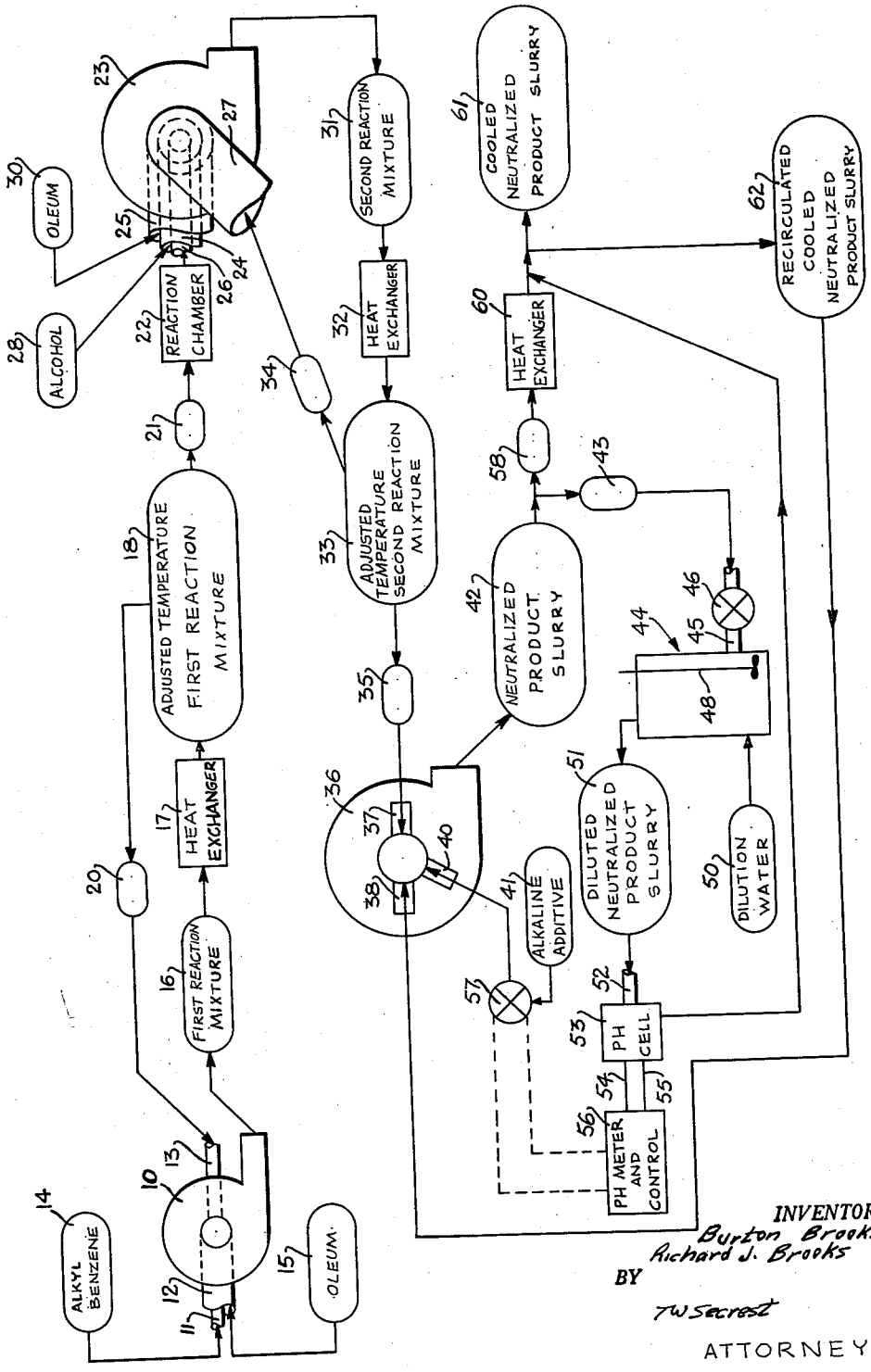
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PROCESS FOR PREPARING A MIXTURE OF AN ALKYL BENZENE SULFONATE AND AN ALCOHOL SULFATE

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PROCESS FOR PREPARING A MIXTURE OF AN ALKYL BENZENE SULFONATE AND AN ALCOHOL SULFATE

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This invention is for the series sulfonation of an aromatic and the sulfation of an alcohol so as to produce a sulfonic acid and an organic sulfuric acid which can be neutralized together to make a surface active material.

An object of this invention is to provide a process for the conversion of alkyl benzene and tallow alcohol into acids.

Another object is to provide a process for said conversion and which process requires less equipment than previously employed processes.

A still further object is to provide a process for said conversion and which process produces a more homogeneous product.

Another desirable object is the provision of a process and apparatus for said conversion and which apparatus can be made in a compact unit.

A still further and important object is to provide a process which produces a higher quality product than previously employed processes in that nearly all of the alcohol is sulfated.

A further object is to provide a process and apparatus wherein the apparatus is less expensive than previously used apparatus.

These and other important objects and advantages will be more particularly brought out by reference to the following specification, drawing and claims.

In this process alkyl benzene and a sulfonating agent are reacted to form a first reaction mixture. Then, this first reaction mixture is mixed with a fatty alcohol and a sulfonating agent to form a second reaction mixture. This second reaction mixture comprises alkyl benzene sulfonic acid and the organic sulfuric acids of the fatty alcohol. The second reaction mixture is mixed with an alkaline material such as sodium hydroxide to form a salt mixture. The salt mixture can be employed as a detergent or surface active material.

Referring to the FIGURE of the drawing it is seen that the apparatus employed for carrying out this invention comprises a centrifugal pump 10 having two concentric inlet pipes 11 and 12 which terminate inside of the pump. These pipes terminate a fraction of an inch from the impeller blade. For example, the pipes may terminate one-eighth of an inch away from the blade. Also leading into the centrifugal pump is an inlet pipe 13. This pipe may be in a concentric relation with pipes 11 and 12 or may terminate inside of pump 10. For example, the pipe 13 may terminate near the periphery of the impeller. Alkyl benzene 14 having from ten to eighteen carbon atoms in the side chain is introduced into the pump 10 through pipe 11. A sulfonating agent such as oleum or sulfuric acid 15 is introduced into the pump through pipe 12. The alkyl benzene 14 and the sulfonating agent are substantially simultaneously contacted and mixed to form a first reaction mixture 16. This reaction mixture 16 is fed into a heat exchanger 17 wherein the temperature of the reaction mixture is adjusted to a temperature in the range of 110–130° F. to form an adjusted temperature first reaction mixture 18. This mixture 18 is split into two fractions. A first fraction 20 is recycled and introduced through pipe 13 into the pump 10 so as to be agitated and mixed with the sulfonating agent and alkyl

benzene to form the first reaction mixture. The volume of this first fraction is at least fifteen times as large as the combined volume of the alkyl benzene 14 and the oleum 15 introduced into the pump 10. A second fraction 21 is introduced into a reaction chamber 22 and allowed to digest in said chamber for a period of time varying from approximately five to thirty minutes.

In this apparatus there is a second centrifugal pump 23 having two concentric pipes 24 and 25 leading into the inlet side of the pipe. The two pipes 24 and 25 terminate a fraction of an inch from the impeller of the pump. For example, these pipes may terminate about one-eighth of an inch from the pump. Also leading into the pump 23 is a pipe 26 which may be in concentric relationship with the pipes 24 and 25 or may terminate inside of the pump casing and near the periphery of the impeller. A fourth pipe 27 leads into the pump 23 and may be in concentric relationship with the pipes 24 and 25 or may terminate inside the pump casing near the periphery of the impeller. A fatty alcohol 28 is introduced through pipe 24 to pump 23 and a sulfonating agent such as sulfuric acid or oleum 30 is introduced through pipe 25 into the pump 23. The second fraction 21 upon leaving the reaction chamber 22 is introduced through pipe 26 into the pump 23. The alcohol 28 and the oleum 30 are substantially simultaneously contacted and mixed inside the pump by the activation of the impeller and in conjunction with the fraction 22 to form a second reaction mixture 31. This second reaction mixture 31 is introduced into a heat exchanger 32 wherein the temperature is adjusted to a temperature in the range of 90–130° F. so as to form an adjusted temperature second reaction mixture 33. This mixture 33 is split into two fractions, a first fraction 34 and a second fraction 35. The first fraction 34 is introduced through pipe 27 into the pump 23 so as to be mixed with the alcohol, oleum and said second fraction 21 to form the second reaction mixture 31. The volume of the first fraction 34 is at least fifteen times the total volume of the first fraction 21, the alcohol 28 and the oleum 30. The second fraction 35 comprises alkyl benzene sulfonic acid and an organic sulfuric acid of the alcohol.

In this apparatus there is a third centrifugal pump 36. Leading into this pump are three pipes 37, 38 and 40. These pipes may be in concentric relationship with each other or they may terminate in different places inside the pump housing. The second fraction 35 is introduced through the pipe 37 into the pump 36. An alkaline additive 41 in introduced through the pipe 40 into the pump 36. This alkaline additive 41 may be a twenty-two (22%) percent aqueous sodium hydroxide mixture. This aqueous sodium hydroxide mixture is agitated with the second fraction 35 comprising the sulfonic acids and the organic sulfuric acids to form the sodium salts of the acids which are in neutralized product slurry 42.

As is realized the neutralization of the acids in the second fraction 35 by the alkaline additive 41 is difficult with respect to controlling the pH of the neutralized product slurry 42. In order to satisfactorily control this neutralization step there is employed a pH sensing and control apparatus. In this system the sulfonic and sulfuric acids are neutralized with a strong aqueous caustic slurry in the range of 15–50% sodium hydroxide or potassium hydroxide. A product having approximately pH 7 is desired. In order to accurately measure the pH there is bled off a first fraction 43. This fraction is introduced into mixing cell 44. In inlet pipe 45 leading into the mixing cell 44 there is a valve 46 for regulating the amount of the bleed off fraction 43. In the mixing cell is a stirrer 48 for mixing the neutralized product 43 with dilution water 50 to form an aqueous neutralized product having approximately twenty-five (25%) per-

cent solids concentration, i.e., the salts of the neutralized sulfonic and organic sulfuric acids. From the mixing cell, the diluted neutralized product slurry **51** is fed through pipe **52** into pH measuring cell **53**. In this cell are two pH electrodes **54** and **55** connected with a pH control meter **56**. The pH control meter **56** controls a valve **58** which controls the amount of the alkaline additive **41** being fed into the neutralizer pump **36** through the pipe **40**.

As previously stated the neutralized product slurry **42** is split into a first fraction **43** and a second fraction **58**. In this apparatus is a heat exchanger **60**. The second fraction **58** is introduced into the heat exchanger **60** so to cool the neutralized product slurry to form a cooled neutralized product slurry **61**. Some of this cooled slurry **61** is bled off as recirculated cooled neutralized product slurry **62** and introduced through pipe **38** and the centrifugal pump **36** so as to lower the temperature of the neutralized product slurry **42**. The diluted neutralized product slurry **51** upon leaving the pH cell **53** is added to the cooled neutralized product slurry **61**.

In carrying out this process there is employed alkyl benzene having from ten to eighteen carbon atoms in the side chain. An appropriate sulfonating agent is oleum varying from about 15 to 30% sulfur trioxide, or 100% sulfuric acid may also be used. The source of alcohols is fatty alcohols. Fatty alcohols are saturated alcohols having an even number of carbon atoms and may have from twelve to twenty carbon atoms. For example, suitable fatty alcohols are so called "tallow alcohols." Tallow alcohols contain myristyl alcohol, cetyl alcohol and stearyl alcohol. On a weight basis tallow alcohol comprises approximately 60–70% stearyl alcohol; 30–35% cetyl alcohol and less than about 5% myristyl alcohol.

The materials out of which the apparatus can be made are glass, type 316 stainless steels and Alloy 20 stainless steel. The mixing equipment employed is a centrifugal pump having a rated capacity of seventy-five gallons per minute at a seventy-five foot head with a nine inch impeller.

Having presented a general picture of our sulfonation and sulfation process and the apparatus for carrying out the same, we will now present specific examples for series sulfonation and sulfation of reactants. However, it is to be understood that these examples are by way of illustration only and are not to be taken as limitations on the process. Furthermore, as the examples are presented in mol ratio it is to be understood that the mol ratio is an estimate. The reason for this is it is not possible to secure fatty alcohol having known molecular weights.

Example I

In this example there was sulfonated a hydrocarbon comprising in the main an alkyl aryl hydrocarbon, more particularly, alkyl benzene with the alkyl group having from twelve to fifteen carbon atoms. A typical analysis of this alkyl benzene is:

Gravity, API (ASTM D287)	29.5–31.0.
Viscosity at 100° F. SU (ASTM D88)	44–50.
Color, Saybelt (ASTM D156)	19 minimum.
Bromine number (SM–15–13)	0.5 maximum.
Aniline point, °F. (ASTM D611)	46–56.
Sediment and water (ASTM D96)	Nil.
Appearance	Bright and clear at 70° F.
Distillation, °F. (ASTM D447)	
5% recovered	530–535.
95% recovered	560–565° F.
Doctor test (FS–5203)	Negative.

Additional typical tests:

Molecular weight	(Approx. 246).
Specific gravity 60/60	0.877.
Flash point (Pensky Xartin) °F.	255–260.
ASTM distillation (D447), °F.—	
Start	512.
5	533.
10	535.
30	540.
50	545.
70	551.
90	558.
95	563.
End point	570.

The alcohol sulfated was a fatty or tallow alcohol having an approximate analysis as previously given.

Approximately 1.03 pounds per minute of twenty (20%) percent oleum to approximately 1.0 pound per minute of this alkyl benzene was introduced into the first centrifugal pump to make a reaction mixture of the same. Or, approximately, 2.6 mols of twenty (20%) percent oleum to one mol of alkyl benzene. The reactants were injected through concentric pipes into the suction side of the pump which was operating at a speed of about 1750 r.p.m. The temperature of the reactants was room temperature and at this temperature both of the reactants were liquids. In addition to introducing the sulfuric acid and the hydrocarbon into the pump there was simultaneously recycled a partially reacted mixture into the pump to lower the temperature of the reaction mixture.

The reaction mixture, upon leaving the pump, passed to the first heat exchanger where the temperature of the mixture was regulated to a temperature in the range of about 110°–130° F.

Upon being cooled to the desired temperature the reaction mixture was split into two fractions, a first fraction which was recirculated through the first centrifugal pump along with the reactants in a manner previously explained, and a second fraction which passed through the reaction chamber. In this recycling step the rate of flow of the recycled reaction solution compared to the volume of the entering reactants was approximately 15 to 1 (15:1). The residence or digestion time of the mixture in the reaction chamber was approximately thirty minutes.

The reaction mixture upon leaving the reaction chamber was introduced into a second centrifugal pump. Also introduced into the second pump were tallow alcohol and oleum. The alcohol was maintained at a temperature above room temperature so as to keep it in a liquid state. The alcohol and oleum were introduced through concentric pipes. The weight ratio of the oleum to the alcohol was approximately 1.3 pounds of oleum to one pound of alcohol and the mol ratio was approximately 3.6 mols of oleum to 1.0 mol of alcohol. The reaction mixture, alcohol and oleum were mixed to form a second reaction mixture which was introduced into a second heat exchanger wherein the temperature was adjusted to a temperature in the range of approximately 90–130° F. The adjusted temperature second reaction mixture was split into two fractions. The first fraction was introduced back into the second centrifugal pump along with the entering first reaction mixture, the alcohol and the oleum feeds. The volume of this first fraction was approximately fifteen times the combined volume of the alcohol and oleum. The second fraction was introduced into the third centrifugal pump along with a twenty-two (22%) percent aqueous sodium hydroxide solution. The second fraction and the sodium hydroxide reacted to form a neutralized product slurry.

The residence time of the second reaction mixture was very short and of the order of approximately one minute.

The product as analyzed on the dry basis had the following composition.

Component:	Percent by weight
Unreacted alkyl benzene	0.3
Unreacted tallow alcohol	1.1
Tallow alcohol sulfate	29.0
Alkyl aryl sulfonate	28.4
Sodium sulfate	41.2
	100.0

Example II

The process outlined in above Example I was modified with respect to the mol ratio of the oleum, alkyl benzene, and alcohol, and also with respect to the reaction temperatures and reaction time.

In this example the same alkyl benzene was used as was used in Example I. The weight ratio of the oleum to the alkyl benzene was approximately 3.5 pounds of oleum to 3.0 pounds of alkyl benzene whereby the mol ratio was approximately 3.1 mols of oleum to 1.0 mol of the alkyl benzene. The temperature of the reaction mixture was regulated to a temperature of approximately 120° F. The recycle ratio of the reaction mixture to the combined alkyl benzene and oleum was approximately fifteen volumes to one volume. The time in the reaction chamber was approximately ten minutes.

The reaction mixture was mixed with oleum and alcohol whereby there was approximately 2.1 pounds of oleum to 3.0 pounds per minute, of alcohol and the mol ratio was approximately 2.0 mols of oleum to 1.0 mol of alcohol. At the second heat exchanger the temperature of the second reaction mixture was adjusted to approximately 118° F. The reaction time in following from the second centrifugal pump, through the second heat exchanger and then to the third centrifugal pump was approximately two minutes. The recycle ratio of the second reaction mixture to the combined volumes of the alcohol and oleum was approximately 15 to 1.

The analysis of the product was as follows on the dry basis.

Component:	Percent by weight
Unreacted alkyl benzene	0.2
Unreacted tallow alcohol	1.8
Tallow alcohol sulfate	30.2
Alkyl aryl sulfonate	31.2
Sodium sulfate	36.6
	100.0

Example III

In this example an alkyl benzene comprising mainly a twelve carbon alkyl chain was employed. The same system as employed in Example I was used, but with lauryl alcohol sulfonated in the second stage.

Approximately, 2.9 pounds per minute of the alkyl benzene and 3.5 pounds per minute of the twenty (20%) percent oleum were introduced through concentric pipes into the first centrifugal pump. The mol ratio of the oleum to the alkyl benzene was approximately 3.2 mols of the oleum to 1.0 mol of the alkyl benzene. The temperature of the reaction mixture was adjusted to approximately 120° F. The reaction mixture was passed through the reaction chamber in approximately seven minutes. The ratio of the recycled reaction mixture to the combined volume of the alkyl benzene and oleum was approximately twenty-five volumes to one. The reaction mixture was mixed with approximately 2.8 pounds of oleum and 3.0 pounds of lauryl alcohol per minute whereby the mol ratio was approximately 1.9 mols of oleum to 1.0 mol of alcohol. The temperature of the second reaction mixture was adjusted to about 115° F. The average reaction time of the second reaction mixture, i.e., the time between the second centrifugal pump, through the second heat exchanger and to the third centrifugal pump was approximately two minutes. The second reaction mixture was mixed with twenty-two (22%) percent aqueous sodium hydroxide solution to give a product having the following analysis on the dry basis.

Component:	Percent by weight
Unreacted decyl benzene	0.2
Unreacted lauryl alcohol	1.8
Lauryl alcohol sulfate	28.8
Alkyl aryl sulfonate	33.6
Sodium sulfate	35.6
	100.0

Example IV

In this example an alkyl benzene comprising mainly fifteen carbon atoms in the alkyl chain was reacted with oleum. The system was essentially the same as the system in Example I.

There was introduced into the centrifugal pump approximately 3.0 pounds per minute of the pentadecyl benzene and 3.1 pounds per minute of the oleum. On a mol ratio basis this was approximately 3.2 mols of oleum per mol of the pentadecyl benzene. The temperature was adjusted to a temperature in the range of approximately 130° F. The time of the reaction mixture in the reaction chamber was approximately thirty minutes. The recycle ratio of the reaction mixture to the combined volume of the oleum and the alkyl benzene was approximately thirty to one.

The reaction mixture was introduced into the second centrifugal pump wherein it was mixed with 2.3 pounds of oleum and 3.0 pounds of tallow alcohol per minute. This was a mol ratio of approximately 2.2 mols of oleum to 1.0 mol of tallow alcohol. The temperature of the second reaction mixture was adjusted to approximately 115° F. The recycle ratio of the second reaction mixture to the combined volume of the oleum and the alcohol was approximately thirty volumes to one. The second reaction mixture was mixed with a twenty-two (22%) percent aqueous sodium hydroxide solution to give a neutralized product slurry having on the dry basis the following analysis.

Component:	Percent by weight
Unreacted pentadecyl benzene	0.4
Unreacted tallow alcohol	1.8
Tallow alcohol sulfate	26.2
Alkyl aryl sulfonate	31.6
Sodium sulfate	40.0
	100.0

It is to be understood from the above the series sulfonation of an alkyl benzene and a fatty alcohol may be carried out under a reasonable latitude of operating conditions. For example, in the first stage the mol ratio of twenty (20%) percent oleum to alkyl benzene may vary from about 2.5 to 3.4 mols of oleum to one mol of alkyl benzene; the temperature of the reaction mixture from about 110–130° F.; and, the time in the digestion coil from about five to thirty minutes: and, in the second stage the mol ratio of the oleum to the fatty alcohol can vary from about 1.9–3.6 mols of the oleum to one mol of the fatty alcohol; the temperature of the reaction mixture from about 90–130° F.; and, the reaction time from approximately one to three minutes. The mol ratios of the reactants may be so adjusted that there is an excess of the sulfonating agent in the first stage. In the second stage there may not be sufficient sulfonating agent added to react with the alcohol. However, due to the excess of the sulfonating agent from the first stage there may still be an excess of the sulfonating agent in the second stage. However, it is to be understood that the variation of the ratios of the sulfonating agent to the alkyl benzene and the tallow alcohol are varied within certain limits. For example, the mol ratio of the oleum to the alkyl benzene should not be below about 2.5:1 as there is not sufficient reaction taking place and the mol ratio should not be

above 3.4:1 as degradation of the sulfonic acid product takes place. The temperature range of 110–130° F. for the reaction mixture is imposed because below about 110° F. the rate of reaction is too slow while above 130° F. the sulfonic acid product is burned and degraded. In the second stage the mol ratio of the oleum to the fatty alcohol should not be less than about 1.9 as the conversion is too low and the mol ratio should not rise above about 3.6 as the organic sulfuric product is burned and degraded. The temperature in the second stage should not fall below about 90° F. as the reaction rate is too low and the temperature should not rise above about 130° F. as burning and degradation of the product takes place. In the second stage the ratio of the oleum to the fatty alcohol, the temperature of the reaction, and the time duration of the reaction are of importance and must be controlled to preclude the organic sulfuric acid of the alcohol from reverting to form the alcohol and sulfuric acid. In other words in the second sulfation stage it is desirable to have a short reaction time so as to preclude the reversible reaction occurring. Also, it is to be understood that in place of the oleum there may be used 100% sulfuric acid.

Having presented our invention what we claim is:

1. A process for preparing a mixture of an alkyl benzene sulfonate and an alcohol sulfate which comprises continuously mixing an acid, selected from the group consisting of about 100% concentrated sulfuric acid and about 15 to 30% oleum, and an alkyl benzene wherein the alkyl radical has from about ten to about eighteen carbon atoms, with preformed product in a mol ratio of acid to alkyl benzene of 2.5:1 to 3.4:1 and a volume ratio of preformed product to acid and alkyl benzene of at least about 15:1 to form a reaction mixture, maintaining the temperature of said reaction mixture within the range of 110° to 130° F. by cooling, dividing the reaction mixture into a first fraction and a second fraction, returning said first fraction as said preformed product, digesting said second fraction from about 5 to about 30 minutes to form a digested reaction mixture, continuously mixing additional acid from said group and a saturated fatty alcohol having from about 12 to about 20 carbon atoms with said digested reaction mixture and preformed second product in a mol ratio of acid to alcohol of 1.9:1 to 3.6:1 and a volume ratio of preformed second product to the combined volume of the additional acid and alcohol of at least about 15:1 to form a second reaction mixture, maintaining the temperature of said second reaction mixture within the range of 90° to 130° F. by cooling, dividing the second reaction mixture into a first fraction and a second fraction, returning the first fraction of said second reaction mixture as said second preformed product, and neutralizing the second fraction of said second reaction mixture, wherein the average reaction time from the introduction of the alcohol to the neutralization of the second fraction of said second reaction mixture is less than approximately 3 minutes.

2. A process for preparing a mixture of an alkyl benzene sulfonate and an alcohol sulfate which comprises continuously mixing an acid, selected from the group consisting of about 100% concentrated sulfuric acid and about 15 to 30% oleum, and an alkyl benzene wherein the alkyl radical has from about ten to about eighteen carbon atoms, with preformed product in a mol ratio of acid to alkyl benzene of 2.5:1 to 3.4:1 and a volume ratio of preformed product to acid and alkyl benzene of at least about 15:1 to form a reaction mixture, maintaining the temperature of said reaction mixture within the range of 110° to 130° F. by cooling, dividing the reaction mixture into a first fraction and a second fraction, returning said first fraction as said preformed product, digesting said second fraction from about 5 to about 30 minutes to form a digested reaction mixture, continuously mixing additional acid from said group and a saturated fatty alcohol having from about 12 to about 20 carbon atoms with said digested reaction mixture and preformed second product in a mol ratio of acid to alcohol of 1.9:1 to 3.6:1 and a volume ratio of preformed second product to the combined volume of the additional acid and alcohol of at least about 15:1 to form a second reaction mixture, maintaining the temperature of said second reaction mixture within the range of 90° to 130° F. by cooling, dividing the second reaction mixture into a first fraction and a second fraction, returning the first fraction of said second reaction mixture as said second preformed product, and neutralizing the second fraction of said second reaction mixture with a member selected from the group consisting of sodium hydroxide and potassium hydroxide, wherein the average reaction time from the introduction of the alcohol to the neutralization of the second fraction of said second reaction mixture is less than approximately 3 minutes.

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