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## PROCESS OF PRODUCING POLYVALENT-METAL HYDROCARBON SULFONATE

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21 Claims. (Cl. 260-504)

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This invention relates to lubricating and rust preventing compositions, and also to processes for manufacture of such compositions.

Important objects of the invention are to produce compositions which are exceptionally efficient for lubrication purposes, especially in severe service engines, and for the prevention of rust under severe conditions of use. Another object is to provide methods for the easy manufacture of constituents employed in such compositions, particularly the production of oil-soluble, water-insoluble petroleum sulfonates substantially free from inorganic salts and water-soluble or kindred sulfonates which are generally conducive to rust formation, and to undue wear and corrosion in internal combustion engines.

In the preparation of some rust preventing compounds and lubricants, and in the preparation of some lubricants for severe service uses and for similar lubricating uses, it has been a practice for several years to employ various metal salts of sulfonic acids derived from petroleum fractions in connection with sulfuric acid treatment of such petroleum fractions. These sulfonic acids, and their salts are well known in the petroleum industry. Those most commonly used for the present purpose are the oil-soluble acids known as mahogany acids which are found in solution in a supernatant oil layer which accumulates above an acid sludge layer upon settling of a batch of petroleum lubricating oil following sulfuric acid treatment. The sulfuric acid treatment of petroleum lubricating oil results also in the production of other sulfonic acids, known as "green acids," which are primarily water-soluble and are, therefore, found chiefly in the acid sludge layer. However, some of these water-soluble green acids are found in the presence of the oil-soluble mahogany acids in the oil layer and are objectionable for certain purposes. Possibly these vagrant water-soluble sulfonic acids pass into the oil layer because they are at the same time slightly oil-soluble, or because they are to that extent solubilized by the action of the mahogany acids. As a result, these objectionable water-soluble green acids are carried over as sulfonate into the oil-soluble sulfonate which is commonly placed upon the market as the sodium salts of the mahogany acids. For the purpose of preparing rust preventing compounds and severe service lubricants, these sodium mahogany acid salts are commonly converted by metathesis into alkaline earth metal sulfonates, usually the calcium salts. The calcium salts of the true mahogany acids appear to be almost entirely insol-

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uble in water although oil-soluble. But the resultant calcium salts of the green acids, which are readily water-soluble, are apparently also oil-soluble in the presence of mahogany acid salt. Because of their water-solubility, they are objectionable in rust preventives and in lubricating oils where moisture may be encountered, because they appear to weaken the resistance to water of an oil film on metal, possibly through favoring the formation of a water-continuous emulsion; whereas the water-insoluble, oil-soluble calcium salts of the true mahogany acids, when operating in the presence of water to form emulsions, result in emulsions where oil is the continuous phase. In the case of oil-continuous emulsions, the oil preferentially wets iron or steel surfaces with the result that the water present in the emulsion does not wet the metal and rusting is avoided. On the other hand, where the chemical environment produces water-continuous emulsions, the water phase displaces the oil from the metal surface, thereby reducing or destroying the rust inhibiting effect of the oil. Even though the oil-soluble, water-insoluble sulfonates greatly predominate, nevertheless, appreciable proportions of water-soluble sulfonates result in corresponding rusting effects, even a relatively small proportion of the water-soluble sulfonate resulting in excessive water corrosion, to the extent that products fail to give the full degree of protection required in severe service, such as in military and naval operation.

A primary object of the present invention is to eliminate the water-soluble sulfonates above-described, or at least to reduce them to such an insignificant proportion that their presence is not detrimental. Another important object is to produce a finished sulfonate free from inorganic salts such as sodium chloride, calcium chloride and sodium sulfate that may be formed by metathesis or be present as impurities.

I have discovered that the water-soluble sulfonates which ordinarily are present in commercial oil-soluble sulfonates of the mahogany acid type, such as those commonly placed on the market in the form of oil-soluble sodium sulfonates, can be so completely eliminated from the alkaline earth metal product produced by metathesis as to be either not present at all or at least present in such reduced quantities that their presence and effect are not detrimental. This purification of the oil-soluble sulfonates is accomplished by diluting the batch of sulfonates undergoing metathesis or purification with a small percentage, for example, around 2% or 3% or in the order of

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about 0.2% to 10% of the total batch being treated, of a water-insoluble, oil-soluble aliphatic alcohol or other oxygen-bearing organic solvent having appropriate boiling point and sufficiently low viscosity and preferably capable of producing viscosity reduction effects. By suitable boiling point, it is intended to signify a material whose boiling point is below the decomposition temperature of the sulfonate so that the diluent material may be eliminated from the product by vaporization. In general, this signifies a boiling point not materially in excess of 350° F., inasmuch as the initial decomposition temperature of a sulfonate such as calcium sulfonate is in the neighborhood of 450° F. The object in using material of relatively low viscosity is to reduce the viscosity of the sulfonate so that it does not thicken or curd during the conversion operations.

This class of diluents is best represented commonly by amyl alcohol (e. g. fusel-oil) and butyl alcohol. Both of these materials boil several degrees above the boiling point of water, and they are almost entirely insoluble in water. However, other alcohols that may be employed are the hexanols, the pentanols, and also the octanols (especially 2-ethylhexanol).

In general, I may use any oxygen-containing organic compound possessing four or more carbon atoms, which is oil-soluble, water-insoluble and possesses a boiling point not appreciably above 350° F. and preferably not exceeding about 400° F. So far as is known, all aliphatic alcohols containing four or more carbon atoms and having a sufficiently low boiling point are usable. Some times it is desirable or permissible to leave the alcohol or a substantial proportion thereof in the finished sulfonate composition. In such a case, the boiling point of the alcohol may not be a limiting factor in its use, as in the case of 2-ethylhexanol.

In its broadest aspect, one phase of the invention resides in employing as a diluent in the purification or conversion of the sulfonates an oil-soluble, water-insoluble organic compound consisting only of carbon, hydrogen and oxygen, the diluent or solvent having a boiling point below the decomposition temperature of the sulfonates. In general, these materials contain at least four carbon atoms per molecule, and, in order to avoid too high a viscosity, they will ordinarily contain not more than about eight carbon atoms per molecule. More specifically, and primarily, the invention resides also in the definitely preferred class of oil-soluble, water-insoluble aliphatic alcohols whose boiling point is below the decomposition point of the sulfonates. These materials also contain at least four carbon atoms per molecule and ordinarily not to exceed eight carbon atoms per molecule in order to avoid excessive viscosity. The two members which constitute an outstanding preferred class are butyl alcohol and amyl alcohol, these being especially preferred because of their relatively low boiling point, low viscosity and great effectiveness, and also because of their ready availability and relatively low cost. While aliphatic alcohols of four or five carbon atoms may be preferred, I may also use alcohols of the polymethylene series such as cyclohexanol and methyl cyclohexanol, and of the benzene series such as phenol and cresol. Alcohols of the aliphatic type containing ring constituents, such as benzyl alcohol and furfuryl alcohol, may be also used. These materials are normally liquid and are in general solvents for the mineral oils and oil-soluble sulfonates involved.

In employing the term "water-insoluble," it is intended to signify relative insolubility, that is, entire immiscibility or only partial miscibility at the temperature being employed, as contrasted with complete miscibility in any proportion. The term "water-soluble" is used to signify either true or complete solubility, or a high state of dispersion which approaches true solubility and is adequate for the respective purpose.

In producing an oil-soluble, water-insoluble sulfonate according to the present invention, any appropriate commercial product in the form of the usual sodium sulfonate concentrate may be employed; that is, any sodium mahogany acid salt which characteristically contains a considerable proportion of mineral oil commonly carried over into the commercial product from the mineral oil fraction which was originally treated in preparing the sulfonate. Such a commercial sulfonate is ordinarily quite viscous or even semi-solid at normal temperatures and contains varying amounts of mineral oil, for example, 15% to as much as 75% of the oil. This commercial concentrate is often further diluted with mineral oil as desired to reduce viscosity and facilitate handling. It is sometimes desirable however, to employ no additional mineral oil or as small a proportion as possible in order to reduce the bulk being handled or to produce a product of very viscous or resinous consistency.

The sodium sulfonates in the oil carrier are all water-soluble or dispersible in water. In practicing my invention, one volume of sulfonate-oil mixture is dispersed in 1 to 5 or more volumes of water, preferably at or near the boiling point of water. This solution or dispersion is the water-continuous type. For the purpose of conversion into an oil-soluble, water-insoluble metal sulfonate, a water solution of an appropriate metal salt is then added and mixed with the aqueous sulfonate-oil dispersion at a temperature of about 210° F., agitation being employed to insure complete distribution. Characteristically, a water-soluble calcium salt is used, such as calcium chloride in a water solution of 40% concentration, a proportion of the solution being added sufficient to provide at least a slight excess of calcium chloride. Other proportions of solution to afford a satisfactory working volume of water and containing the salt in concentrations to yield any desired excess may be employed. The agitated heated mass usually quickly develops into a characteristic thick or doughy mass of oil-continuous emulsion as the water-insoluble calcium sulfonate forms. As a result subsequent settling produces relatively little separation, or at least very poor separation. Consequently, the water-soluble calcium sulfonates which are formed from the green acid salts during metathesis are mechanically retained in the mass of oil-continuous emulsion. Also, the water phase dispersed as droplets throughout the oil-continuous mass contains the dissolved inorganic salts representing original impurities such as sodium sulfate, sodium chloride produced by metathesis, and excess calcium chloride. It is extremely difficult or practically impossible to wash out or settle out the briny water phase at this stage by the conventional methods. Heretofore, it has been the practice to evaporate the entire amount of water entrained in the oil-calcium sulfonate mass, and to remove as much as possible of the inorganic salts and other impurities from the dehydrated oil-sulfonate mixture by mechanical means, such as centrifuging or filtering in the presence of a filter aid such as

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diatomaceous earth. Naphtha is sometimes added before, during or after the dehydration in order to facilitate handling and removal of crystallized salts and other impurities. Such operations are laborious, expensive, and usually do not remove all inorganic salts from the finished product. Obviously, little or no rejection of water-soluble metal sulfonates is accomplished.

According to the improvement of this invention, a small quantity of the described oil-soluble, water-insoluble diluent alcohol or other indicated oxygen-bearing organic compound is added before, during or after the metathesis, with agitation so as to be thoroughly distributed throughout the mass being treated. Sufficient organic compound is added to obtain good breaking of the emulsion, which seems to vary somewhat with the sulfonate, the amounts of oil and water present and amount of excess calcium chloride used. Ordinarily, 0.2% to 3.0% of commercial fusel-oil (iso-amyl alcohol) based on the volume of the kettle contents is employed. For somewhat faster operation, a greater proportion such as 5% or even up to 10% may be added, especially where the alcohol is to be recovered upon subsequent evaporation. Upon completing distribution of the alcohol in sufficient quantity through the mass, and stopping agitation, the phases quickly break, and separation by settling follows with comparative rapidity. The separation is so complete that a distinct line forms between the resultant supernatant oil phase in which most of the alcohol and all of the water-insoluble, oil-soluble calcium sulfonates have dissolved, and the lower water phase in which water-soluble calcium sulfonate has dissolved along with excess calcium chloride and the resultant sodium chloride formed in the conversion, together with any other water-soluble impurities present, such as sodium sulfate and sodium sulfite. Separation of the phases may be accomplished, if desired, by centrifuging the mass after mixing in the alcohol, using for example a de Laval separator; but I have found settling in a suitable vessel as described below to be satisfactory when the proper alcohol is used in suitable amount.

After settling either the supernatant oil layer containing the diluent alcohol and the dissolved water-insoluble sulfonates may be decanted from the water layer, or the water layer may be withdrawn from the treating vessel leaving only the oil and alcohol layer. In either event, the oil layer is heated to expel any entrained water and the diluent alcohol, which alcohol may be passed to a recovery system if desired. Should an alcohol have been employed whose boiling point too closely approximates the decomposition temperature of the sulfonate, the evaporation of the diluent may be conducted under appropriate vacuum.

The resultant solvent-free concentrate of calcium sulfonate in oil apparently contains little or no water-soluble sulfonate and no inorganic salts. In other words, a mahogany acid soap concentrate comparatively free from green acid soaps and inorganic salts is produced. Or, in any event, the oil-containing concentrate possesses insufficient objectionable sulfonates or other impurities to interfere with the rust preventing and/or detergent properties of compounds produced therefrom.

If it should be that, in the heating of the oil layer to expel the diluent, a product is yielded that requires clarification, it may be centrifuged, or a small amount of filter aid such as diatomaceous earth may be added and commingled with the

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mass, the mass being then filtered to yield a clear final product. For example, small amounts of crystallized salts, trapped in the oil-sulfonate solution following expulsion of solvent and of water that contained the salts and was entrained in the oil-sulfonate layer during settling, will be removed. So complete however is removal of such salts in the water layer, which separates upon the described alcohol treatment, that, in batches containing 900 lbs. of excess  $\text{CaCl}_2$  and other salts, less than 50 lbs. (sometimes as little as 10 lbs.) is trapped through the medium of entrained water, this being easily removed by centrifugation; whereas in the prior processes as much as 90% of the inorganic salts is commonly retained in the oil layer and must be removed as well as possible by mechanical means.

The employment of the described alcohol or other oil-soluble, water-insoluble oxygen-bearing compound described offers the further advantage that the oil-alcohol solution of the oil-soluble sulfonates may be readily water washed and re-washed without emulsification difficulties, should it appear desirable at any time so to treat the oil layer in order to remove the last traces of water-soluble sulfonate and inorganic salts from the oil solution. Additional quantities of the organic diluent compound are usually required at each wash as a greater proportion of the electrolyte is removed, unless adequately large proportions of compound are initially used.

Another advantage in the employment of the alcohol or other described oxygen-bearing compound is that it may be added to a sulfonate concentrate before the addition of water, or either before or after dilution with additional oil when such is employed, whereby the organic solvent is present to take up the water-insoluble sulfonate as formed by metathesis, or at other stages, or portions may be added at various stages as required.

In general, the greater the excess of calcium chloride used or the higher the salts concentration in the water phase, the less the amount of alcohol required, but to take the fullest advantage of this in order to conserve alcohol presents the danger of excessive contamination in the event the settling or decanting operations are not perfect. I prefer to use a larger volume of water and a smaller excess of calcium chloride together with a larger proportion of alcohol when a product of maximum purity is desired, such as for use in compounding rust preventives for military and naval equipment.

As a specific example of one mode of practicing my invention, 4050 lbs. (477 gallons) sodium sulfonate of commerce, known as Griffin Chemical Company's Gammanol L-100, containing approximately 64% sodium sulfonate, 26% lubricating oil and 10% water and inorganic salts, was charged into a steam heated kettle of 2200 gallons capacity. 1000 gallons of water was added and the kettle contents were heated to boiling and agitated to insure thorough dispersion of the commercial sodium sulfonate. Then 600 lbs. of commercial calcium chloride flakes (82%  $\text{CaCl}_2$ ) dissolved in 80 gallons of water was added to the kettle with agitation and continued boiling. Then four (4) gallons of commercial fused oil (about 90% iso-amyl alcohol) was added with agitation to insure thorough mixing. Next, 500 gallons of refined mineral oil (500 seconds Saybolt Universal viscosity at 100° F.) was added and the kettle contents again brought to boiling with agitation. Soon after the contents again reached boiling

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temperature, both heating and agitation were stopped and the kettle contents were allowed to stand for 12 hours. Two sharply defined layers developed during standing, and the bottom layer consisting of water and dissolved impurities was drawn off accurately and discarded. Heat was then applied to the kettle and the retained upper layer was heated with agitation to 275° F. to remove fusel oil and water. Agitation with dry steam for a few minutes at 250° F. was employed. As the kettle contents were being heated, 50 lbs. powdered  $\text{Ca}(\text{OH})_2$  were added to the kettle to insure a neutral or alkaline product. After dehydration at about 275° F. 1070 gallons of the same oil as the 500 gallons added previously was added with agitation. The resulting blend was heated to 250° F. to 275° F. and passed through a Sharples Super-Centrifuge at the rate of 400 gallons per hour. The centrifuge bowl was cleaned three times while running the batch, first after 30 minutes, then after 2 hours, and at the end of the run. The total solids removed from the centrifuge bowl weighed 18.6 lbs. and consisted largely of excess  $\text{Ca}(\text{OH})_2$ .

A yield of 1980 gallons of clear calcium sulfonate concentrate was obtained, containing approximately 15% calcium sulfonate. Addition of 12 parts of this concentrate to 88 parts of a well refined mineral oil blend of 53 seconds Saybolt Universal viscosity at 100° F. gave a compounded oil meeting the requirements for rust preventive oil for small arms as given in U. S. Army specification 2-120. The addition of 12 to 18 parts of this concentrate to a number of different brands of heavy duty crankcase oil conforming to U. S. Army specification 2-104B gave in each case an interior engine preservative oil complying with U. S. Army Ordnance specification AXS-934. The addition of 20 parts of this concentrate to 80 parts of refined mineral oil of 65 seconds viscosity at 210° F. gave a rust preventive oil complying with U. S. Army Ordnance specification AXS-674, Revision 2. The addition of 5 parts of the concentrate along with 1 part tertiary amyl phenol sulfide to 94 parts of a well refined motor oil blend, having a viscosity of 62 seconds at 210° F. and a viscosity index of 78 gave a heavy duty crankcase oil complying with U. S. Army specification 2-104B. The addition of 20 parts of the concentrate to 80 parts of petrolatum having a melting point of 138° F. and a penetration of 210 gave a resulting rust preventive compound complying with Army-Navy Aeronautical specification AN-C-124. The addition of 10% to 25% of the concentrate to sodium base greases used for automotive chassis lubrication not only imparted exceptional resistance to corrosion from moisture and salt water immersion, but also improved the resistance to disintegration by water to the point where such modified soda base greases compared satisfactorily in this respect with aluminum, barium, and lithium base greases. The addition of 5% to 20% of the concentrate to calcium, aluminum, barium, magnesium, zinc, and lithium base greases, respectively, imparted both markedly improved anti-rusting properties and reduced tendency to bleed or separate on standing.

While my purified petroleum sulfonates or mahogany salts are usually the calcium products, the invention includes also the preparation of other alkaline earth metal sulfonates especially the barium salts and also the strontium salts. Such sulfonates may be readily prepared by employing water-soluble barium or strontium salts

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instead of calcium chloride or other water-soluble calcium salt. The process of converting and purifying petroleum sulfonates described herein is applicable to the production of water-insoluble, oil-soluble sulfonates of metals other than the alkaline earth metals. Such metals include aluminum, zinc, magnesium, lead, cobalt, nickel and the like. In brief, my process makes it possible to manufacture efficiently and economically the sulfonates of any of the polyvalent metals.

For the purpose of production of rust preventives, as above indicated, the described water-insoluble, oil soluble polyvalent metal sulfonate concentrate in oil is diluted with such carriers as may be desired for the intended purpose. The diluent may be selected from any appropriate mineral oil lubricating fraction according to the ultimate use of the product. For example, the diluent may range anywhere from a very light petroleum fraction, such as one having a viscosity of 50 to 60 seconds Saybolt Universal at 100° F. for low temperature work, up to one having a viscosity of 2000 seconds Saybolt Universal at 100° F. (corresponding generally with a lubricating oil of an S. A. E. 70 grade) such as may be required for high temperature lubrication in aircraft engines and the like. In preparing such an oil, a quantity of the sulfonate product obtained by the above-described purification method will be employed to yield in the final product a proportion of the calcium sulfonate or other water-insoluble, oil-soluble metal sulfonate amounting to between about 0.5% and about 6% based on the blended product. Ordinarily, a satisfactory working proportion will be about 3%, or between about 2% and about 4%.

Inasmuch as lubricating properties are possessed by the petroleum fractions employed for solution therein of the sulfonates purified by the present improvement, the resultant rust-preventive products may be simultaneously employed as lubricants. In the case of aircraft and other engines as above mentioned, where heavier grades of lubricating oils are employed in producing the rust preventing composition, the engines may be subsequently operated with the rust preventive material as a lubricant. If desired, other constituents may be incorporated in such oils to adapt them to special lubrication uses such as severe service conditions encountered in aircraft engines, Diesel engines, and the like. In those instances, other additives well known to the lubricating industry may be introduced, including (1) detergent soaps such as represented by oil-soluble calcium soaps and similar metal soaps of synthetic carboxylic acids produced by the oxidation of paraffinic hydrocarbons, and (2) oxidation inhibitors such as sulfurized alcohols, sulfurized hydrocarbons, thiophosphates, phenolic thioethers, phosphites, suitable metal derivatives of these materials, and like materials known to the industry.

Similarly, purified sulfonates of the present invention may be employed in the preparation of sulfonate-containing lubricating oil for severe service uses and the like which are not necessarily required for rust preventing purposes. Thus, typical lubricating oils may contain from about 0.5% to about 2%, for example 0.75%, of the purified alkaline earth metal sulfonate of this invention, together with from about 0.5% to 2% or 3%, for example about 1%, of oxidation inhibitors as above-described, or detergent soaps as above-described, or otherwise, to meet any given requirement. In many of these instances,

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the employment of purified water-insoluble, oil-soluble alkaline earth metal sulfonates from petroleum, as above-described, are especially valuable in counteracting tendencies toward undue corrosion in internal combustion engines, especially those of the severe service type such as the indicated aircraft and Diesel engines.

The purified sulfonates produced as described may be used in other compositions than those above disclosed. For example, they may be used as rust preventives in carriers which are normally solid and applied as films having appreciable thickness either by hot application or as solutions in readily volatile solvents. Such sulfonates may be used also in grease-like materials for rust preventing or lubricating purposes, or otherwise. For example, an appropriate quantity of the oil-sulfonate product may be added to petrolatum, and, if required, this composition thinned with petroleum lubricating fractions to whatever consistency desired. The petrolatum itself possesses lubricating properties.

When any of the products above-described are to be used under conditions where foaming is apt to be encountered, purified sulfonates may be produced, as above-described, by employing the indicated octyl alcohol and terminating the subsequent expulsion of the octyl alcohol so as to leave around 0.5% to 2% of octyl alcohol in the oil-sulfonate solution whereby to impart anti-foaming characteristics. The same will be true of any other organic solvent which is employed and possesses anti-foaming characteristics. I have also found that the presence of 0.25% to 2% of octyl alcohol or other high molecular weight alcohol in the finished lubricant increases very greatly the effectiveness of the sulfonate addition in combating corrosion from hydrobromic acid. For example, the addition of 2.5% calcium sulfonate to a heavy duty motor oil containing 0.75% calcium soap of oxidized petroleum acids and 0.75% calcium salt of tertiary amyl phenol sulfide was sufficient to protect the crankcase interior of engines against rusting from moisture condensation, but was insufficient to protect against dilutes aqueous hydrobromic acid. The addition of 0.75% of octyl alcohol (2-ethylhexanal) to the foregoing oil containing 2.5% sulfonate, as described, gave perfect protection against hydrobromic acid corrosion as required in Army-Navy Aeronautical specification AN-VV-C-576 and Army Ordnance specification AXS-934. The addition of the octyl alcohol in any amount to the heavy duty oil described, without the addition of the sulfonate, failed to correct the corrosion from hydrobromic acid. Other alcohols, alcohol-esters such as "Carbitol" and "Cellosolve" (monoethyl ethers of diethylene and ethylene glycol respectively, made by Carbide and Carbon Chemical Corporation), and their alkylated derivatives, may be used to increase the effectiveness of the sulfonate addition in combating hydrobromic and hydrochloric acid corrosion of iron surfaces.

At present I have no theory regarding the operability of the indicated class of organic compounds which are useful for breaking the emulsion formed when sodium sulfonate is converted to alkaline earth or heavy metal sulfonates by metathesis, whereby good separation between the oil layer and water layer results. Obviously, it is not wholly a matter of viscosity reduction imparted by the low viscosity of the solvent diluent, because petroleum naphtha, which possesses low viscosity and is water-insoluble and oil-soluble,

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is not effective. Nor are the water-soluble propyl alcohols effective, nor other lower molecular weight alcohols. Conceivably, the results are derived as combined effects of the characteristics of low viscosity, oil-solubility, substantial water-insolubility, and possibly even the effect of very slight water-solubility which appears to be a characteristic of the materials employed and defined as water-insoluble.

My process is not to be confused with the commonly used process of concentrating or purifying sodium sulfonate wherein crude sodium sulfonate is extracted with methyl, ethyl, or isopropyl alcohol containing carefully controlled proportions of water. In the latter process, the solvent is miscible with water and immiscible with oil, and is designed to extract the sodium sulfonates away from the oil. While both green acid and mahogany acid sodium soaps can be concentrated from the crude sodium sulfonates with water-iso-propyl alcohol mixtures, any tendency to separate green acid from mahogany acid soaps is in the wrong direction. Water-iso-propyl (or ethyl or methyl) alcohol mixtures have a greater solvent power for the green acid soaps than for the mahogany acid soaps. The so-called "purified sodium sulfonate" produced in the conventional manner therefore usually has a higher ratio of green acid to mahogany acid soap than was present in the crude sulfonate; whereas my process gives a purified sulfonate in which the ratio of green acid to mahogany acid soap is less than was present in the crude sulfonate. In the conventional process, a portion of the more desirable mahogany acid soaps is lost in the rejected oil phase, whereas in my process all of the more desirable mahogany acid soaps are recovered and the less desirable green acid soaps are expelled in the rejected water phase. The amount of alcohol containing four or more carbons used in my process is from only a few tenths of a percent to 5 percent as a maximum, usually, based on the volume being processed, as compared with from 50% to 200% of aqueous alcohol solvent in the conventional process for purifying sodium sulfonate. Also, judging from the small amount required of alcohol containing four or more carbons per molecule, it would appear that the function of the alcohol in my process is not to act so much as a selective solvent as it is to break an otherwise stable oil-continuous emulsion, and to permit water-soluble impurities to be expelled in an easily removed water phase.

While I have described my process as being applicable to petroleum sulfonates produced by sulfuric acid treatment of petroleum fractions, my process is also applicable to sulfonates produced synthetically by sulfonation of hydrocarbons or other compounds from coal tar products or any other source. Also my process is applicable to sulfates (often called sulfonates) produced by reacting sulfuric acid or sulfur trioxide with alcohols and/or unsaturated compounds belonging to the classes of hydrocarbons, acids, esters, ketones, ethers, glycerides, waxes, etc.

It is to be understood that, in view of the above disclosures, other modifications will become apparent to those skilled in the art to which these improvements pertain. Therefore, all modifications within the scope of the appended claims are intended to be protected thereby.

I claim as my invention:

1. In a process of producing water-insoluble, oil-soluble polyvalent-metal hydrocarbon sulfonate, the steps which comprise: forming a mix-

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ture containing water, said polyvalent metal sulfonate and an emulsion-breaking, oil-soluble liquid compound consisting of carbon, hydrogen and oxygen and containing four to about eight carbon atoms per molecule to facilitate separation of a water-insoluble sulfonate-containing phase from an aqueous phase; and recovering the sulfonate phase.

2. The process of claim 1 wherein the mixture containing said emulsion-breaking liquid is heated approximately to the boiling point of the mixture to facilitate said separation.

3. The process of claim 1 wherein said emulsion-breaking liquid is an aliphatic alcohol.

4. The process of claim 1 wherein said emulsion-breaking liquid is a butyl alcohol.

5. The process of claim 1 wherein said emulsion-breaking liquid is an amyl alcohol.

6. The process of claim 1 wherein an alkaline earth metal hydroxide is heated with said separated sulfonate-containing phase in the presence of said emulsion-breaking liquid to render said sulfonate alkaline.

7. The process of claim 1 wherein said polyvalent-metal sulfonate is an alkaline earth metal sulfonate.

8. The process of claim 1 wherein the quantity of emulsion-breaking liquid employed is about 0.2% to 10% of the mixture.

9. A process as in claim 1 wherein the separated sulfonate-containing phase is washed with water in the presence of said emulsion-breaking liquid.

10. In a process of producing water-insoluble, oil-soluble polyvalent-metal hydrocarbon sulfonate, the steps which comprise: forming a mixture containing water, said polyvalent-metal sulfonate, a petroleum oil of lubricating viscosity and an emulsion-breaking, oil-soluble liquid compound consisting of carbon, hydrogen and oxygen and containing four to about eight carbon atoms per molecule, said water, sulfonate and oil tending to form an oil continuous emulsion, and said emulsion-breaking liquid facilitating separation of a water-insoluble sulfonate and petroleum oil containing phase from an aqueous phase; and recovering the sulfonate and oil containing phase.

11. The process of claim 10 wherein the mixture containing said emulsion-breaking liquid is heated approximately to the boiling point of the mixture to facilitate said separation.

12. The process of claim 10 wherein said emulsion-breaking liquid is an aliphatic alcohol.

13. The process of claim 10 wherein said emulsion-breaking liquid is a butyl alcohol.

14. The process of claim 10 wherein said emulsion-breaking liquid is an amyl alcohol.

15. The process of claim 10 wherein an alkaline earth metal hydroxide is heated with said

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separated sulfonate oil containing phase in the presence of said emulsion-breaking liquid to render said sulfonate alkaline.

16. The process of claim 10 wherein said polyvalent-metal sulfonate is an alkaline earth metal sulfonate.

17. The process of claim 10 wherein the quantity of emulsion-breaking liquid employed is about 0.2% to 10% of the mixture.

18. A process as in claim 10 wherein the separated sulfonate oil containing phase is washed with water in the presence of said emulsion-breaking liquid.

19. A process of producing oil-soluble, water-insoluble, polyvalent-metal petroleum type sulfonate, substantially free from water-soluble constituents, comprising: preparing a mixture in water of oil-soluble, water-soluble, alkali metal petroleum sulfonate containing petroleum oil; supplying to said mixture an oil-soluble, organic emulsion-breaking liquid compound consisting of carbon, hydrogen and oxygen and containing from four to about eight carbon atoms per molecule; also supplying to said mixture a water-soluble, polyvalent metal salt to convert said alkali metal sulfonate to said oil-soluble, water-insoluble polyvalent-metal sulfonate, whereby said liquid compound facilitates separation of an oil phase containing said polyvalent-metal sulfonate and oil from an aqueous phase containing said water and water-soluble constituents; and recovering the resultant polyvalent-metal sulfonate and oil phase.

20. A process in accordance with claim 19, in which the emulsion-breaking compound is introduced into said mixture prior to introducing said polyvalent metal salt.

21. A process in accordance with claim 19 in which the emulsion-breaking compound is introduced into said mixture after formation of said polyvalent-metal sulfonate.

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**Certificate of Correction**

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ULRIC B. BRAY

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 9, line 46, for the word "dilutes" read *dilute*; line 48, for "hexanal" read *hexanol*; line 57, for "alcohol-esters" read *or alcohol-ethers*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of March, A. D. 1949.

**[SEAL]**

THOMAS F. MURPHY,

*Assistant Commissioner of Patents.*