

This invention relates to a process for the production of solid or paste-form products by reaction of stoichiometric quantities of several reactants in a fast reaction and spraying of the reaction products in a spray unit.

5 Typical examples of fast chemical reactions in the context of the present invention are the neutralization of acids, the saponification of esters and also alkylation reactions, particularly alkylations of tertiary amines.

10 Neutralization reactions of sulfonic acids or fatty acids take place spontaneously. Problems in the conduct of the reaction can arise when the reactants, i.e. acids and alkalis, are immiscible with one another and/or when the neutralization product formed is a solid or paste-form product. In cases such as these, the quality of the
15 neutralization is determined by the intensity with which the reactants are mixed and/or by the intensity with which the reaction mixture is intermixed.

On an industrial scale, the neutralization of sulfonic acids to washing-active sulfates or sulfonates takes place
20 discontinuously in neutralization vessels or continuously in recirculation systems. In the latter case, the sulfonic acid is introduced together with the alkali into already neutralized product with intensive mixing by stirrers, centrifugal pumps and static mixing elements, the ratio of
25 recirculation volume to freshly added sulfonic acid and alkali being in the range from 10:1 to 20:1. In the neutralization of hydrolysis-sensitive products, such as sulfuric acid semiesters of fatty alcohols and fatty alcohol ethers, consistently good intermixing and blending
30 of the neutralization mixture have to be guaranteed to rule out product losses. Both with discontinuous operation and with continuous operation, heat exchange elements have to be used to dissipate the heat of reaction in order to rule out overheating of the product.

35 Neutralization products containing around 60% by

weight washing-active substance (WAS) can be produced by this process. Most of the remaining 40% by weight consists of water which has to be removed, for example by spray drying, during incorporation of the washing-active sulfates/sulfonates in powder-form detergents.

A reduction in the water content to reduce energy consumption during drying would be desirable and could even be achieved by the use of relatively highly concentrated alkalis in the neutralization reaction.

Simple material balances show that neutralization products containing around 80% washing-active substance and around 20% water can be produced in the neutralization of sulfonic acids with 50% sodium hydroxide. In addition, the energy balance of the neutralization reaction shows that around 40 to 50% of the water formed during the neutralization reaction and the water introduced into the reaction mixture with the 50% sodium hydroxide can be evaporated with the heat of reaction. Where 50% sodium hydroxide is used, therefore, neutralization products containing around 90% washing-active substance and only around 10% water are theoretically formed, the heat of reaction being utilized for drying. Under these conditions, the neutralization products of sulfonic acids based on fatty alcohol and fatty acid esters may readily be processed to free-flowing powders. By utilizing the heat of reaction, however, other unwanted volatile substances can also be removed from the products. Reduction of the dioxane content of fatty alcohol ether sulfates is mentioned as an example of this.

However, the industrially used process described above for the neutralization of sulfonic acids does not allow the use of highly concentrated alkalis because the reaction product or neutralization product becomes increasingly more viscous and, ultimately, paste-like with increasing content of washing-active substance. Beyond a content of around 60% by weight washing-active substance, sulfates/sulfonates

can no longer be pumped and uniform blending and intermixing of the reaction components and the reaction mixture, respectively, and safe dissipation of the heat of reaction are no longer manageable.

5 The production of soaps by the neutralization of fatty acids with alkalis is comparable with the neutralization of sulfonic acids for the production of washing-active sulfates/sulfonates. In this case, however, the neutralization reaction is complicated not only by the paste-like
10 flow behavior of the soap formed during the reaction. Since the aqueous alkalis and the fatty acids are not soluble in one another, a correspondingly high degree of dispersion is necessary to establish a sufficiently large mass transfer surface between the two liquid phases and,
15 hence, a sufficiently high reaction velocity. Conventional processes for the production of basic soaps from fatty acids may be divided into two process steps, namely:

1. combining, homogenizing or emulsifying the reactants insoluble in one another and carrying out the neutralization or saponification reaction in stirred tanks, reaction
20 columns or loop reactors;
2. multistage drying of the basic soap with an active-substance content of around 60% to 80%.

Like the neutralization of sulfonic acids with alkalis,
25 the neutralization of fatty acids with alkali is a spontaneous reaction providing the two reactants insoluble in one another can be combined in sufficiently finely dispersed form. The reaction can be started at room temperature, the reaction mixture or rather the reaction products
30 undergoing intense heating.

As in the neutralization of sulfonic acids, the material and energy balances for the neutralization of fatty acids show that, where 50% sodium hydroxide is used, it is possible to produce basic soap containing around 80%
35 active substance and around 20% water in a single process

step.

Instead of pure fatty acids, fatty acid methyl esters may also be reacted to soaps by saponification with sodium hydroxide. In this reaction, methanol is formed as secondary product and has to be removed from the basic soap or toilet soap. This is generally done by evaporation or stripping with steam. The processes used for the production of soaps from methyl esters correspond to the processes for the production of soaps from fatty acids, involving an additional process step, namely the removal of methanol. In contrast to the neutralization of fatty acids, the reaction velocity in the saponification of methyl esters depends to a large extent on the reaction temperature. Whereas the saponification reaction progresses only slowly at room temperature, it is greatly accelerated by relatively high temperatures (for example 100°C). It takes place almost instantaneously providing the methyl ester and the alkali can be brought into contact in finely dispersed form at 130 to 140°C.

EP-A-0 083 122 describes a process of the type mentioned at the beginning in which two streams of reactants respectively consisting of acid and alkali and, independently thereof, a gas stream are delivered to a spray nozzle; the neutralization reaction between the sprayed reactants takes place after leaving the nozzle. The mass ratio between gas and reactants is of the order of 0.4. However, the process can only be operated within narrow parameters if a high degree of neutralization is to be achieved and blockage of the spray nozzles is to be prevented. In addition, the known process requires nozzles of complicated construction with a plurality of concentric bores for the separate delivery of reactants and gaseous medium.

The present invention relates to a process of the type mentioned at the beginning which requires spray units of

simple construction, can be operated with widely variable outputs (for example 1.5 to 200 kg/h product for one of the nozzles used in the process according to the invention) and is substantially trouble-free in operation because blockage of the spray unit is avoided.

According to the invention, this object is achieved in that a gaseous medium is added to each of the separate reactant streams, optionally after heating, the reactant streams are then combined and finally are forced through the spray unit at a rate of 0.1 to 15 m/sec., as calculated from the gas-free reactant streams and based on the free cross-section of the spray unit, the masses of reactants and gaseous medium being gauged in such a way that a mass ratio of gaseous medium to product stream of 0.04 to 0.3 (kg/kg) is obtained.

The process according to the invention may be applied anywhere where solid or paste-form products are formed in the course of fast chemical reactions, as for example in the neutralization of acids, particularly carboxylic acids, sulfuric acid semiesters and sulfonic acids, and in the saponification of esters, for example lower alkyl esters of fatty acids, particularly to the corresponding alkali salts using concentrated aqueous alkalis. The process according to the invention is also suitable for the production of alkali salts, more especially the sodium salt, of monochloroacetic acid and for the production of quaternary ammonium compounds by alkylation of tertiary amines, for example with alkyl halides. The process according to the invention is used with particular preference in the production of solid, free-flowing washing-active products.

Solid or paste-form, washing-active products which may be produced in accordance with the invention include inter alia the neutralization products of alkyl aryl sulfonic acids, α -sulfofatty acid esters and fatty acids and also the sulfuric acid semiesters of alkoxylated, more especial-

ly ethoxylated, fatty alcohols and phenols and sulfosuccinic acid and the saponification products of fatty acid esters, particularly fatty acid methyl esters. The neutralization or saponification is preferably carried out with concentrated aqueous alkalis, for example with sodium hydroxide containing around 50% by weight NaOH. Gases inert to the reactants and reaction products, such as air, nitrogen and steam, are particularly suitable as the gaseous medium. Steam is used particularly when the reactant streams or one of the reactant streams is/are to be heated before being combined. The distance between the point at which the gas-treated reactant streams are combined and the spray unit depends upon the process conditions and material systems and should be kept as small as possible. It may readily be determined by the expert in simple tests; it is merely important to ensure that the nozzle is not blocked by premature neutralization or saponification reactions.

In the context of the invention, aqueous alkalis are understood in particular to be the hydroxides, carbonates and hypochlorites of sodium and potassium in aqueous solution or suspension and also mixtures thereof. With the hypochlorites, it is possible at the same time to obtain a bleaching effect desirable for many products.

The upper limit to the velocity of the combined reactant streams, based on the free cross-section of the spray unit, is determined by the sonic velocity of the gas and the adjusted ratio of gas mass flow to product mass flow, calculation being based on the gas-free reactant streams.

Through the addition of a gaseous medium into the reactant streams before they are combined, the process according to the invention is independent of the type and construction of the particular spray nozzles used. Spray neutralization or saponification in a simple tube is even

possible. To achieve thorough mixing and to obtain a fully neutralized, homogeneous product, higher mass ratios between gaseous medium and product stream are necessary where spraying is carried out using a tube than where it is carried out using nozzles which are also normally used for spraying liquids. Suitable nozzles are, for example, hollow cone, solid cone and flat jet nozzles with corresponding swirl elements or swirl slots or with a tangential inlet into a swirl chamber.

Suitable nozzle types and particulars of their dimensions can be found in the relevant literature, for example in K. Chaster, Spray Drying Handbook, John Wiley & Sons, New York, 1979.

The dimensions of the nozzle opening are dependent on the required throughput.

The process according to the invention is particularly suitable for the production of solid, free-flowing washing-active products, preferably for the production of washing-active alkali sulfates or sulfonates. Reactant streams, particularly acid streams, containing a solution or suspension of buffers are preferably used for this purpose. The type of buffers used are known to the expert on the subject of hydrolysis-sensitive surfactants.

In another advantageous embodiment of the invention, sodium perborate is added as buffer for the production of products which have to be bleached to improve their colour, particularly fatty acid (lower) alkyl ester sulfonates; this buffer also acts as a bleach, thereby eliminating the need for a separate process step.

In another advantageous embodiment of the invention, the heat of neutralization or the energy which has to be introduced into the saponification of esters is utilized to evaporate the water of reaction and the water generally introduced through the aqueous alkalis, so that solid, free-flowing washing-active products can be obtained. In

addition, the heat of neutralization or rather the energy mentioned may be used completely to remove low-boiling solvents, for example methanol, present or formed in the reaction system.

5 According to one particularly advantageous feature of the process according to the invention, products having dioxane contents below 200 ppm, based on the solids content, are obtained in the production of fatty alcohol ether sulfates by neutralization of sulfuric acid semiesters of
10 fatty alcohol ethoxylates with aqueous alkalis.

 The process according to the invention is also suitable for the production of alkali salts of substituted fatty acids by neutralization or for the production of quaternary ammonium compounds by alkylation of the corresponding
15 tertiary amines, particularly with alkyl halides.

 Through the process according to the invention, the reactants are intensively mixed while they are being combined and the reaction mixture is finely dispersed
20 immediately after the intensive mixing by spraying through a nozzle. The mixing and fine dispersion can be effected by the kinetic energy of the reactants (flow velocity) and by the potential energy of the reaction mixture (pressure). Both are promoted by the gaseous medium to be added. The
25 addition of the medium to the reactants before they are combined prevents the formation of relatively large product units during the combination phase. This enhances the necessary micromixing of the reactants and simplifies the following spraying step.

30 In the case of exothermic reactions, as for example in the neutralization of sulfonic acids and fatty acids, the gaseous medium, in addition to intensifying the mixing process, also serves to dissipate the heat of reaction and to reduce the reaction temperature. If, on the other hand,
35 a relatively high reaction temperature is necessary to

increase the reaction velocity to achieve high conversions under the conditions of a spraying process, the gaseous mixture may also be preheated in addition to the reactant streams and may be used to establish the necessary reaction temperature by direct heat exchange with the reaction medium. The hydrolysis of fatty acid methyl esters with concentrated aqueous alkalis is mentioned as an example of this. The addition of the gaseous medium to the reactant streams enables spraying to be carried out at low pressures, even where paste-like or solid products are formed. The performance of the nozzle may be varied by simple changes in the volume streams of the gaseous medium.

In the practical application of the process according to the invention, the reactants stored in the appropriate storage tanks are introduced in stoichiometrically dosed quantities using piston pumps into an unmodified commercially available nozzle or spray tube. The gaseous medium is introduced into the reactant streams before the reactants are combined immediately before the nozzle. In the neutralization of sulfonic acids and fatty acids, air or nitrogen at room temperature is used as the gaseous medium. The basic hydrolysis of the methyl ester may take place on the methyl ester side for example using nitrogen at room temperature and, on the alkali side, using superheated steam (150-160°C) as the gaseous medium.

The reaction temperature may be directly controlled through the mass or volume flows of the reactants and the temperature thereof. In addition, the reaction temperature may be influenced by the mass or volume flow of the gaseous medium and the temperature thereof.

Adjustment of the pH value of the product in the technically interesting range (pH 7 to pH 9) is complicated by the very small quantities and residence times of the reactants in the nozzle and by the marked dependence of the pH value on the mass ratio between acid and concentrated

aqueous alkalis. For example, a slight reduction in the quantity of alkylbenzenesulfonic acid used (by 1%) leads to an increase in the pH value from pH 4 to pH 11.

5 By addition of buffers, such as citric acid and, in particular, sodium perborate (buffer effect of boric acid), a distinct flattening of the neutralization curve is obtained through the buffer effect,

10 If, for example, 6% sodium perborate is added to alkyl benzenesulfonic acid and the resulting suspension delivered to the nozzle, variations in the reactant streams of 2% only produce changes in the pH values between 7 and 9.

15 The low mass ratio between auxiliary and product is of advantage in the process described herein. Mass ratios of 0.3 kg and, in particular, of less than 0.3 kg gaseous medium per kg end product are sufficient to achieve very thorough mixing and to obtain a fully neutralized, homogeneous spray product in the production of a fully neutralized product in the neutralization of sulfonic acids. Table 1
20 below shows the operating conditions where different nozzle types and nozzle diameters are used in the neutralization of alkyl benzenesulfonic acid with 50% sodium hydroxide solution.

11 0 319 819

Table 1

Operating conditions in the neutralization of alkyl benzenesulfonic acid

Nozzle type	Bore diameter [mm]	Pressure before nozzle [bar]	Product velocity [m/s]*	Ratio of gas to product mass flow (kg/kg)
30° hollow	1.2	8.8	7.1	0.08
cone nozzle	1.2	10.7	15.0	0.07
(Schlick	2.7	2.8	1.4	0.10
Model 100/200)	2.7	6.9	6.9	0.05
	3.4	2.8	0.9	0.09
	3.4	5.7	4.4	0.04
	5.0	3.1	1.1	0.08
	5.0	4.1	2.0	0.04
Tube	3.0	6.9	1.5	0.20
	3.0	9.7	2.7	0.19
	6.0	2.7	0.4	0.23
	6.0	4.9	1.4	0.15
Annular gap	$d_a = 5.0$	$d_i = 3.0$	0.8	0.29
(Schlick	$d_a = 5.0$	$d_i = 3.0$	3.1	0.13
Model 942)				

* based on the free cross-section of the nozzle orifice

The process according to the invention is illustrated by the following Examples. A nozzle of the model 942 type made by Schlick with the dimensions shown in Table 1 was used.

5

Example 1

Spray neutralization of alkyl benzenesulfonic acid (ABS)

Starting materials: ABS (basis C_{12/14}), m approx. 60 kg/h,
t approx. 60°C

10

sodium hydroxide containing 50% by
weight NaOH, t approx. 40°C

spraying pressure : 4.5 bar

N₂-demand : 2 m³/h

15

Spray product (quantities in % by weight):

WAS : 84.8

US : 1.6

Na₂SO₄ : 0.8

H₂O : 11.5

20

pH value : 9.6
(1% solution, based on WAS)

Klett colour value: 59

25

(5% solution, based on WAS,
4 cm cell, blue filter no. 42)

Example 2

Spray neutralization of fatty alcohol sulfonic acid (FAS)

Starting materials: FAS (basis $C_{12/16}$), m approx. 60 kg/h,
t approx. 60°C

sodium hydroxide containing 50% by
weight NaOH, t approx. 40°C

spraying pressure : 4.5 bar

N_2 -demand : 2 m³/h

Spray product (quantities in % by weight):

WAS : 71.2

US : 8.6

Na_2SO_4 : 6.3

NaCl : 0.1

H_2O : 12.6

pH value : 9.5

(1% solution, based on WAS)

Klett colour value: 63

(5% solution, based on WAS,

4 cm cell, blue filter no. 42)

Example 3

Spray neutralization of fatty acid methyl ester sulfonic acid (MES)

5 Starting materials: MES (basis $C_{16/18}$), m approx. 20 kg/h,
t approx. 80°C
sodium hydroxide containing 48% by
weight NaOH, t approx. 40°C
spraying pressure : 8.5 bar
10 N_2 -demand : 2 m³/h

Spray product (quantities in % by weight)

	mono	:	52.3
	di	:	27.7
15	mono + di	:	80.0
	US	:	6.4
	Na ₂ SO ₄	:	6.2
	water	:	10.3
20	pH value	:	9.0
	(1% solution, based on WAS)		

Klett colour value: 305
(5% solution, based on WAS,
25 4 cm cell, blue filter no. 42)

Example 4

Spray neutralization of fatty alcohol ether sulfonic acid (FAES)

- 5 Starting materials: FAES (basis $C_{12/14}$; 2 mol EO) containing approx. 380 ppm dioxane, t approx. 30°C sodium hydroxide containing 50% by weight NaOH, t approx. 30°C
- 10 N_2 -demand : 2 m³/h
spraying pressure : 5 bar

Spray product (quantities in % by weight):

	WAS	:	77.2
	US	:	3.8
15	Na ₂ SO ₄	:	1.2
	H ₂ O	:	9.4
	dioxane	:	under 200 ppm

20 pH value : 10.1
(1% solution, based on WAS)

Klett colour value: 37
(5% solution, based on WAS;
4 cm cell, blue filter no. 42)

Example 5

Spray neutralization of fatty acid

- Starting materials: palmitic acid, m 60 kg/h, t 70°C
- 5 sodium hydroxide containing 42% by weight NaOH, t 40°C
- spraying pressure : 3.5 bar
- N₂-demand : 2 m³/h
- 10 Spray product (quantities in % by weight):
- | | | |
|------------------|---|------|
| Na soap | : | 69.9 |
| H ₂ O | : | 26.8 |
| palmitic acid | : | 0 |
- 15 pH value : 9.7
- (1% solution or Na soap)

Example 6

Saponification of fatty acid methyl esters

Starting materials: C₁₄ methyl ester, m 30 kg/h, t 125°C
5 sodium hydroxide containing 50% by
weight NaOH, t 110°C
spraying pressure : 6.5 bar
N₂-demand : 1 m³/h
steam demand : 1 m³/h
10 nozzle temperature (preheating 150°C)

Spray product (quantities in % by weight):

Na soap	:	86.6
H ₂ O	:	13.7
C ₁₄ methyl ester:		0.1-0.2
methanol	:	2.0
pH value	:	9.3
(1% solution, Na soap)		

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CLAIMS

1. A process for the production of solid or paste-form products by reaction of stoichiometric quantities of several reactants in a fast reaction and spraying of the reaction products in a spray unit, characterized in that a gaseous medium is added to each of the separate reactant streams, optionally after heating, the reactant streams are then combined and, finally, are forced through the spray unit at a rate of 0.1 to 15 m/second, as calculated from the gas-free reactant streams and based on the free cross-section of the spray unit, the masses of the reactants and the gaseous medium being gauged in such a way that a mass ratio of gaseous medium to product stream of from 0.04 to 0.3 (kg/kg) is obtained.
2. A process as claimed in claim 1, characterized in that acids are neutralized with concentrated aqueous alkalis.
3. A process as claimed in claim 1, characterized in that esters are saponified with concentrated aqueous alkalis.
4. A process as claimed in any of claims 1 to 3 for the production of solid, free-flowing washing-active products.
5. A process as claimed in any of claims 1 to 4 for the production of washing-active alkali sulfates or sulfonates, characterized in that one of the reactant streams, particularly the acid stream, contains a solution or suspension of buffers.
6. A process as claimed in claim 5, characterized in that sodium perborate is used as the buffer.
7. A process as claimed in any of claims 1 to 6 for the production of solid, free-flowing washing-active products.
8. A process as claimed in any of claims 1 to 7 for the production of products which are free from low-boiling solvents.
9. A process as claimed in any of claims 1 to 8 for the production of fatty alcohol ether sulfates having a dioxane content of less than 200 ppm, based on the solids content,



by neutralization of sulfuric acid semiesters of fatty alcohol ethoxylates with aqueous alkalis.

10. A process as claimed in claim 1, characterized in that monochloroacetic acid is reacted with concentrated alkali hydroxides.
- 5 11. A process as claimed in claim 1, characterized in that tertiary amines are alkylated.



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