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PRODUCTION OF ALKYLATED ARYL SULFONATE DETERGENTS

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1

This invention relates to the manufacture of alkylarylsulfonates having an alkyl group of at least 12 carbon atoms attached to the sulfonated aromatic ring. The invention deals with an improved method of manufacturing sulfonates of this type having desirable detergent properties and provides a commercially practical method for producing alkylated sulfonates of the benzene series in high yields and excellent quality.

A great deal of work has been done on the production of alkylaryl sulfonates of a wide variety of different types for use as detergents, and mono- and di-alkylated benzenes such, for instance, as benzene, toluene, ethyl benzene, cumene and tertiary butyl benzene alkylated so as to introduce an alkyl radical of 12 or more carbon atoms have been suggested as suitable starting materials for the production of such sulfonates. In the prior methods of preparing these sulfonates difficulties have been encountered in obtaining high yields of products of good detergent properties. The sulfonation step of the process is particularly subject to side reactions, and, especially in the case of the sulfonation of dialkyl aromatic hydrocarbons having an alkyl group of 12 to 24 carbon atoms and an alkyl group of 1 to 4 carbon atoms directly attached to a benzene ring, dealkylation with splitting off of the long chain alkyl radical is liable to take place. Oxidation accompanied by sulfur dioxide formation is another undesirable side reaction to which these alkyl benzenes are particularly subject during sulfonation. With alkyl aromatic hydrocarbons in which the higher alkyl group is a highly branched chain tertiary alkyl radical derived from an olefin polymer, the sulfonation reaction is further complicated by the tendency of such alkyl radicals to undergo disproportionation or depolymerization, etc., and by the formation of undesirable by-products as a result of polymerization, or other reactions of the unsaturates so formed and/or present in the feed. These side reactions tend to introduce in the product hydrocarbon impurities which are especially difficult to remove and which are not only quite detrimental to the detergent properties of the final sulfonate but also tend to give the sulfonate an undesirable odor and to make it gummy and hard to handle in powder form. It has now been found that it is important to control not only the sulfonation step of the process but also the neutralization of the sulfonic acids in order to produce high yields of sulfonates having good detergent properties.

An important object of the present invention is to provide a process of producing sulfonate salts of alkyl benzenes having an alkyl group

2

which contains at least 12 carbon atoms, in which process the foregoing undesirable side reactions are obviated or reduced and high yields of products of improved detergent properties are obtained. Still other objects and advantages of the invention will be apparent from the following description wherein the application of the invention to the sulfonation of alkylbenzenes produced by alkylating benzene, toluene, ethyl benzene, cumene or a butyl benzene with an olefin polymer of at least 12 carbon atoms per molecule will be emphasized because these sulfonations present special difficulties which are overcome by the new process. It will be understood, however, that, as previously pointed out, the process is equally applicable to the sulfonation of corresponding mono- and di-alkyl benzenes having less highly branched or straight chain alkyl groups of 12 to 24 carbon atoms derived from other sources.

In accordance with the invention, the production of sulfonate salts of alkyl aryl hydrocarbons having an alkyl group of at least 12 carbon atoms is carried out under a combination of carefully coordinated sulfonating and neutralizing conditions which avoid the difficulties encountered in prior methods of operation. Because it is extremely difficult to effectively separate oily impurities from the sulfonates of the invention which are very strong emulsifying agents, it is highly desirable that the sulfonation be as complete as possible while still avoiding excessive sulfonation leading to the formation of polysulfonates as well as preventing the previously mentioned undesirable dealkylation and other side reactions. To this end, the sulfonation of alkyl benzenes having an alkyl group of 12 to 24 carbon atoms is carried out under the following combination of conditions which give high yields of detergents of high quality without the use of added solvent:

Sulfonation temperature	5° C. to 50° C.
Contact time	1 min. to 5 hrs.
Pressure	5 to 50 p. s. i. g.
Oleum strength	15% to 30%.
Mole ratio of free SO_3 to alkylate	0.7:1 to 1.4:1.

The combination of neutralizing conditions which must be used with these sulfonation conditions in order to obtain good results according to the invention are as follows:

Concentration of the base added	20% to 30% by weight.
Temperature	50° C. to 90° C.
pH	7 to 10.

When the sulfonation is controlled so that the

operating variables are maintained within these limits, one obtains a yield above 96% of monosulfonic acid salts of low oil content and high detergency.

The particular sulfonating conditions within the limits of the foregoing combination of conditions which it will be best to use with a particular alkyl benzene will depend upon whether it is of the monoalkyl benzene type or is a dialkyl benzene having an alkyl group of 1 to 4 carbon atoms in addition to the long chain alkyl radical of 12 to 24 carbon atoms which characterizes all the alkyl benzenes used in the process of the invention. Due to their greater sensitivity to side reactions during sulfonation, these dialkyl benzenes are sulfonated under milder conditions coming within the foregoing ranges than is necessary with the corresponding monoalkyl benzenes, namely:

Sulfonation temperature	5° C. to 20° C., preferably 10° C. to 20° C.
Contact time	1 to 60 min., preferably 2 to 40 min.
Pressure	5 to 50 p. s. i. g., preferably 10 to 35 p. s. i. g.
Oleum strength	15% to 30%, preferably 20% to 30%.
Mole ratio free SO_3 to alkylate	1.15:1 to 1.4:1, preferably 1.2:1 to 1.3:1.

With dialkyl benzenes wherein the higher alkyl radical is derived from olefin polymers of 12 to 24 carbon atoms per molecule, it is particularly desirable to control the sulfonation so the conditions are maintained within the indicated preferred narrower ranges.

When using the described dialkyl benzenes as starting materials, temperatures above 20° C. cannot be used without encountering excessive dealkylation which gives products of low equivalent weight having a detrimental oil content and reduced detergency. The increased oil content of the products produced at temperatures above 20° C. is particularly undesirable because of the tackiness which it imparts to the dry products. Due to their greater stability, monoalkyl benzenes can be sulfonated at higher temperatures, 40° C. to 50° C. being useful. With both mono- and di-alkyl benzenes having alkyl groups of 12 to 24 carbon atoms, temperatures of at least 5° C. are necessary for effective mixing and reaction as at lower temperatures the mixture is too viscous when using oleum of the concentration necessary according to the invention. In this connection it should be noted that the process of the invention is preferably carried out in the absence of solvents such, for example, as sulfur dioxide, etc. since they complicate the recovery of the product, the reaction product used being the effective solvent in the new process.

The contact time used in sulfonation must be at least 1 minute and preferably is at least 5 minutes in order to insure the desired completeness of sulfonation. Contact times greater than about 60 minutes are undesirable, however, in the sulfonation of the described dialkyl benzenes because they needlessly decrease plant capacity and may increase side reactions which take place, leading to products of higher oil content having equivalent weights too far below the theoretical with consequent poorer detergency. Average reaction times of 10 to 40 minutes are preferred for such dialkyl benzenes. With the monoalkyl benzenes used in the process, it is feasible to increase the reaction time to about 5 hours. In fact, in batch sulfonation of these monoalkyl benzenes, one convenient method of operation is to react for 2 hours at about 25° C. and then increase the temperature to 50° C. for an additional 2 hours. When carrying out the sulfonation continuously, however, reaction times of the same order as those used for the dialkyl benzenes are preferably employed.

Whichever type of alkyl benzene having an alkyl group of 12 to 24 carbon atoms is used as starting material in the process, the sulfonation must be conducted under substantial superatmospheric pressure of at least 5 pounds per square inch, gage, in order to obtain effective reaction under the conditions of the new process. At lower pressures the sulfonation is incomplete and the preferred range of pressures is from 5 to about 50 p. s. i. g., most preferably about 10 to 15 p. s. i. g.

Oleum strengths between 15% and 30% corresponding to about 103% to about 107% sulfuric acid strength, are used for sulfonation of both types of starting alkyl benzenes. Lower concentrations give products of such low sulfonate content as to seriously reduce their effectiveness as detergents unless the process is complicated by special arrangements for removing a part of the sulfuric acid before neutralization and/or purification of the product by separation of inorganic sulfates. Oleum of too high a concentration is undesirable because it gives a product which is difficult to dry.

The mole ratio of free sulfur trioxide to dialkyl benzene must be maintained at 1.15 or higher in order to reduce the residual oil in the sulfonation product to the required degree. Ratios above 1.4 to 1 are undesirable as they give products of lower sulfonate content after neutralization and also needlessly increase the cost of operation. This range of ratios is also desirable when sulfonating monoalkyl benzenes having an alkyl group of at least 12 carbon atoms in a continuous manner but lower ratios, e. g. 0.7:1, can be used in batch sulfonation of these alkyl benzenes where longer contact times are employed.

When the sulfonation conditions are maintained within the foregoing ranges the reaction may be carried out intermittently as well as by the indicated continuous or batchwise method. A convenient method of continuous sulfonation comprises simultaneously feeding the alkyl benzene and oleum in the specified proportions into a circulating stream of reacted mixture flowing through a suitably cooled reactor while drawing off at a point ahead of the feed inlets a volume of reacted mixture equivalent to the feed. The reactor may, for instance, be a high speed mixer, or a cooler with or without a time tank through which the reaction mixture is circulated by a pump connected with the inlet and outlet, or other suitable form of apparatus. In such a method of operation a ratio of recycled mixture to feed of the order of about 5 to 25 volumes per volume, preferably about 10 to 20 volumes per volume, has been found to be suitable. In sulfonating batchwise it is preferred to use a reactor equipped to withstand the required elevated pressures and provided with efficient cooling and stirring means. The reactor is preferably charged with the alkyl aromatic hydrocarbon to be sulfonated, after which the oleum is run in at a rate such as will insure a reaction time within the previously indicated range. Still other methods of carrying out the sulfonation within the critical range of operating conditions of the invention may, of course, be used.

Most preferably, the sulfonation mixture is neutralized immediately upon withdrawal from the sulfonation reactor since in this way an advantageous mixture of sulfonates and sulfates corresponding to the base used in neutralization is obtained. To obtain products of high quality, the neutralization must be effected by adding the sulfonation mixture to a solution of the neutralizing agent under controlled conditions of concentration and proportion of base, temperature and pH, as previously pointed out, to prevent undesirable sulfur dioxide evolution and mixing difficulties associated with excessive viscosity of the mixture. Thus, with both mono- and di-alkyl benzenes having an alkyl group of 12 or more carbon atoms, the neutralization of the sulfonic acids must be carried out under the following conditions when using an inorganic hydroxide.

Concentration of the base added	20% to 30% by weight.
Temperature	50° C. to 90° C.
pH	7 to 10.

A wide variety of different bases may be used for neutralization. Alkali metal hydroxides, particularly sodium or potassium hydroxide, or ammonium hydroxide, or mixtures thereof, are particularly suitable although alkaline earth metal hydroxides such as calcium and magnesium hydroxides, or organic bases such as amines, including alkanolamines such as the ethanolamines, morpholine and the like, may also be used.

The neutralized product is a light colored slurry which may be used as such or drum or spray dried with or without addition of builders such as sodium tripolyphosphate or the like to obtain a free flowing, nonhygroscopic powder of good odor and high detergency in both hard and soft water.

The following examples illustrating typical applications of the invention show some of its advantages and make clear how the new process may be carried out.

Example I

To show the effect of sulfonation temperature, a series of runs was made using a dodecyl toluene mixture produced by alkylating toluene with a tetramer fraction of propylene polymers. The sulfonating agent in all cases was 15.5% to 23.1% oleum (103.5% to 105.2% sulfuric acid). The mole ratio of sulfur trioxide to dodecyl toluene was 1.21 to 1.35, and the residence time was 16 to 19 minutes at a pressure of 5 p. s. i. g. The sulfonation was carried out continuously by pumping the oleum and dodecyl toluene via proportioning pumps into a high speed rotary mixer provided with cooling coils, the product flowing continuously to a water-cooled, stirred neutralizer where it was neutralized at 80° C. with 30% aqueous sodium hydroxide at a pH of about 8.

Temperature	6° C.	10° C.	20° C.	30° C.	40° C.	50° C.
Equivalent weight of sodium sulfonate	351	372	369	343	324	313
Residual oil in product (wt. percent of dodecyl toluene fed)	2.4	4.2	5.1	9.0	17	24.3
Sulfur dioxide formation (moles per equivalent of sulfonic acid)	0.12	0.12	0.12	0.14	0.20	0.23
Relative detergency in washing cotton in soft water	------	95	93	93	89	89

Example II

The effect of variations in the operating pressure in the sulfonation reactor is shown by the following results obtained by sulfonating a propylene tetramer-toluene alkylate in the apparatus used in Example I. In the experiments essentially equivalent sulfonation conditions, except for pressure, were used as follows:

Temperature, ° C.	10
Time of contact, min.	6
Oleum strength, per cent	23
Mole ratio of SO_3 to alkylate	1.35

Pressure (p. s. i. g.)	0	1	5	12	25
Equivalent weight of sodium sulfonate	----	362	372	372	368
Residual oil in product (wt. percent of alkylate fed)	16	11	4.2	3.7	4.2
Relative detergency of sodium sulfonate (at concentration of 2 grs. total solids per 100 grs. water at 60° C. in washing cotton in soft water)	----	-----	95	95	-----

Example III

The favorable results which may be obtained at sulfonation times in the range of 5 to 60 minutes, provided the other reaction variables are maintained within the required limits, are shown by the following figures for the sulfonation of dodecyl toluene in the continuous reactor of Example I, using 23.1% oleum (105.2% sulfuric acid) at 10° C., a pressure of 5 to 15 p. s. i. g., and a mole ratio of free SO_3 to dodecyl toluene at 1.35.

Average contact time (min.)	6	13	25	40
Equivalent weight of sodium sulfonate	361	374	364	363
Residual oil in product (wt. percent of of dodecyl toluene fed)	4.1	4.3	4	3.7
Relative detergency of sodium sulfonate (at a concentration of 0.2 gr. total solid per 100 grs. water at 60° C. in washing cotton in soft water)	95	97	95	------

Example IV

The effect of sulfuric acid concentration in the sulfonation of dodecyl toluene produced by alkylating toluene with a tetramer fraction of propylene polymers is shown by the following results of tests in which temperatures of 10° C. and 20° C. were used at a contact time of 6 minutes, a pressure of 15 p. s. i. g., and a mole ratio of free sulfur trioxide to dodecyl toluene of 1.35:1.

Oleum concentration, wt. percent	23	23	31	31
Temperature, ° C.	10	20	10	20
Equivalent weight of sodium sulfonate	372	369	365	362
Residual oil in product (wt. percent of dodecyl toluene fed)	4.2	5.1	14.	3.3
Active ingredient content of dry product, wt. percent	38	28	42	46
Relative detergency of sodium sulfonate	95	93	------	------

Example V

The following test runs show the effect of varying the mole ratio of free sulfur trioxide to dodecyl toluene when sulfonating with oleum of 23.1% concentration at 10° C., a pressure of 15 p. s. i. g., and an average contact time of 6 minutes in the continuous sulfonator of Example I.

Mole ratio of SO_3 to dodecyl toluene	1.04	1.15	1.25	1.41
Equivalent weight of sodium sulfonate	363	374	375	372
Residual oil in product (wt. percent of dodecyl toluene fed)	22	4.4	4.8	3.7
Sulfonate content of neutralized and dried product, wt. percent	37	40	39	36
Relative detergency	------	------	------	95

Example VI

A dodecyl benzene fraction boiling between 120° C. and 162° C. at 5 mm. from the alkylation of benzene with propylene tetramers was sulfonated by the continuous method described above, the reaction conditions and results being as follows:

Sulfonation temperature, °C	50
Contact time, min.	6
Pressure, p. s. i. g.	31
Oleum concentration, per cent	30
Mole ratio of SO_3 to alkylate	1.29
Neutralization temperature, °C	60
Concentration of NaOH, per cent	25
pH	7 to 10
Equivalent weight of sodium sulfonate	350
Residual oil (wt. per cent of dried product), per cent	0.83
Sulfonate content of dried product, wt. per cent	47.5
Relative detergency in soft water when built with 50% $Na_5P_3O_{10}$ and 1% CMC to 18% sodium sulfonate content	108

The relative detergency values given in the foregoing results are comparative values for standard Launderometer test washings of General Dyestuff soiled cotton cloth No. 26 at 60° C. for 10 minutes using 0.2 gram per 100 grams of neutralized and dried sulfonation product consisting of a mixture of sodium sulfonate and sodium sulfate with the results expressed as per cent soil removal compared with an arbitrary standard of removal as 100%.

While in the foregoing examples the sulfonation of dodecyl benzene and dodecyl toluenes has been emphasized, it will be seen from the following results that equally good results may be obtained by sulfonating other alkyl benzenes wherein one of the alkyl groups contains 12 to 24 carbon atoms, using sulfonation and neutralization conditions within the specified ranges of the invention.

Example VII

Alkyl benzene	N-dodecyl benzenes	Dodecyl ethyl benzene from alkylation of ethyl benzene with propylene tetramer (mol. wt. 262 found)	C_{15}–C_{18} alkyl toluene from alkylation of toluene with propylene pentamers and hexamers	sec.-tetradecyl toluene	sec.-octadecyl toluene
Temperature, ° C.	50	15	20	22	22
Time of contact, min.	60	2	2	2	2
Mole ratio of free SO_3 to alkyl benzene	1.3	1.2	1.2	1.2	1.2
Equivalent weight of sodium sulfonate:					
Actual	345	352	380–422	392	430
Theoretical	348	364	394–434	390	447
Residual oil in product, percent	0.56	1.9	ca 1	1.3	1.4
Relative detergency on cotton	103	88	101–106	107	104

It will thus be seen that the process of the invention offers many advantages over prior methods of producing detergents from alkyl aromatic compounds and is capable of considerable variation with respect to the type of alkyl benzenes which may be used since, although particularly useful with dialkyl benzenes having alkyl groups of 1 to 4 and 12 to 24 carbon atoms therein, it is also advantageous for the preparation of high quality detergents from monoalkyl benzenes having 12 to 24 carbon atoms in the alkyl group. It will therefore be understood that the new process is not limited to the details disclosed by way of example nor by any theory proposed in explanation of the improved results which are obtained.

This application is a continuation-in-part of copending application Serial No. 17,814, filed March 29, 1948, now abandoned.

We claim as our invention:

1. A process of producing a sulfonic acid salt of an alkyl benzene having an alkyl group of 12 to 24 carbon atoms and not more than one other alkyl group, said other alkyl group containing not more than four carbon atoms, which comprises reacting said alkyl benzene in the absence of added solvent with oleum of 15% to 30% initial concentration in proportions such that the mole ratio of free sulfur trioxide to alkyl benzene is 0.7:1 to 1.4:1, maintaining the reaction mixture at a temperature of 5° C. to 50° C. and a superatmospheric pressure of 5 to 50 p. s. i. g., removing from the reaction zone reacted mixture after a contact time of 1 min. to 5 hrs., and feeding the withdrawn reaction mixture into an aqueous solution of a base of 20% to 30% concentration while maintaining in the neutralizer a temperature of 50° C. to 90° C. and a pH of about 7 to 10.

2. A process of producing a sulfonic acid salt of an alkyl benzene having an alkyl group of 12 to 24 carbon atoms and not more than one other alkyl group, said other alkyl group containing not more than four carbon atoms, which comprises reacting said alkyl benzene in the absence of added solvent with oleum of 22% to 30% initial concentration in proportions such that the mole ratio of free sulfur trioxide to alkyl benzene is 1.15:1 to 1.4:1, maintaining in the reaction mixture a temperature of 5° C. to 50° C. and a superatmospheric pressure of 5 to 50 p. s. i. g., removing from the reaction zone reacted mixture after a contact time of 1 to 60 min., and feeding the withdrawn reaction mixture into an aqueous solution of a base of 20% to 30% concentration while maintaining in the neutralizer a temperature of 50° C. to 90° C. and a pH of about 7 to 10.

3. A process of producing a sulfonate of a dialkyl benzene having one alkyl group of 12 to 24 carbon atoms and another alkyl group of 1 to 4 carbon atoms which comprises reacting said dialkyl benzene in the absence of added solvent with oleum of 22% to 30% initial concentration in proportions such that the mole ratio of free sulfur trioxide to dialkyl benzene is 1.2:1 to 1.3:1, maintaining in the reaction mixture a temperature of 10° C. to 20° C. and a superatmospheric pressure of 10 to 20 p. s. i. g., removing from the reaction zone reacted mixture after a contact time of 5 to 40 min., and feeding the withdrawn reacted mixture directly into an aqueous solution of a base of 20% to 30% concentration while maintaining in the neutralizer a temperature of 50° C. to 90° C. and a pH of about 7 to 10.

4. A process of producing a sulfonate of a dialkyl benzene having one alkyl group of 12 to 24

carbon atoms derived from an olefin polymer of branched chain structure and another alkyl group of 1 to 4 carbon atoms which comprises reacting said dialkyl benzene in the absence of added solvent with oleum of 22% to 30% initial concentration in proportions such that the mole ratio of free sulfur trioxide to dialkyl benzene is 1.2:1 to 1.3:1, maintaining in the reaction mixture a temperature of 10° C. to 20° C. and a superatmospheric pressure of 10 to 50 p. s. i. g., removing from the reaction zone reacted mixture after a contact time of 5 to 40 min., and feeding the withdrawn reacted mixture directly into an aqueous solution of a base of 20% to 30% concentration while maintaining in the neutralizer a temperature of 50° C. to 90° C. and a pH of about 7 to 10.

5. A process of producing a sulfonate of a dialkyl benzene having one alkyl group of 12 to 24 carbon atoms and another alkyl group of 1 to 4 carbon atoms which comprises continuously feeding into a circulating stream of reacted mixture said dialkyl benzene and oleum of 22% to 30% concentration in proportions such that the mole ratio of free sulfur trioxide to dialkyl benzene fed is 1.2:1 to 1.3:1 and the volume ratio of recycled reacted mixture mixed with the feed is 10:1 to 20:1, maintaining in the reaction mixture a temperature of 10° C. to 20° C. and a superatmospheric pressure of 10 to 50 p. s. i. g., continuously removing from the reaction zone reacted mixture equivalent to the feed after an average contact time of 5 to 40 minutes, and immediately neutralizing the withdrawn reacted mixture with an aqueous solution of sodium hydroxide of 20% to 30% concentration while maintaining in the neutralizer a temperature of 50° C. to 90° C. and a pH of about 7 to 10.

6. A process of producing a sulfonate of an alkyl toluene wherein the alkyl group is derived from a propylene polymer having 12 to 24 carbon atoms per molecule which comprises continuously feeding into a circulating stream of reacted mixture an alkyl toluene product of the alkylation of toluene with a propylene polymer of 12 to 24 carbon atoms and oleum of 22% to 30% concentration in proportions such that the mole ratio of free sulfur trioxide to alkyl toluene fed is 1.2:1 to 1.3:1 and the volume ratio of recycled reacted mixture mixed with the feed is 10:1 to 20:1, maintaining in the reaction mixture a temperature of 10° C. to 20° C. and a superatmospheric pressure of 10 to 50 p. s. i. g., continuously removing from the reaction zone reacted mixture equivalent to the feed after an average contact time of 5 to 40 minutes, immediately neutralizing the withdrawn reacted mixture with an aqueous solution of an inorganic hydroxide of 20% to 30% concentration while maintaining in the neutralizer a temperature of 60° C. to 90° C. and a pH of about 7 to 10, and drying the resulting slurry to obtain a free flowing detergent mixture.

7. A process of producing a sulfonic acid salt of a monoalkyl benzene having an alkyl group of 12 to 24 carbon atoms which comprises reacting said monoalkyl benzene in the absence of added solvent with oleum of 15% to 30% initial concentration in proportions such that the mole ratio of free sulfur trioxide to alkyl benzene is 0.7:1 to 1.4:1, maintaining the reaction mixture at a temperature of 40° C. to 50° C. and a superatmospheric pressure of 5 to 50 p. s. i. g., removing from the reaction zone reacted mixture after a contact time of 1 min. to 5 hrs., and feeding the withdrawn reaction mixture into an aqueous solution of a base of 20% to 30% concentration while maintaining in the neutralizer a temperature of 50° C. to 90° C. and a pH of about 7 to 10.

8. A process of producing a sulfonic acid salt of a mono-alkyl benzene having the alkyl group derived from an olefin polymer of branched chain structure having twelve carbon atoms which comprises continuously feeding into a circulating stream of reacted mixture said dodecyl benzene and oleum of 15% to 30% concentration in proportions such that the mole ratio of free sulfur trioxide to dodecyl benzene fed is 1.15:1 to 1.4:1 and the volume ratio of recycled reacted mixture mixed with the feed is 10:1 to 20:1, maintaining in the reaction mixture a temperature of 40° C. to 50° C. and a superatmospheric pressure of 5 to 50 p. s. i. g., continuously removing from the reaction zone reacted mixture equivalent to the feed after an average contact time of 5 to 40 minutes, immediately neutralizing the withdrawn reacted mixture with an aqueous solution of sodium hydroxide of 20% to 30% concentration while maintaining in the neutralizer a temperature of 60° C. to 90° C. and a pH of about 7 to 10.

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