon as both solutions are in the mix, CO_2 is introduced near the bottom of the kettle and allowed to bubble slowly through the mix throughout the operation. About 50 pounds is sufficient for a batch of this size, and serves to maintain the balance of CO_2 in the carbonate during processing. Although the use of CO_2 is preferred, it is not absolutely necessary.

Stirring and heating are continued until the temperature has reached 380° F. , at which point the water is substantially removed. The product is then filtered.

The theoretical Ca content of $\text{Ca}(\text{SO}_3\text{R})_2\text{CaCO}_3$ in a 1 to 1 dilution with mineral oil is 3.93%. Repeated batches made by the method described above have shown a Ca content of around 4%.

It will be obvious to those skilled in the art that the carbonate-calcium chain can be lengthened to give yet greater calcium content, and that many anions other than the carbonate may be employed. These anions, however, to be of practical benefit, must be polybasic and weak enough that their presence in the oil in the free state will not destroy the basicity of the calcium cation.

A good example of the latter class is the alkali metal borate such as borax.

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Example 2

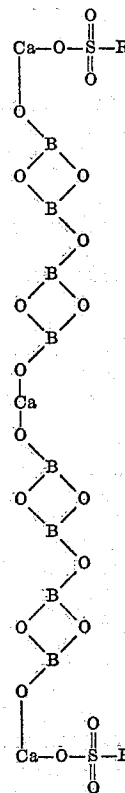
1428 pounds of sodium sulfonate (Na content approximately 3.5%) and 1428 pounds of the above neutral lubricating stock are blended with heating and stirring in a blending kettle. At $180\text{--}190^\circ\text{ F.}$ an aqueous solution of 763 pounds borax in sufficient water to effect complete solution and an aqueous solution of 333 pounds anhydrous CaCl_2 in 1,000 pounds of water are added simultaneously and separately in the same manner as in Example 1 with the exception that no CO_2 is employed. Heating and stirring are continued to expel water exactly as in Example 1 and the resultant product is filtered.

This product has the formula $\text{Ca}(\text{SO}_3\text{R})_2\text{CaB}_4\text{O}_7$ and is a bright viscous dark-colored oil-soluble compound.

On analysis this compound showed 3.79% Ca, 2.65% B, and had a sulfated ash of 21.35%.

Theoretical: 3.70 Ca 2.65 B.

The structural formula is believed to be as follows:



In the foregoing, it is readily seen that an important feature of the invention is the conversion of sodium to calcium sulfonate and the creation of alkaline reserve in the same operation without the aid of alkaline earth oxides or hydroxides.

The oxidation inhibitor that has heretofore been added as a separate ingredient may be introduced by incorporating a dithiophosphate in the sulfonate molecule itself.

Example 3

1428 pounds of sodium sulfonate (Na content about 3.5%) and 1428 pounds neutral lubricating stock were blended as in the other examples. 555 pounds anhydrous CaCl_2 were dissolved in 1,000 pounds water. 222.3 pounds P_2S_5 were added slowly to a solution of 159 pounds anhydrous Na_2CO_3 in 750 pounds water at boiling temperature. A vigorous reaction ensued, with a resultant dark brownish green solution. 265 pounds anhydrous Na_2CO_3 were dissolved in 750 pounds water.

At $180\text{--}190^\circ\text{ F.}$, the CaCl_2 and Na_2CO_3 solutions were added simultaneously to the agitating oil sulfonate mass, and immediately after, the $\text{P}_2\text{S}_5\text{Na}_2\text{CO}_3$ solution was added as quickly as possible, the speed being gov-

erned by the foaming of the mass, which makes it necessary to add the solution in small portions.

As before, the mass is heated with constant agitation to 380°–400° F. to remove the water, then filtered.

The resultant product was a bright, dark-colored oil-soluble product which gave the following analysis:

Ca 5.7% P 2.315%

The detailed combination of the Ca is:

1.5% is thiophosphate

1.28% is neutral sulfonate

2.92% is alkaline reserve

Due to the fact that the principal reactions of converting the sodium mahogany sulfonate to the alkaline earth metal sulfonate and loading it with alkaline reserve takes place in a simple reaction, it appears evident that the method of this invention lends itself readily to the continuous production of the alkaline loaded sulfonates.

The additives of this invention may be added to any of the ordinary petroleum lubricating oils by primarily heating and stirring the mixture of oil and additive until the additive is dissolved. In general, the amount of additive employed may be any amount up to about 20% by weight of the oil. A satisfactory amount has been found to be about 5%. All percentages expressed herein are by weight.

Having described my invention as related to the embodiments set out herein, it is my intention that the invention be not limited by any of the details of description unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

I claim:

1. A novel method of making an additive for a lubricating oil which comprises: (a) concurrently introducing into a quantity of an alkali metal petroleum sulfonate two separate salt solutions, the first of said salt solutions

consisting of an aqueous solution of an alkaline earth metal halide and the second of said salt solutions consisting of an aqueous solution of an alkali metal salt selected from the group consisting of an alkali metal carbonate and an alkali metal borate, (b) admixing said salt solutions with said sulfonate, (c) the molar ratio of the said alkaline earth metal halide to the member selected from the group consisting of alkali metal carbonate and alkali metal borate being $(N+1):N$, where N is the number of mols of the alkali metal salt, (d) heating said admixture of materials sufficiently to maintain a temperature above about 200° F. and for a period of time sufficiently long to drive off all the water, and (e) recovering the resulting product.

2. The method according to claim 1, wherein the temperature of the alkali metal sulfonate is maintained between about 180 and 200° F. while said two solutions are being added.

3. The method according to claim 1 wherein the alkali metal carbonate is sodium carbonate.

4. The method according to claim 1 wherein the alkali metal borate is sodium borate.

5. The method according to claim 1 wherein said admixture is heated to a temperature between 200° F. and 400° F.

6. The method according to claim 1 wherein the alkali metal sulfonate is diluted with a neutral oil prior to admixing with said solutions.

7. The oil additive prepared by the method of claim 1.

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