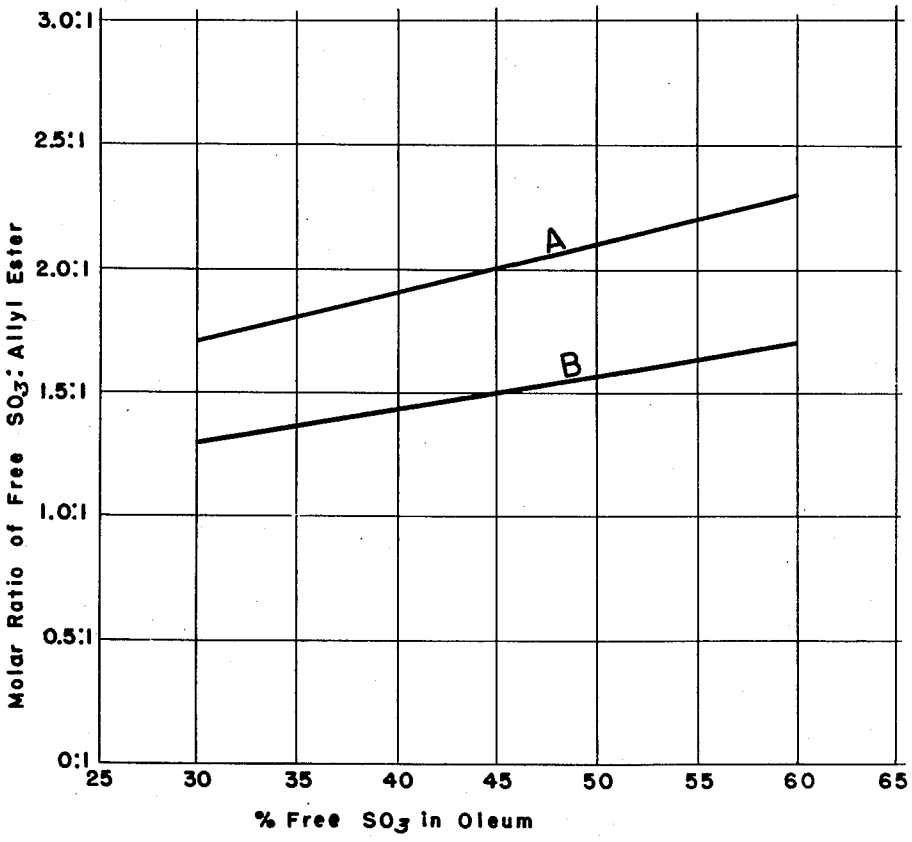
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SULFONATION OF OLEFINES

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SULFONATION OF OLEFINS

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This invention relates to sulfonation of olefines in the production of wetting, sudsing and detergent agents, and to products so produced.

It is known that useful surface-active agents may be produced by the reaction of sulfonating agents such as sulfuric acid, oleum, chlorsulfonic acid, sulfur trioxide and the like on many high molecular organic compounds such as alcohols, olefines, alkylolamides, unsaturated acids, aromatic hydrocarbons, alkyl aromatic hydrocarbons and related compounds. In many cases, it is necessary to use an excess of sulfonating agent over and above the amount theoretically required for the reaction in order to bring about a high degree of sulfonation, the term "sulfonation" being used broadly herein to designate reaction with such acidic sulfur derivatives as the above, whether true sulfonates, sulfuric acid esters or mixtures thereof are produced by the reaction. For example, it is disclosed in copending application of John S. Brod, Serial No. 38,405, bearing even date herewith, that light colored monoglyceride sulfonates of high wetting, sudsing and detergent power may be produced from allyl esters of soap-forming monocarboxylic acids containing from 8 to 18 carbon atoms; in order to obtain these desirable products, sulfonation is effected with oleum of specified strength and amount under specified conditions. The resulting acid sulfonation mixture may be used as such or it may if desired be neutralized with certain specified precautions.

Using the procedures described in the above-mentioned application of Brod, a considerable excess of acid normally remains unreacted at the conclusion of the sulfonation step, and this is eliminated in the final steps of the process. This elimination is most simply accomplished by neutralization of the acid mixture, whereby the sulfonic acid of the allyl ester is converted into useful salt and the excess free SO_3 and H_2SO_4 are converted into sodium sulfate or other salt of relatively little value. It is an object of the present invention to provide means whereby this excess of unreacted acid may be more profitably utilized. More specifically, it is an object to provide means whereby it may be utilized in producing agents richer in surface-active products which possess wetting, sudsing and detergent properties and poorer in inorganic salts of relatively little value. It is a further object to provide means whereby mixed compounds of high wetting, sudsing and detergent power may be prepared from acid sulfonation mixtures wherein an excess of unreacted sulfonating agent remains.

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In addition to utilizing residual sulfonating power possessed by acid sulfonation mixtures, an important object of our invention is to provide means for satisfactorily sulfonating olefines and obtaining useful surface-active agents therefrom. It has been known previously that certain sulfonated olefines are good wetting, sudsing and washing agents, but their sulfonation has in the past been unusually difficult. Chlorsulfonic acid has proved undesirable for this purpose, because of the low yields obtained therewith and extensive side reactions. Weak oleums, or low temperatures of reaction usually result in sulfuric acid ester formation, while strong oleums or high temperature cause discoloration and side reactions, and in both cases the resulting products require purification before they become suitable for most uses. So far as we are aware sulfonates having good sudsing, wetting and detergent power without further purification have in the past been made from olefines only by treatment with concentrated sulfuric acid in the presence of acetic anhydride, and this process is expensive and hence not commercially attractive. An object of our invention is to provide an improved means of effecting the sulfonation of the said olefines, employing as the sulfonating agent the residual SO_3 and H_2SO_4 which remains after the sulfonation of the allyl esters.

As a broad aspect of the invention, our object is to provide an improved process of sulfonating high molecular olefines, during which process the action of the sulfonating agent is "cushioned" by the presence of a sulfonic acid of a monoglyceride or a similar ester.

Other objects will appear in the course of the description which follows.

In the application of Brod, it is shown that sulfonation of high molecular allyl esters occurs smoothly, rapidly and to a high degree of completeness when oleum containing from 30 per cent to 60 per cent free SO_3 is used in such amount that the molar ratio of free SO_3 added:allyl ester lies above line B of Fig. 1 hereof (wherein the molar ratio of free SO_3 added:allyl ester is plotted on the ordinate scale and the strength of the oleum, expressed as the per cent free SO_3 therein, is plotted on the abscissa scale) at the completion of the addition of the reactants, and in such manner that at no time during the addition does this ratio lie substantially above line A; i. e., the ester may be in considerable excess in the early stages of the reaction, this excess decreasing as the addition of the reactants nears completion, or alternatively the ratio of free SO_3

added:ester may remain relatively constant throughout; but in neither case should the acid at any time be in substantially greater excess than shown by line A. Thus when oleum containing about 60 per cent free SO_3 is used, this molar ratio should be at least 1.7:1 when all of the oleum has been added to the allyl ester, but at no time during the addition should it substantially exceed 2.3:1. It is further disclosed therein that the oleum and the ester should be promptly, thoroughly and continuously mixed, that the temperature of the reaction mixture should be maintained between 10° C. and 60° C., and preferably between 30° and 50° C., and that neutralization of the acid mixture, if desired, should be carried out at a temperature not substantially above 50° C. and in such manner that the mixture should not be substantially alkaline at any time during the neutralization, and that at the end of the neutralization the pH of the mixture should preferably lie between about 4.5 and about 7.

Under these sulfonating conditions, the excess acid present at the end of the sulfonating reaction, prior to neutralization, is not capable of satisfactorily sulfonating additional amounts of allyl ester. Yet we have found that it does possess great sulfonating power toward high molecular olefines, and that as a result the acid reaction mixture can be used to prepare further amounts of valuable wetting, sudsing and washing agents. This result is surprising, in view of the above-mentioned inability of the acid mixture to sulfonate additional amounts of allyl ester satisfactorily. Furthermore, if the allyl ester is premixed with, say, half of its own weight or more of olefine, prior to treatment with the sulfonating agent, low yields and poor products result. Only small proportions of olefine can be treated successfully by premixing before sulfonation. Best results, with larger proportions of olefine, are obtained by adding the olefine after sulfonation of the allyl ester has reached completion.

When the residual sulfonating power of an acid sulfonation reaction mixture is being exploited as herein described, it is often desirable to control the reaction by using as a thinning agent a saturated volatile aliphatic liquid diluent which is substantially inert to oleum, such for example as ethers, hydrocarbons, and chlorinated hydrocarbons as described by Brod. In order to facilitate subsequent removal from the system, if desired, we prefer to use a thinning agent having a boiling point below that of water. The amount of thinning agent required varies, depending upon its own character and the character of the material being sulfonated. For example, a thinning agent such as ethylene dichloride must commonly be used in an amount equal to at least one third of the olefinic ester; in the case of a less efficient thinning agent, larger amounts must be used for optimum results.

The following examples, in which all parts are by weight, illustrate in greater detail ways in which we practice our invention, but it will be understood that these examples are illustrative only and that the invention is not limited to the details thereof except as indicated in the appended claims.

Example 1.—The allyl esters of mixed fatty acids from coconut oil were sulfonated in an externally cooled vessel equipped with an efficient stirrer the blades of which scraped the sides of the vessel. One hundred parts of the allyl ester, dissolved in 100 parts of ethylene dichloride, were added to this vessel with continuous stirring, and simultaneously there were added 117 parts of oleum containing 58% free SO_3. The rates of addition were such that the weight ratio of oleum to allyl ester solution never substantially exceeded 117:200, and the temperature of the reaction mixture was maintained between 30° and 35° C. throughout the major part of the reaction. The molar ratio of free SO_3 added:allyl ester was 2.1:1. To this mixture there were then added, slowly and with constant stirring, 80 parts of hexadecene-1. The mixture was stirred for 2 minutes following this addition, during which time the temperature remained between 25° and 30° C. Neutralization was then carried out by simultaneously and slowly adding the reaction mixture and a 28% caustic soda solution in closely equivalent amounts to water containing cracked ice, regulating the additions so as to maintain the temperature below 40° C. and the pH between 5.5 and 6.5. Analysis showed that 83% of the ester and 73% of the olefine had been sulfonated. The product possessed sudsing, wetting and washing power. The sodium sulfate content of the product was only about two thirds as high as it would normally be if no hexadecene were added.

Example 2.—One hundred parts of the allyl ester of mixed fatty acids of coconut oil were added to 80 parts of ethylene dichloride and the mixture was sulfonated as in Example 1, using 120 parts of 60% oleum, keeping the temperature between 30° and 35° C. and keeping the weight ratio of oleum:allyl ester solution not substantially more than 120:180 at any time. The molar ratio of free SO_3:ester was 2.2:1. To this acid mixture there were added slowly and with constant stirring, 80.6 parts of tetradecene. The mixture was stirred for one minute following this addition, during which the temperature did not exceed 30° C. The reaction mixture was then added to 1200 parts of crushed ice and was neutralized with caustic soda until alkaline to methyl orange. Analysis indicated that 63% of the ester and 81% of the tetradecene had been sulfonated.

When coconut fatty acid esters of allyl alcohol have been sulfonated with oleum containing about 60 per cent free SO_3 in such amount that the molar ratio of free SO_3:ester is from about 1.7:1 to about 2.3:1, and when high molecular olefines are added to this acid reaction mixture after the primary reaction has taken place, reaction with the added olefine is rapid. With efficient stirring, one or two minutes is a long enough time to allow for the reaction. The use of hexadecene-1 has been illustrated in Example 1. Amounts of hexadecene as high as 150 per cent of the weight of allyl ester have been successfully used in such sulfonations, but we find that it is as a rule preferable that the weight of olefine should not exceed about 80 to 100 per cent of the weight of the allyl ester, otherwise the degree of sulfonation falls and the performance of the resulting product suffers.

In complex mixtures, such as those obtained by adding olefines to allyl ester-oleum sulfonation mixtures, it is difficult to determine with certainty the character and proportions of the various compounds finally present. Thus we are unable to state to what extent the olefines are converted into true monosulfonates, to what extent into sulfuric acid esters and to what extent both sulfonation and sulfation occur in the same olefine molecule. In general, high temperatures and strong acids favor true sulfonation, and low temperatures and weak acids favor sulfation, but

it will be understood that we use the term "sulfonation" generically herein to include the formation of sulfuric acid esters as well as the formation of sulfonic acids. Whatever the composition, our invention makes it possible to attain high yields of highly efficient wetting, sudsing and washing agents, and ones which do not require purification in order to be useful. This is the more important because, as has been explained before, previous methods of sulfonation of olefines have either been discouragingly expensive, or have given products of poor performance, whereas our invention makes possible the utilization of the residual sulfonating power of allyl ester sulfonation mixtures and the utilization of olefines to produce useful surface active agents.

By "high molecular" olefines we mean those of from about 8 to about 30 carbon atoms, for example those which can be derived from petroleum sources or by hydrogenation of carbon monoxide or by polymerization of alkylenes. However, more efficient sulfonated products are normally obtained from straight chain olefines and from alpha olefines, and particularly from those containing about 12 to 18 carbon atoms, hence such olefines are preferred.

Our process not only permits putting to use the excess sulfonating power remaining in allyl ester-oleum acid mixtures, but it also lessens the cost, per unit of active material in the final product, of using relatively costly thinning agents. Instead of increasing viscosity as might be expected and thereby increasing the amount of thinning agent required, the presence of an olefine in the sulfonation mixture has the opposite effect, decreasing viscosity.

We have described our invention largely as though it were confined to the utilization of the residual sulfonating power of mixtures of oleum and allyl ester. In such cases, an excess of acid must necessarily be used in order to attain the desired degree of sulfonation of the ester. This is true also in the sulfonation of high molecular esters of other low molecular olefinic monohydric alcohols, by which we mean alcohols containing not more than 5 carbon atoms, such as methallyl, ethallyl, crotyl alcohols, etc. It will be seen that the principles of our invention apply to the case of sulfonation of such esters, and also to sulfonation by means other than oleum and of materials other than olefinic esters. In numerous cases an excess of sulfonating agent is either essential to, or at least not harmful to, the primary sulfonation reaction, and such excess may be used and the residual sulfonating power may be utilized as we have described. Furthermore, it will be seen that following the sulfonation of a high molecular ester of a low molecular olefinic alcohol with oleum, either in the presence of or in the absence of a thinning agent, the residual sulfonating power of the free SO_3 or of the H_2SO_4 may be utilized by adding an olefine thereto, and that additional amounts of oleum or free SO_3 or H_2SO_4 may if necessary be added thereto in order to effect a high degree of sulfonation of the olefine. In this way the previously-formed free sulfonic acid of the olefinic ester, or more broadly a previously-formed sulfuric reaction product of a high molecular aliphatic compound (said reaction product being characterized by one alkyl group of about 8 to about 18 carbon atoms) acts as a cushion to render less drastic the sulfonation reaction and larger proportions of olefine may be handled than hereinbefore disclosed. Thus for example the sulfuric reaction product of lauric allyl amide may be utilized as a cushioning agent in the sulfonation of olefines.

Monoglyceride sulfonic acids or the sulfonic acids of similar esters of high molecular fatty acids and low molecular olefinic monohydric alcohols may be made by processes other than those described herein, and it will be understood that the cushioning effect of these sulfonic acids may be utilized in the sulfonation of high molecular olefines in accordance with the present invention, regardless of the origin or mode of manufacture of the monoglyceride sulfonic acid. In preparing olefine sulfonates by subjecting higher olefines to sulfonation reaction in the presence of monoglyceride sulfonic acid (made by any desired method) we prefer that the temperature should not substantially exceed 60° C.

In practicing our invention, it is common to neutralize the finished sulfonation mixture, although for some uses this may be unnecessary or even undesirable. A neutralizing agent is commonly chosen such that the resulting salt or salts shall be water-soluble. Alkali metal salts of the sulfonated products, particularly the sodium salts, are the most widely applicable of the salts, but alkaline earth and heavy metal salts also are frequently sufficiently soluble to be useful. Salts of ammonium and of various organic bases are also used. Neutralization may thus be with alkali hydroxides, alkaline salts, oxides or hydroxides of alkaline earths or of heavy metals, ammonia and other nitrogen bases.

While the carbon-to-sulfur linkage of true sulfonic acids is stable, the carbon-to-oxygen-to-sulfur linkage of sulfuric acid esters is subject to hydrolysis, this hydrolysis being favored by acids and by high temperature. On the other hand, the carboxylic acid ester linkage of sulfonated allyl esters readily hydrolyzes in hot alkaline solutions. It will thus be seen that precautions are commonly necessary in the neutralization step; that these precautions involve avoidance of high temperature, and that the degree of acidity or of alkalinity desirable depends upon the character of the particular compounds in question. In general, when olefines are used according to the process herein described to utilize the residual sulfonating power of oleum-allyl ester sulfonation mixtures, neutralization temperature should not substantially exceed 50° C. and should preferably be 20° C. or lower; the alkaline neutralizing agent should be added to the acid mixture with efficient stirring, in such manner and at such a rate that at no time during the neutralization is the mixture substantially alkaline; and the final pH of the mixture should not be substantially less than 4.5 nor substantially more than 7.

Temperature control during neutralization may be effected in various ways, such as by external or artificial cooling, or by neutralizing in the presence of a large proportion of previously neutralized material, or by coupling such procedure with artificial cooling.

Following neutralization, the sulfonated products may be treated in conventional manner to remove unsulfonated organic matter, inorganic salts, water, etc., or they may if desired be used without drying or further purification. One of the great advantages inherent in our invention is that in this manner detergents are obtained which without purification have a high content

of active sulfonated compound and a low content of relatively inactive inorganic salt.

Conventional modifications in procedure to make the sulfonation process continuous lie naturally within the scope of our invention.

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

1. The process of preparing wetting, sudsing and washing agents which comprises admixing a high molecular allyl ester with oleum containing from 30 per cent to 60 per cent free sulfur trioxide by weight to effect reaction between said ester and said oleum, the oleum being added to the ester in such manner and amount that the molar ratio of free sulfur trioxide added:allyl ester lies above line B of Figure 1 when all of the oleum has been added, but at no time during the addition lies substantially above line A, while restraining the temperature of the reaction mixture from rising substantially above 60° C.; thereafter admixing the acid mixture with a high molecular olefine, to cause reaction therewith while restraining the temperature of the reaction mixture from rising substantially above 60° C.; and thereafter neutralizing the product to form a water-soluble salt by mixing therewith an alkaline neutralizing agent in such manner that the mixture is at no time substantially alkaline and while restraining the temperature from rising substantially above 50° C.

2. The process of claim 1 wherein the olefine is essentially a straight chain olefine.

3. The process of claim 1 wherein the olefine is essentially an alpha olefine.

4. The process of claim 1 wherein the olefine contains from about 12 to about 18 carbon atoms.

5. The process of claim 1 wherein the allyl ester and the oleum are admixed in the presence of a thinning agent consisting essentially of a saturated volatile aliphatic liquid substantially inert to oleum.

6. The process of claim 1 wherein the allyl ester and the oleum are admixed in the presence of ethylene dichloride.

7. The process of claim 1 wherein the oleum and the allyl ester are admixed in the presence of a thinning agent consisting essentially of a saturated volatile aliphatic liquid substantially inert to oleum, the weight of said thinning agent being at least one third as great as the weight of allyl ester, and wherein the olefine is essentially a straight chain alpha olefine of from about 12 to about 18 carbon atoms, the weight of said olefine not substantially exceeding the weight of allyl ester.

8. The process of claim 7 wherein the thinning agent is ethylene dichloride.

9. The process of preparing wetting, sudsing and washing agents which comprises admixing a high molecular allyl ester with oleum to effect reaction therewith, the oleum containing about 60 per cent free SO_3 by weight and being added to the allyl ester in such manner and amount that the molar ratio of free SO_3 added:allyl ester is at least 1.7:1 when all of the oleum has been added but at no time during the addition substantially exceeds 2.3:1, restraining the temperature of the reaction mixture from rising substantially above 60° C., admixing the acid reaction mixture with a high molecular olefine to effect reaction therewith while restraining the temperature of the said reaction mixture from rising substantially above 60° C., and thereafter neutralizing the product to form a water-soluble salt by mixing therewith an alkaline neutralizing agent in such manner that the mixture is at no time substantially alkaline while restraining the temperature from rising substantially above 50° C.

10. The process of preparing wetting, sudsing and washing agents which comprises admixing oleum with a high molecular allyl ester in the presence of a thinning agent consisting essentially of a saturated volatile aliphatic liquid substantially inert to oleum, thereby to effect reaction of said oleum with said ester, the oleum containing about 60 per cent free SO_3 by weight and being added to the allyl ester in such manner and amount that the molar ratio of free SO_3 added:allyl ester is at least 1.7:1 when all of the oleum has been added but at no time during the addition substantially exceeds 2.3:1, restraining the temperature of the reaction mixture from rising substantially above 60° C., admixing the acid reaction mixture with a high molecular olefine to effect reaction therewith while restraining the temperature of the said reaction mixture from rising substantially above 60° C., and thereafter neutralizing the product to form a water-soluble salt by mixing therewith an alkaline neutralizing agent in such manner that the mixture is at no time substantially alkaline while restraining the temperature from rising substantially above 50° C.

11. The process of claim 10 wherein the amount of thinning agent is equal to at least one third of the weight of allyl ester, and wherein the olefine is essentially a straight chain alpha olefine of from about 12 to about 18 carbon atoms, the weight of said olefine not substantially exceeding the weight of allyl ester.

12. The process of claim 10 wherein the thinning agent is ethylene dichloride in an amount equal to at least one third of the weight of allyl ester, and wherein the olefine is essentially a straight chain alpha olefine of from about 12 to about 18 carbon atoms, the weight of said olefine not substantially exceeding the weight of allyl ester.

13. Water-soluble salts of acids of the group consisting of sulfonic acids, sulfuric acid esters and mixtures thereof, obtained by the process of claim 1 and characterized by marked sudsing and washing power.

14. The process of preparing sudsing and washing agents which comprises sulfonating a high molecular olefine by subjecting said olefine to reaction with a sulfonating agent selected from the group consisting of oleum, free SO_3, sulfuric acid and mixtures thereof, the said sulfonation being effected in the presence of the sulfonic acid of an ester of a low molecular olefinic alcohol with a high molecular soap-forming monocarboxylic acid; allowing said olefine and said sulfonating agent to react while restraining the temperature of the reaction mixture from rising substantially above 60° C., and thereafter neutralizing the product to form a water-soluble salt by mixing therewith an alkaline neutralizing agent in such manner that the mixture is at no time substantially alkaline and while restraining the temperature from rising substantially above 50° C.

15. The process of claim 14 wherein the ester of a low molecular olefinic alcohol is an ester of allyl alcohol and wherein the said process is carried out in the presence of a thinning agent consisting essentially of a saturated volatile aliphatic liquid substantially inert to oleum.

16. The process of preparing sudsing and

washing agents which comprises sulfonating a high molecular olefine by subjecting it to reaction with a sulfonating agent selected from the group consisting of oleum, free SO_3, sulfuric acid and mixtures thereof, the said reaction being effected in the presence of the previously-formed sulfuric reaction product of a high molecular aliphatic compound, said reaction product being characterized by one alkyl group of about 8 to about 18 carbon atoms.

17. A mixture of a sulfonated olefine and the sulfuric reaction product of a high molecular aliphatic compound, said reaction product being characterized by one alkyl group of about 8 to about 18 carbon atoms and said mixture being obtained by the process of claim 16 and possessing marked sudsing and washing power.

18. The process of preparing wetting, sudsing and washing agents which comprises admixing an ester of a low molecular olefinic alcohol and a high molecular soap-forming mono-carboxylic acid with oleum containing from 30 per cent to 60 per cent free sulfur trioxide by weight to effect reaction between said ester and said oleum, the oleum being added to the ester in such manner and amount that the molar ratio of free sulfur trioxide added:allyl ester lies above line B of Figure 1 when all of the oleum has been added, but at no time during the addition lies substantially above line A, while restraining the temperature of the reaction mixture from rising substantially above 60° C.; thereafter admixing the acid mixture with a high molecular olefine, to cause reaction therewith while restraining the temperature of the reaction mixture from rising substantially above 60° C.; and thereafter neutralizing the product to form a water-soluble salt by mixing therewith an alkaline neutralizing agent in such manner that the mixture is at no time substantially alkaline and while restraining the temperature from rising substantially above 50° C.

19. A mixture of the sodium salt of a high molecular sulfonated olefine and the sodium salt of the sulfonation product of a high molecular allyl ester, said mixture being obtained by the process of claim 1 and being characterized by marked sudsing and washing power.

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