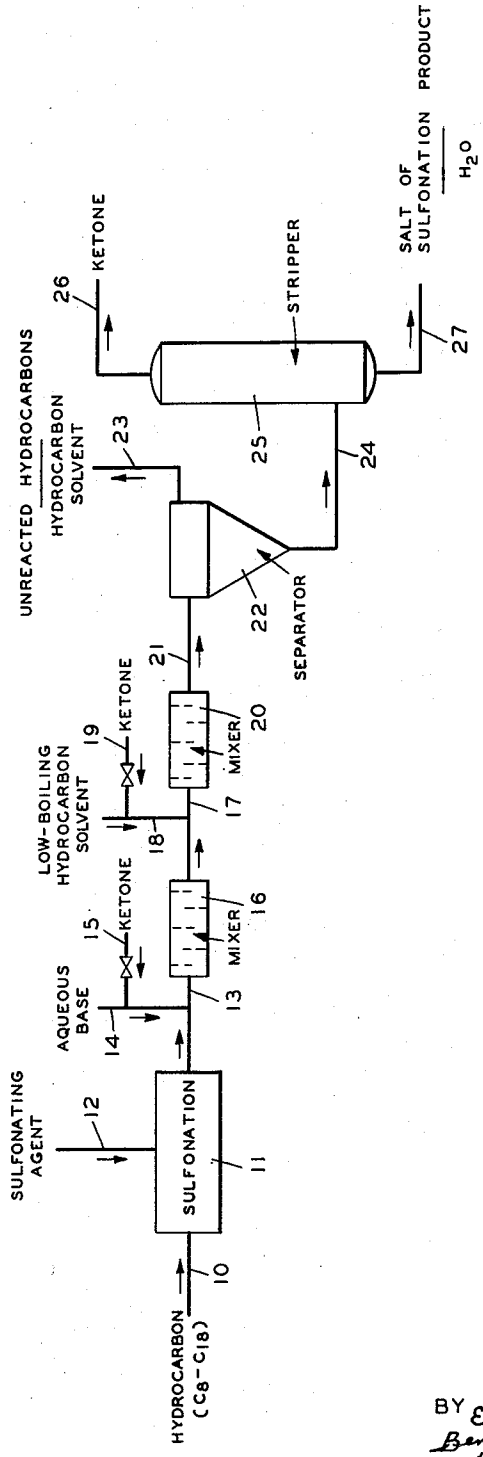
Jan. 18, 1955 G. G. LAUER 2,700,052

PREPARATION OF DETERGENT COMPOSITIONS

Filed March 25, 1952



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United States Patent Office 2,700,052 Patented Jan. 18, 1955

2,700,052

PREPARATION OF DETERGENT COMPOSITIONS

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Application March 25, 1952, Serial No. 278,400

16 Claims. (Cl. 260—504)

This invention relates to a process for preparing detergent compositions. More particularly, the invention relates to a process for preparing sulfonates in the form of salts of sulfonation products, of high purity and effectiveness, having detergent and wetting properties, which may be used for laundering and cleansing purposes in soft or hard water, and which do not leave undesirable deposits of unreacted materials on the surface of the object which is being cleansed.

This application is a continuation-in-part of my prior and co-pending application Serial No. 2,578, filed January 16, 1948, now abandoned.

The use of water-soluble sulfonates as detergents and wetting agents is well known. Heretofore, it has been proposed to prepare these sulfonates by treating mineral and petroleum oils with varying concentrations of sulfuric acid, and subsequently neutralizing the resulting sulfonation products with an alkali to obtain water-soluble sulfonates, suitable for use as detergent and wetting agents. It has been found, however, that the reaction of unsaturated hydrocarbons, in the presence of saturated hydrocarbons, with sulfuric acid or other sulfonating agents for the production of sulfonates or sulfates and their salts, invariably leaves in the product of reaction certain quantities of unreacted saturated hydrocarbons and/or polymerized material which are not attacked, even by very highly concentrated acids. The presence of these unreacted compounds in the sulfonates thus produced, has resulted in obtaining detergent compositions of limited cleansing and wetting properties, and consequent low market value.

It is, therefore, a primary object of the present invention to provide a process for preparing improved sulfonates having detergent and wetting properties.

Another object of the invention is to provide a process for preparing water-soluble sulfonates, having the aforementioned properties, which do not leave undesired deposits of unreacted materials when used as detergent or cleansing agents.

Still another object of the invention is to provide a process for preparing water-soluble sulfonates, having the aforementioned properties, from a hydrocarbon feed-stock in which unsaturated hydrocarbons are converted to these sulfonates, substantially free of unreacted saturated hydrocarbons and other unreacted materials.

With the above and other objects and features in view, the invention broadly comprises the improved process of preparing water-soluble sulfonates, in the form of a salt of a sulfonation product possessing the aforementioned properties, by treating a feed-stock comprising unsaturated and saturated hydrocarbons having from 8 to 18 carbon atoms per molecule with selected sulfonating agents under controlled conditions, to form a reaction product comprising a sulfonated oil; next contacting this reaction product with an aqueous solution of a base and a ketone to form a sulfonation salt and unreacted hydrocarbons; and finally separating the unreacted hydrocarbons by extracting these unreacted hydrocarbons with a relatively light hydrocarbon treating agent. In another modification of the process of the invention, the aforementioned sulfonation reaction product may be contacted with an aqueous solution of a base to form the corresponding salt and unreacted hydrocarbons, followed by contacting the salt with a mixture of the light hydrocarbon treating agent and ketone, to effect separation of unreacted hydrocarbons from the sulfonation product, as more fully hereinafter described. Particular novelty has been found to exist in the use of a ketone in the process of the invention, either in combination with an aqueous solution of the base in the aforementioned sulfonation step, or in combination with the relatively light hydrocarbon treating agent in the extraction step, wherein unreacted hydrocarbons are separated from the sulfonate. In this respect, I have found that alkali salts of the sulfonation product formed by contacting the aforementioned sulfonated hydrocarbons with an aqueous solution of a base exert a solutizing effect upon unreacted hydrocarbons, for the most part saturated hydrocarbons present in the formed sulfonation product, and hence subsequent extraction of these unreacted hydrocarbons by means of a light hydrocarbon material is extremely difficult. In adding a ketone, which is water-miscible in combination with either the aqueous solution of the base or the light hydrocarbon material, I have found that the solutizing power of the formed alkali salts of the sulfonation product upon the unreacted material is markedly lowered, and hence subsequent removal of the unreacted material from the resulting sulfonation salt is facilitated.

The invention will now be described in conjunction with the drawing, in which the sole figure is in the form of a flowsheet, diagrammatically illustrating the process of the invention and one form of the apparatus employed and capable of carrying out one embodiment thereof. It should be noted, however, that it is not intended that the invention be limited to the embodiment as illustrated, but is capable of other embodiments which may extend beyond the scope of the apparatus illustrated.

Referring to the drawing, a suitable acid reactive hydrocarbon feed-stock, such as mineral oil or a petroleum oil hydrocarbon fraction comprising unsaturated and saturated hydrocarbons having from 8 to 18 carbon atoms per molecule, is passed via line **10** into a sulfonation zone **11**. Sulfonation zone **11**, in the drawing, is representative of a reaction vessel or series of reaction vessels or similar conventional apparatus, into which a strong sulfonating agent is introduced through line **12**. This sulfonating agent may comprise a strong sulfonation reagent such as sulfuric acid having a concentration of at least 80%. Other sulfonating agents such as fuming sulfuric acid containing approximately 1% to 20% by weight of sulfur trioxide, aceto-sulfuric acid, or chlorosulfonic acid may be used. In all instances, it is preferred to use a strong sulfonating agent of suitable strength which is liquid at the desired reaction temperature. It should be noted, that the aforementioned reagents such as sulfuric acid or chlorosulfonic acid, etc. are herein referred to in their commonly accepted form, as sulfonating agents regardless of whether they may form true sulfonates or sulfuric acid esters (sulfates) or mixtures of both, according to the conditions of sulfonation.

In sulfonation zone **11**, the hydrocarbon-feed introduced through line **10**, and the sulfonating agent introduced through line **12**, are brought into rapid and intimate contact by any conventional contacting means, at a reaction temperature maintained in the range from about —20° C. to about 45° C. in the manner known to those skilled in the art. This sulfonating step is preferably carried out at atmospheric pressure but may be also carried out at super-atmospheric pressures if desired, within the above temperature range. The quantities of sulfonating agent admixed with quantities of C_8 to C_{18} hydrocarbons undergoing sulfonation treatment, may vary from ratios of approximately 1:3 to approximately 1:1, depending in each instance upon the quantities of unsaturated hydrocarbons present in the feed stock. Thus as the quantities of unsaturated hydrocarbons present in the feed are increased, the quantities of sulfonating agents employed are also proportionately increased. In some instances, it may be also desirable to add inert diluents to the sulfonating agent employed, such as ethyl ether or ethylene dichloride. In the latter event, the ratios of diluent to the hydrocarbon feed may be relatively high such as 5:1 or even higher.

From sulfonation zone **11**, the mixture of reactants is withdrawn through line **13**. This mixture comprises sulfonated oils containing unreacted hydrocarbons which

consist of either saturated hydrocarbons or both saturated and unsaturated hydrocarbons. To the sulfonated oil flowing through line **13**, there is next added under suitable temperature control effective to diminish the violence of the reaction, an aqueous solution of a base and a water-miscible ketone, introduced through line **14** with which line **13** connects, in an amount sufficient to neutralize the sulfonated oils (and any excess quantities of the sulfonating agent present) withdrawn from zone **11**, and to convert these oils to their corresponding salts. As previously indicated, the presence of the ketone in the aforementioned aqueous solution of the base tends to lower the solutizing power of the formed salts of the sulfonation product upon the unreacted material, thus facilitating the subsequent removal of the unreacted saturated or unreacted saturated and unsaturated hydrocarbons, as hereinafter described. For this purpose, I have found that I may employ such aqueous solutions of inorganic bases as alkali or alkali earth oxides, hydroxides, or carbonates. I may also employ aqueous solutions of organic bases such as trimethylamine, diethanolamine, or triethanolamine and the like. It should be noted that the dilution of the aforementioned bases may be affected not only by the addition of suitable quantities of water, but may also be attained by admixture with proper quantities of ice. The use of ice may be desirable in some instances in order to reduce the violence of the reaction resulting from the aforementioned neutralization. As indicated above, the ketone introduced with an aqueous solution of the aforementioned base into line **13** through line **14**, comprises a water-miscible ketone or a mixture of such ketones. While any water-miscible ketone may be successfully employed in the aforementioned step to lower the solutizing power of the formed alkali salts of the sulfonation product upon unreacted material, it is preferred, however, to employ ketones or mixtures of ketones such as acetone or methyl ethyl ketone. In addition, while the quantities of the water-miscible ketone or mixture of such ketones, which is added to the aqueous solution of the aforementioned base, may be varied in order to reduce the solutizing power of the formed alkali salts of the sulfonation product upon unreacted material to the degree desired, it is preferred, generally, to employ an aqueous solution of the base which contains from approximately 10% to 60% of the ketone by volume. It will be understood, that in each instance the quantities of the base and ketone used, may necessarily be varied to obtain optimum neutralization conditions, accompanied by a sufficient reduction of the solutizing power of the aforementioned salts upon unreacted material, as illustrated in the examples hereinafter shown. Ketones admixed with the base in line **14**, are introduced via valved-line **15**, with which line **14** connects.

In order to effect complete admixture of the aforementioned sulfonation product, and the aqueous solution of the base and ketone, these components are preferably transferred through line **13** to a mixer **16**. In mixer **16** the components are brought into intimate contact for a time sufficient to effect complete neutralization of the sulfonation product to form an aqueous solution containing the corresponding salts of the aforementioned reaction product, ketones and unreacted materials (these materials comprising saturated or both saturated and unsaturated hydrocarbons). This mixture is next withdrawn from mixer **16** through line **17**. In order to facilitate subsequent separation of the unreacted material, the mixture is next treated with a relatively light hydrocarbon solvent treating agent which is introduced into line **17**, via line **18**, in an amount sufficient to absorb therein substantially all of the unreacted material. This treating agent is preferably a low boiling hydrocarbon or hydrocarbon fraction having a boiling point lower than that of the unreacted hydrocarbons which are to be removed from the aforementioned formed sulfonation salts. Hence, I may preferably employ such hydrocarbons as liquid propane, butane, or pentane fractions, although higher boiling hydrocarbons or hydrocarbon fractions such as hexane or light naphthas, may also be successfully employed. While the proportions of the hydrocarbon treating agent and the solution comprising the formed sulfonation salts, excess ketones, and unreacted material may be varied, it is generally desirable to add the hydrocarbon treating agent to the solution in line **17** in a ratio of approximately 1:2. At this point, it should be noted that it is possible as previously indicated to modify the process of the invention by introducing the aforementioned water-miscible ketone, or ketone mixtures, together with the hydrocarbon treating agent into line **17** via line **18**, by closing off valved-line **15** and introducing the ketone component into line **18** via valved-line **19**. In such event, the quantities per volume of the ketone introduced via line **19**, may be present in a ratio of approximately 1:1 to 1:10 per volume of the aqueous solution of the neutralized sulfonation product in line **17**.

In order to effect complete admixture of the hydrocarbon solvent treating agent and the constituents in line **17**, these components are preferably transferred into a mixer **20**. From mixer **20**, this mixture is transferred through line **21** into a settling vessel, represented in the drawing by separator **22**. In separator **22**, the mixture is permitted to settle for a period of time sufficient to effect substantially complete separation, into an upper oil layer comprising a mixture of the hydrocarbon solvent treating agent and unreacted hydrocarbons, which is withdrawn through line **23** for further use or treatment outside the scope of the present process, and a lower layer comprising an aqueous solution of water-soluble salts of the sulfonation product and the ketone treating agent, which is withdrawn through line **24**. The aqueous solution in line **24** is next transferred to a stripper **25** (or any conventional separation media) which is operated under conditions effective to distill overhead the ketone treating agent which is withdrawn through line **26**. The purified aqueous solution of the aforementioned salts of the sulfonation product is withdrawn as bottoms through line **27** and may be transferred to any suitable storage facilities, or if so desired, can be dried by any suitable means, such as a spray dryer, to obtain the detergent composition in the solid form.

The aqueous solution of the salt of the sulfonation product in line **27** is free of unreacted hydrocarbons and has been found highly suitable as a detergent composition having outstanding detergent and wetting properties. This detergent is water-soluble, and has been found to have exceptional efficacy when used for laundering or cleansing purposes in either soft or hard water, without leaving undesirable deposits of unreacted materials or foreign matter on the surface or the object which is being cleansed. It will be understood, of course, that the detergent may also be used in highly dilute aqueous solutions, depending upon the degree of cleansing or wetting properties desired.

The following specific examples will serve to illustrate, but are not intended in any way to limit unduly the broad scope of the invention in the preparation of the aforementioned detergent compositions.

Example I

100 parts of a blend containing chiefly unsaturated C_8–C_{18} hydrocarbons having an average molecular weight of 200 and an iodine number of 93 obtained from the product produced in the catalytic hydrogenation of carbon monoxide, are slowly added to 50 parts of commercially water-free sulfuric acid with constant stirring for several minutes at a temperature of about 0°–20° C. and then poured over ice. The cooled mixture is next neutralized at a temperature below 45° C. with a 40% solution of sodium hydroxide containing approximately 30% acetone by volume. These constituents are thoroughly mixed and next contacted with approximately 75 parts of n-pentane to remove unreacted saturated hydrocarbons. The treated mixture is then subjected to phase separation to obtain an upper oil layer containing unreacted material dissolved in pentane, and a lower aqueous phase containing the formed sulfonation salt in admixture with acetone. The aqueous phase is next distilled at a temperature sufficiently high to take the ketone overhead. Thus a slightly hygroscopic material is obtained as bottoms having a yellowish appearance and which is found to possess excellent detergent and wetting properties.

Example II

To 100 parts of the blend in Example I, are slowly added 75 parts of commercial chlorosulfonic acid under similar conditions of temperature and reaction time as in Example I. The mixture is next poured over ice and neutralized with a 40% solution of sodium hydroxide. These constituents are thoroughly mixed and contacted with a mixture consisting of 60 parts of methyl ethyl ketone and 75 parts of n-pentane. The treated mixture is next sub-

jected to phase separation to obtain an upper phase containing unreacted saturated hydrocarbons dissolved in pentane, and a lower aqueous phase containing methyl ethyl ketone and a sulfonate in the form of the salt of the reaction product. This aqueous phase is next distilled at a temperature sufficiently high to take the ketone overhead, leaving the salt as bottoms possessing properties similar to that of the salt obtained in Example I.

Having thus described my invention, what I claim and desire to secure by Letters Patent is:

1. A process for preparing a salt of a sulfonation product wherein said salt possesses detergent and wetting properties which comprises the steps of: contacting a feedstock comprising unsaturated and saturated hydrocarbons having from 8 to 18 carbon atoms per molecule with a sulfonating agent containing a free acid group, whereby unsaturated hydrocarbons are reacted without reacting saturated hydrocarbons, to form a reaction product comprising a sulfonated oil; contacting said sulfonated oil with a treating agent comprising an aqueous solution of a base to form a mixture comprising a salt of said sulfonated oil and unreacted saturated hydrocarbons; subjecting said mixture to extraction treatment with a treating agent comprising a light hydrocarbon to obtain an extract phase comprising unreacted saturated hydrocarbons and hydrocarbon treating agent and a raffinate phase comprising said salt of the sulfonated oil; introducing a water-miscible ketone in combination with one of said treating agents in said aforementioned treating steps; separating said extract and raffiniate phases; and separating said salt of the sulfonated oil from said raffinate phase.

2. A process for preparing a salt of a sulfonation product wherein said salt possesses detergent and wetting properties which comprises the steps of: contacting a feedstock produced in the catalytic hydrogenation of carbon monoxide comprising unsaturated and saturated hydrocarbons having from 8 to 18 carbon atoms per molecule with a sulfonating agent containing a free acid group at a temperature between about —20° C. and about 45° C., whereby unsaturated hydrocarbons are reacted without reacting saturated hydrocarbons, to form a reaction product comprising a sulfonated oil; contacting said sulfonated oil with a treating agent comprising an aqueous solution of a base to form a mixture comprising a salt of said sulfonated oil and unreacted saturated hydrocarbons; subjecting said mixture to extraction treatment with a treating agent comprising a light hydrocarbon to obtain an extract phase comprising unreacted saturated hydrocarbons and hydrocarbon treating agent and a raffinate phase comprising said salt of the sulfonated oil; introducing a water-miscible ketone in combination with one of said treating agents in said aforementioned treating steps; separating said extract and raffinate phases; and separating said salt of the sulfonated oil from said raffinate phase.

3. A process for preparing a salt of a sulfonation product wherein said salt possesses detergent and wetting properties which comprises the steps of: contacting a feedstock comprising unsaturated and saturated hydrocarbons having from 8 to 18 carbon atoms per molecule with a sulfonating agent containing a free acid group, whereby unsaturated hydrocarbons are reacted without reacting saturated hydrocarbons, to form a reaction product comprising a sulfonated oil; contacting said sulfonated oil with an aqueous solution of a base and water-miscible ketone to form a mixture comprising a salt of said sulfonated oil and unreacted saturated hydrocarbons; subjecting said mixture to extraction treatment with a light hydrocarbon treating agent to obtain an extract phase comprising unreacted saturated hydrocarbons and hydrocarbon treating agent and a raffinate phase comprising said salt of the sulfonated oil; separating said extract and raffinate phases; and separating said salt of the sulfonated oil from said raffinate phase.

4. A process for preparing a salt of a sulfonation product wherein said salt possesses detergent and wetting properties which comprises the steps of: contacting a feedstock produced in the catalytic hydrogenation of carbon monoxide comprising unsaturated and saturated hydrocarbons having from 8 to 18 carbon atoms per molecule with a sulfonating agent containing a free acid group at a temperature between about —20° C. and about 45° C., whereby unsaturated hydrocarbons are reacted without reacting saturated hydrocarbons, to form a reaction product comprising a sulfonated oil; contacting said sulfonated oil with an aqueous solution of a base and a water-miscible ketone to form a mixture comprising a salt of said sulfonated oil and unreacted saturated hydrocarbons; subjecting said mixture to extraction treatment with a light hydrocarbon treating agent to obtain an extract phase comprising unreacted saturated hydrocarbons and hydrocarbon treating agent and a raffinate phase comprising said salt of the sulfonated oil; separating said extract and raffinate phases; and separating said salt of the sulfonated oil from said raffinate phase.

5. A process in accordance with claim 4 wherein said base is an alkali metal hydroxide.

6. A process in accordance with claim 4 wherein said base is trimethylamine.

7. A process in accordance with claim 4 wherein said base is diethanolamine.

8. A process in accordance with claim 4 wherein said ketone is acetone.

9. A process in accordance with claim 4 wherein said ketone is methyl ethyl ketone.

10. A process in accordance with claim 4 wherein said sulfonating agent is sulfuric acid having a concentration of at least 80%.

11. A process in accordance with claim 4 wherein said sulfonating agent comprises fuming sulfuric acid containing from 1 to 20% by weight of sulfur trioxide.

12. A process in accordance with claim 4 wherein said sulfonating agent is chlorosulfonic acid.

13. A process in accordance with claim 4 wherein said sulfonating agent is aceto-sulfuric acid.

14. A process for preparing a salt of a sulfonation product wherein said salt possesses detergent and wetting properties which comprises the steps of: contacting a feedstock comprising unsaturated and saturated hydrocarbons having from 8 to 18 carbon atoms per molecule with a sulfonating agent containing a free acid group, whereby unsaturated hydrocarbons are reacted without reacting saturated hydrocarbons, to form a reaction product comprising a sulfonated oil; contacting said sulfonated oil with an aqueous solution of a base to form a mixture comprising a salt of said sulfonated oil and unreacted saturated hydrocarbons; subjecting said mixture to extraction treatment with a mixture comprising a light hydrocarbon treating agent and a water-miscible ketone to obtain an extract phase comprising unreacted saturated hydrocarbons and hydrocarbon treating agent and a raffinate phase comprising said salt of the sulfonated oil; separating said extract and raffinate phases; and separating said salt of the sulfonated oil from said raffinate phase.

15. A process for preparing a salt of a sulfonation product wherein said salt possesses detergent and wetting properties which comprises the steps of: contacting a feedstock produced in the catalytic hydrogenation of carbon monoxide comprising unsaturated and saturated hydrocarbons having from 8 to 18 carbon atoms per molecule with a sulfonating agent containing a free acid group at a temperature between about —20° C. and about 45° C., whereby unsaturated hydrocarbons are reacted without reacting saturated hydrocarbons, to form a reaction product comprising a sulfonated oil; contacting said sulfonated oil with an aqueous solution of a base to form a mixture comprising a salt of said sulfonated oil and unreacted saturated hydrocarbons; subjecting said mixture to extraction treatment with a mixture comprising a light hydrocarbon treating agent and a water-miscible ketone to obtain an extract phase comprising unreacted saturated hydrocarbons and hydrocarbon treating agent and a raffinate phase comprising said salt of the sulfonated oil; separating said extract and raffinate phases; and separating said salt of the sulfonated oil from said raffinate phase.

16. A process for preparing a salt of a sulfonation product wherein said salt possesses detergent and wetting properties which comprises the steps of: contacting a feedstock comprising unsaturated and saturated hydrocarbons having from 8 to 18 carbon atoms per molecule with sulfuric acid having a concentration of at least 80% at a temperature between about —20° C. and about 45° C., whereby unsaturated hydrocarbons are reacted without reacting saturated hydrocarbons, to form a reaction product comprising a sulfonated oil; contacting said sulfonated oil with an aqueous solution of an alkali metal hydroxide and acetone to form a mixture comprising a salt of said sulfonated oil and unreacted saturated hydrocarbons; subjecting said mixture to extraction treatment with a light hy-

drocarbon treating agent to obtain an extract phase comprising unreacted saturated hydrocarbons and hydrocarbon treating agent and a raffinate phase comprising said salt of the sulfonated oil; separating said extract and raffinate phases; and separating said salt of the sulfonated oil from said raffinate phase.

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