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ALKALINE EARTH METAL PETROLEUM MAHOGANY SULFONATES

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This invention relates to new and useful improvements in alkaline earth metal petroleum mahogany sulfonates.

Alkaline earth metal petroleum mahogany sulfonates have proven useful as additives for lubricating oils and particularly with respect to the prevention of corrosion of metal parts by acidic materials formed in the use of lubricating oils, especially in internal combustion type engines. They are in most cases used in the form of their mineral oil solutions and preferably including the mineral oil conventionally referred to as "occluded" oil retained by petroleum mahogany sulfonate products in the course of their manufacture.

Since the value of alkaline earth metal petroleum mahogany sulfonate additives is largely determined by the total alkaline earth metal content thereof, so-called "basic" sulfonates have been prepared. These are conventionally made by, for instance, treating a substantially neutral alkaline earth metal petroleum mahogany sulfonate with an aqueous slurry or substantial solution as the case may be, of an alkaline metal hydroxide, followed by dehydration. The resultant sulfonate product is characterized by a relatively high basicity and an alkaline earth metal content considerably higher than that of the ordinary substantially "neutral" alkaline earth metal petroleum mahogany sulfonate. This basicity is often considered to constitute an added beneficial feature of these basic sulfonates as it will tend to neutralize any harmful acids formed in the engine which might otherwise corrode metal parts contacted by the lubricating oil.

Though the basicity of these "basic" sulfonates may tend to neutralize acids formed in the engine, it is relatively easily and quickly removed by water forming the hydroxide of the particular earth alkaline metal. Since water is always present in crankcases of internal combustion engines, the alkalinity originally present in the lubricating oil by reason of a basic sulfonate therein, is thus transferred to the water phase where it may become deleterious to metal surfaces. This is particularly true for such strongly reacting alkaline materials as barium hydroxide. The relatively caustic aqueous phase will react with metal parts, and especially non-ferrous metals and alloys, to corrode the same. Inasmuch as it is practically impossible to obtain at all times a balance between actively available basic and acidic components in the oil of an internal combustion engine, the corrosive influence of the one or the other will be present.

One object of the invention comprises among others a substantially clear, substantially neutral mineral oil solution of alkaline earth metal petroleum mahogany sulfonate having a relatively high alkaline earth metal content. This and further objects of the invention will be apparent from the following description:

I have discovered that when treating an alkaline earth metal petroleum mahogany sulfonate solution in mineral oil, and preferably a basic alkaline earth metal petroleum mahogany sulfonate mineral oil solution, with oxygen at a temperature of about 250–350° F. and preferably about

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275–325° F. in the presence of finely dispersed, substantially basic compound of such metal, being a carbonate (including bicarbonate) or oxide (including hydroxide), a substantially neutral, substantially flowable sulfonate product of high alkaline earth metal content may be obtained.

The alkaline earth metal components in accordance with the invention may be calcium, strontium, barium or magnesium. Basic sulfonates of these metals may be obtained in accordance with conventional practices, including treatment of their neutral sulfonates with aqueous slurries of the corresponding metal oxides or hydroxides, and further including neutralization of petroleum mahogany sulfonic acid mineral oil solutions with such slurries containing in excess of neutralizing amounts of alkaline earth metal oxides or hydroxides. Sulfonates especially useful in accordance with the invention are those of calcium and barium, the latter being the preferred embodiment. Whenever aqueous slurries are used a dehydration is effected, and in order not to unnecessarily prolong the dehydration period, it is desirable to limit the aqueous slurry to one of about 10% by weight of the hydroxide.

Within a preferred embodiment of the invention use is conveniently made of the dispersion of oxides resulting from the dehydration step in the preparation of "basic" sulfonates. Alternatively alkaline earth metal carbonate suspensions (or separately produced oxide suspensions) in a substantially neutral or basic alkaline earth metal mahogany sulfonate mineral oil solution may be treated in accordance with the invention.

The substantially neutral alkaline earth metal sulfonate solution obtained in accordance with the invention is one in a petroleum hydrocarbon or mineral oil, a large portion of which is preferably so-called "occluded" oil, the solution preferably containing without benefit of auxiliary solvent, alkaline earth metal in excess of that normally obtainable for corresponding "basic" alkaline earth metal petroleum mahogany sulfonate.

The sulfonate content of the mineral oil solution constituting a desirable additive obtained in accordance with the invention may be, for instance, at least about 20% and preferably in excess of about 40% by weight of sulfonate. The top amount of alkaline earth metal components is primarily dependent upon total available amount of the particular oxides or carbonates in relation to the extent of applied oxygen treatment.

The oxygen treatment of the basic alkaline earth metal petroleum mahogany sulfonate mineral oil solutions in accordance with the preferred embodiment of the invention is best accomplished by intimately contacting the solution, containing appropriate dispersed oxide or carbonate with gaseous oxygen, and preferably by passing oxygen through the solution. The basic sulfonate solution is advantageously one containing sufficient basically reacting alkaline earth metal components to impart to the solution a free alkalinity in excess of substantially 40 milligrams KOH per gram of said solution. It may contain in excess of 50 milligrams KOH per gram free alkalinity or an equivalent percentage basicity of an excess of 40.5%. The oxygen treatment of the basic sulfonate solution is best effected by passing oxygen through the same while at an elevated temperature of from 250–350° F. and preferably about 275–325° F. The passage of oxygen is preferably continued until not in excess of 8 mg. KOH/g. and preferably not in excess of 6 mg. KOH/g. alkalinity prevails, the latter being considered for practical purposes as constituting substantial neutrality.

The substantially neutral product obtained in accordance with the invention has the advantage that it is sub-

stantially free from any basicity or alkalinity which, when in contact with water, may become a corrosive influence.

The following example is furnished by way of illustration but not of limitation:

Example

A sodium petroleum mahogany sulfonate (molecular weight about 450) was diluted with petroleum hydrocarbon oil to produce a solution of about 40% by weight sulfonate content. This solution was then converted to the corresponding barium sulfonate by double decomposition in the conventional, well known manner with a 20% barium chloride solution.

The barium sulfonate oil solution obtained as above was then admixed with about 10% by weight of barium hydroxide in the form of a 10% aqueous slurry, the resulting mixture being thoroughly stirred for intimate contact between the components, and the temperature being slightly raised to facilitate reaction. The resultant product was then dehydrated, thereby obtaining a basic barium sulfonate solution containing appreciable amounts of dispersed therethrough barium oxide or hydroxide. The dehydration was effected at a temperature of about 250° F. and once accomplished, substantially pure O₂ gas was passed through the solution containing dispersed barium oxide or hydroxide while substantially maintaining the temperature at about 300° F., O₂ addition being stopped (after about 15 hrs.) substantially at the point of residual alkalinity testing about 4 mg. KOH/g. The resultant product was then filtered and after filtration constituted a substantially neutral barium sulfonate in oil solution.

A sample drawn showed the basic sulfonate (filtered test sample) to have a sulfated ash content of about 25.34% by weight as compared to the oxygen treated product with a sulfated ash content of about 35.39% by weight. This corresponds to a barium content of 14.90% by weight for the filtered untreated product and to a barium content of 20.80% by weight for the oxygen treated filtered product, with a barium hydroxide content of 7.0% by weight for the filtered untreated product and 0.80% for the filtered oxygen treated product.

Similar results to those set forth in the foregoing example are obtainable when using other alkaline earth metal petroleum mahogany sulfonates in lieu of the barium sulfonate there specified, or when using alkaline earth metal oxide or carbonate suspensions separately prepared in the basic sulfonate solution of the example after dehydration and filtering thereof. By way of specific example, for instance, when substituting calcium hydroxide or sulfonate, as the case may be, in the fore-

going example, there is obtained a sulfated ash content of about 10.2% by weight for the filtered untreated product as compared to such content for the ultimate filtered oxygen treated product of about 11.2% by weight.

When using a higher temperature of, for instance, about 340° F. during the oxygen treatment in the above example, practically 0 alkalinity was obtained after about 12 hrs. In that case, however, a substantial darkening of the color of the resulting product occurred.

As will be readily understood, it is possible in accordance with the invention to prepare substantially neutral sulfonates of high alkaline earth metal content using two or more of such metals in the preparation of the novel products. It is thus possible for instance to prepare a calcium sulfonate or such basic sulfonate as the case may be, and treat the same with O₂ in the presence of dispersed barium oxide or hydroxide. By way of further illustration, for instance, there may be substituted in the foregoing example substantially neutral calcium petroleum mahogany sulfonate in lieu of the barium sulfonate there specified, the calcium sulfonate being thereafter treated with a barium hydroxide slowly and the remainder of the steps being followed as set forth in the example.

I claim:

1. Process for the production of oil solutions of basic alkaline earth metal petroleum mahogany sulfonates having low alkalinity, which comprises passing oxygen in contact with an anhydrous petroleum oil solution of an alkaline earth metal petroleum mahogany sulfonate containing a substantial quantity of a member selected from the group consisting of oxides and carbonates of said alkaline earth metal dispersed therein at a temperature of about 250-350° F. and continuing said contacting with said oxygen for a period of time sufficient to produce an alkaline earth metal petroleum mahogany sulfonate of an alkaline earth metal content in excess of that contained in the normal alkaline earth metal petroleum mahogany sulfonate and of a substantially reduced alkalinity.

2. Process according to claim 1 in which said contacting is effected at a temperature between about 275 and 325° F.

3. Process according to claim 1 in which said alkaline earth metal is barium.

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