

PROCESS FOR THE PREPARATION OF HIGHLY SULFATED
FATTY ACIDS AND FATTY ACID DERIVATIVES

The present invention relates to a process for the production of highly sulfated fatty acids, hydroxy fatty acids and/or oxalkylated hydroxy fatty acids.

The reaction of fatty acids and fatty acid esters with sulfuric acid or oleum to manufacture water-soluble products or those which are miscible with water, respectively, and which have surface active properties is a wide-spread method in industry. Starting, for example, from castor oil, olive oil, soybean oil, sunflower oil, tallow, or various fish oils, as well as the natural fatty acids bonded therein and obtainable by saponification, and depending on certain reaction conditions so-called "sulfated oils" for many purposes could be manufactured.

A particularly known example of this family is sulfated castor oil which is commercially available until today under the name "Turkey-red oil".

According to a process described in DRP 561 715, it is possible to produce products with an extraordinary resistance to acids and salts by means of short-time sulfatation with large amounts of sulfuric acid under rapid cooling. Analytic tests revealed that these extraordinary wetting agents exhibited an amount of organically bonded sulfur which was substantially higher than could be achieved with other processes.

According to these results efforts were made to achieve a degree of sulfatation which is as high as

possible. The degree of sulfatation indicates how much percent of the fatty acids within the examined product are actually sulfated; in this connection, it is arbitrarily assumed that the total amount of organically bonded sulfuric acid (calculated as SO_3) is present in the form of ricinoleic acid monosulfuric acid ester (H.P. Kaufmann, *Analyse der Fette und Fettprodukte* [Analysis of the fats and fat products], Springer Verlag 1958, page 1495). Due to the properties with respect to application technology a sulfatation degree of at least 50% was, and still is desirable. The terms "highly sulfated" or "high degree of sulfatation" will be used to this effect in the following.

According to known processes, increasing the sulfatation degree to values of more than 50% requires the use of solvents, such as trichloroethylene. In this connection, the solvent on the one hand serves as diluent during sulfation, and, on the other hand, as agent to separate off the non-sulfated portions from the reaction product.

DE-OS 36 06 868 describes a possibility to separate the unsulfated portions from the sulfation mixture without having to use a solvent. According to this publication, foreign substances having a demulsifying effect are added during the production of unsaturated fatty-acid-low-alkyl-ester-sulfonates. It is recommended to use additions of 5 to 400 parts by weight of sorbitan- or glycerol fatty acid ester and 5 to 300 parts by weight of a low-molecular alcohol per 100%-wt. sulfonated ester.

It is accordingly the object of the present invention to provide a process for the production of highly sul-

fated fatty acids, hydroxy fatty acids and/or oxalkylated hydroxy fatty acids, which on the one hand permits to avoid the use of solvents, the toxicity problems associated therewith, and the expenditure arising with respect to devices and equipment, and which, on the other hand, can do without the addition of foreign substances which may impair the end products' properties with respect to application technology.

This object is achieved by the process according to the present invention, in which - subsequent to the sulfatation which is known per se - the reaction mixture comprising the sulfated esters as well as unsulfated starting products is neutralized. Then the neutral ester sulfate is diluted with water, in this connection the brine may optionally be separated off first. After addition of lye whose quantity is equimolar or submolar to the organically bonded sulfuric acid content, the alkaline solution obtained is hydrolyzed at temperatures between 20°C and 160°C, preferably between 40 and 90°C, whereby a water-insoluble oil layer consisting of unsulfated esters separates out of the aqueous phase comprising the desired sulfated fatty acids which can subsequently be isolated.

The ester sulfate obtained from the sulfatation reaction and normally adjusted to neutral is preferably diluted with at least half of the weight amount of water, further preferred double or triple the weight amount of water, relative to the weight of the ester-sulfate-mixture.

The water content of the alkaline mixture at the beginning of the hydrolysis advantageously amounts to 60

to 95%-wt, preferably 70 to 90%-wt, relative to the total mixture.

According to the present invention, the ester sulfate mixture which is optionally desalinated may be mixed with 10 to 50%-wt of an already hydrolyzed ester sulfate, relative to the non-hydrolyzed ester sulfate, and subsequently subjected to further hydrolysis at temperatures of at least 20°C. Hydrolysis may be carried out under pressure or without pressure.

Suitable starting products are unsaturated fatty acid esters, saturated or unsaturated hydroxy fatty acid esters, or the alkoxylation products of saturated or unsaturated hydroxy fatty acid esters of water-soluble mono- or bivalent alcohols, such as methanol, ethanol, n-propanol, i-propanol, ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butylene glycol, and hexylene glycol.

Easily accessible fatty acid esters are preferred, such as oleic acid methyl ester, tall oil fatty acid methyl ester, fish oil fatty acid methyl ester, rapeseed oil fatty acid methyl ester, oleic acid ethyl ester, oleic acid isopropyl ester, ethylene glycol dioleate, 1,2-propylene glycol dioleate, ricinoleic fatty acid methyl ester, ricinoleic fatty acid ethyl ester, and the alkoxylated derivatives of the ricinoleic fatty acid ester - provided that they are water-insoluble.

The mentioned starting products may be used alone or in admixture and are preferably substantially free from fatty acids.

Depending on their origin the starting esters contain portions of unsulfatable saturated esters which, however, do not disturb the process according to the present invention, they can be isolated together with the unsulfated unsaturated esters from the desired sulfated products.

However, free fatty acids and soaps may impair the production process according to the present invention. For this reason, fatty acid esters with the lowest possible cleavage should be used in cases where very high separation efficiency is required.

The achieved degree of sulfatation is of no great importance in the reaction of these esters with sulfuric acid or oleum to the ester sulfates. The reaction may be carried out according to common methods.

The step of dilution according to the present invention under the addition of bases results in phase separation into an upper, oily phase and a lower, aqueous phase comprising the desired sulfated fatty acids. The upper oil-phase, called "neutral oil", mainly comprises unsulfated esters.

Any lye suitable for the cleavage of fats can be used in the alkaline saponification, in particular strong lyes, such as soda lye and potash lye. Since the fatty acid ester sulfates are readily saponifiable, the use of weaker bases, such as ammonia and amines, is possible too.

The amount of lye depends on the desired portion of sulfated soap and alcohol in the ester sulfate solu-

tion, and can freely be selected between a 10% and 100% cleavage of the ester sulfate.

The alkali treatment in the presence of larger amounts of water according to the present invention nearly exclusively results in a saponification of the fatty acid ester sulfate.

If at all, hydrolysis of the unsulfated portions of the mixture takes place to a negligible extent.

The alkaline solution is heated to a temperature between 20°C and 160°C, preferably between 40 and 90°C, until the lye is exhausted and the unsulfated portions separate off in form of the upper neutral oil film.

An amount of lye larger than the equivalent to the organically bonded sulfuric acid content is to be avoided, since in case of lye excess the unsulfated ester would be cleaved too. This undesired saponification can be avoided by the addition of sub-stoichiometric amounts of lye.

If the ester sulfate mixture obtained from the sulfation reaction is to be stored intermediately, it may be of advantage to effect an alkaline stabilization by a slight excess of lye when the acidic ester sulfate is set to neutral, so as to avoid an uncontrolled acidic cleavage. This excess of lye must be considered when the lye is added later so that the total quantity added does not exceed an amount equivalent to the organically bonded sulfuric acid content.

During the saponification reaction the aqueous solution of the sulfatation mixture which - depending on the sulfatation degree - is clear or milky increasingly becomes cloudy, and finally oil separates out. The

phase separation can be accelerated physically, e.g., by means of centrifuges or packed columns.

The period of time until the oil separation starts mainly depends on the kind of fatty acid ester, the inorganic salt content, and the temperature during the treatment. Whereas sulfated esters of primary alcohols rapidly separate the unsulfated portions during the process according to the present invention, the separation in case of sulfated esters of bivalent alcohols takes place slower; the latter having a stronger tendency to permanently absorb the neutral oil portions. Depending on the desired result in each individual case, an optimization of the process can be achieved by variation of the temperature and - via the lye amount - the degree of saponification.

However, it is possible too, and sometimes even recommendable to mix a slow-reacting sulfated ester with a quick-reacting ester, e.g., a sulfated methyl ester. The additionally added sulfated ester may be the same or different with respect to the fatty acid base and/or degree of sulfatation.

It is of advantage with respect to the subsequent hydrolysis and phase separation to use the additional ester suitable therefor directly in the sulfatation reaction so that a mixture already comprising different suitable esters is sulfated and subsequently subjected to the further steps according to the present invention.

The individual stages of the process according to the present invention may be carried out either discontinuously or continuously. In case of short-time heating

of the alkaline ester sulfate solution under pressure, e.g., within a tubular or a falling-film reactor, the required saponification temperature is to be adapted to the reactor arrangement and the flow rate. In this connection, the rule applies that a reduction of the residence time of the ester sulfate solution within the heating device requires an elevation of the saponification temperature.

The process according to the present invention shall be illustrated by way of the following examples which are given in the form of general working instructions I to IV and the corresponding tables.

General working instruction I

A g of an ester sulfate or ester sulfate mixture, respectively, manufactured with concentrated sulfuric acid and neutralized with soda lye and having a degree of sulfatation S_1 at an SO_3 -content of B %, were diluted with 2,000 ml softened water. Subsequently, 45% soda lye the amount of which was equimolar to the SO_3 -content was added (quantity C). After strong mixing, the alkaline solution was heated to approximately 50°C, whereby the solution became very turbid, and finally layers formed. Phase separation resulted in D g unsulfated fatty acid ester.

The sulfated fatty acid sulfate was obtained from the lower, aqueous phase after addition of mineral acid (pH = 4) and common salt. The degree of sulfatation of the starting products and that of the end products (S_1 and S_2) are indicated in Table 1.

In examples h and i hydrolysis was carried out with 45% potash lye and concentrated ammonia solution, respectively.

General working instruction II

A g of an ester sulfate or ester sulfate mixture, respectively, produced with concentrated sulfuric acid and neutralized with soda lye and having a degree of sulfatation S_1 at an SO_3 -content of B %, were diluted with 2,000 ml softened water. Subsequently, 45% soda lye (quantity C) was added the amount of which was submolar with respect to the SO_3 -content. Further processing was carried out as described under I.

The test results are summarized in Table II.

General working instruction III

A g ester sulfate or ester sulfate mixture, respectively, manufactured with concentrated sulfuric acid and neutralized with soda lye and having a degree of sulfatation S_1 at an SO_3 -content of B %, were diluted with 400 ml boiling, softened water. Subsequently, the mixture was heated to 80°C and an equimolar amount (relative to the SO_3 -content) of 45% soda lye (quantity C) was added. After strong mixing, the alkaline, cloudy liquid was placed in a centrifuge and centrifuged at 3,000 rpm for 3 minutes (Martin Christ, Osterode; type UJ3, 330 watts). Finishing was carried out as specified under I.

The results are shown in Table III.

The manufacture of the starting material which builds the basis for the general working instructions I, II, and III is exemplified on the basis of the oleic acid methyl ester:

538 g oleic acid methyl ester (Edenor ME TI 05, HENKEL) were sulfated within 1 hour with 350 g concentrated sulfuric acid under ice cooling (max. 10°C) and rapid stirring. Subsequently, 1676 g of an alkaline-aqueous solution comprising 225 g caustic soda and 120 g common salt were added as quickly as possible in order to neutralize the solution to a pH-value of 5 to 6 and work it up. In this connection, the temperature rose to 80°C. The mixture was allowed to stand at 50 to 60°C, subsequently the salt solution was removed and the obtained ester sulfate was determined with respect to water content and sulfatation degree (yield: 1,000 g).

Water content:	40%
Content of effective substance:	60%
Degree of sulfatation:	appr. 50%

This product was subjected to the processes according to the general working instructions I (examples h, i), II (examples b, c, d), and III (example a). In this connection, unsulfated methyl ester was separated from the aqueous phase and the sulfatation degree increased correspondingly.

General working instruction IV

According to the general working instruction I, A g of an ester sulfate produced with concentrated sulfuric acid and neutralized with soda lye and having an SO₃-

content of B % and a sulfatation degree of S₁ % are diluted with 500 ml softened water. Hydrolysis and further working up were carried out according to the general working instruction I.

The results are shown in Table IV.

Table I **General working instruction I**

	Charge (g) <u>A</u>	H ₂ O- addition (g)	Ratio A:H ₂ O	H ₂ O- content (%)*	SO ₃ (%) <u>B</u>	NaOH 45% (g) <u>C</u>	Unsulph. (g) <u>D</u>	S ₁ (%)	S ₂ (%)
a) Oleic acid methyl ester	1,000	2,000	1:2.0	80.0	8.2	90	201	57	87
b) Tall oil fatty acid methyl ester	1,134	2,000	1:1.76	78.3	8.6	108	182	58	82
c) Oleic acid isopropyl ester	796	2,000	1:2.51	82.9	9.5	82	151	56	83
d) 1,2-propylene glycol dioleate	984	2,000	1:2.03	80.2	7.7	84	106	48	61
e) Ricinoleic acid methyl ester	1,346	2,000	1:1.49	75.8	7.1	106	470	39	71
f) Oxethylated ricinoleic acid methyl ester (3 mole EO)	984	2,000	1:2.03	80.2	6.1	66	130	41	76
g) Oleic acid methyl ester oleic acid isopropyl ester (mixed 1:1)	1,000	2,000	1:2.00	80.0	8.4	93	193	57	85
h) Oleic acid methyl ester	1,500	2,000	1:1.33	74.3	4.8	KOH 45% 112	145	50	89
i) Oleic acid methyl ester	1,500	2,000	1:1.33	74.3	4.8	NH ₃ conc. 106	65	50	68

*H₂O-content prior to hydrolysis, relative to an average water content of the starting product of 40%.

Table IIGeneral working instruction II

	Charge (g) <u>A</u>	H ₂ O- addition (g)	Ratio A:H ₂ O	H ₂ O- content (%)*	SO ₃ (%) <u>B</u>	NaOH,45% (g) <u>C</u>	Unsulf. (g) <u>D</u>	S ₁ (%)	S ₂ (%)
a) Oleic acid methyl ester	750	2,000	1:2.67	83.6	8.2	41	229	43	81
b) "	1,000	2,000	1:2.00	80.0	4.8	21	79	50	80
c) "	1,000	2,000	1:2.00	80.0	4.8	16	68	50	76
d) "	1,000	2,000	1:2.00	80.0	4.8	11	52	50	70

*H₂O-content prior to hydrolysis

relative to an average water content of the starting product of 40%.

Table IIIGeneral working instruction III

	Charge (g) <u>A</u>	H ₂ O- addition (g)	Ratio A:H ₂ O	H ₂ O- content (%)*	SO ₃ (%) <u>B</u>	NaOH,45% (g) <u>C</u>	Unsulf. (g) <u>D</u>	S ₁ (%)	S ₂ (%)
a) Oleic acid methyl ester	300	400	1:1.33	74.3	4.8	16	28	50	88

*H₂O-content prior to hydrolysis

relative to an average water content of the starting product of 40%.

Table IV

	Charge (g) <u>A</u>	H ₂ O- addition (g)	Ratio A:H ₂ O	H ₂ O- content (%)*	SO ₃ (%) <u>B</u>	NaOH, 45% (g) <u>C</u>	Unsulph. (g) <u>D</u>	S ₁ (%)	S ₂ (%)
a) Oleic acid methyl ester	1,000	500	2:1	60	8.2	90	108	57	78

*H₂O-content prior to hydrolysis

relative to an average water content of the starting product of 40%.



C L A I M S

1. Process for the production of highly sulfated fatty acids, hydroxy fatty acids or oxalkylated hydroxy fatty acids characterized by the following steps:

- sulfatation of unsaturated fatty acids and/or saturated or unsaturated hydroxy fatty acid esters and/or oxalkylated saturated or unsaturated hydroxy fatty acid esters,
- neutralization of the reaction mixture,
- optionally separation of the brine,
- dilution of the neutral or alkaline stabilized ester sulfate with water,
- addition of lye the amount of which at maximum is equimolar to the organically bonded sulfuric acid content,
- hydrolysis of the alkaline solution at temperatures between 20°C and 160°C, preferably 40 to 90°C,
- separation of the oil-phase which substantially consists of non-sulfated starting product from the aqueous phase which comprises the highly sulfated fatty acids,
- isolation of the highly sulfated fatty acids.

2. The process according to claim 1 wherein dilution of the neutralized, optionally desalinated ester sulfate mixture is effected with at least half of the weight amount of water, relative to the weight of the sulfatation mixture.

3. The process according to claims 1 or 2 wherein the neutral, optionally desalinated ester sulfate mixture is diluted with double to triple the weight amount of



water, relative to the weight of the sulfatation mixture.

4. The process according to any one of claims 1 to 3 wherein the water content of the alkaline mixture at the beginning of the hydrolysis amounts to 60 to 95%-wt, relative to the total mixture.

5. The process according to any one of claims 1 to 4 wherein the water content of the alkaline mixture at the beginning of the hydrolysis amounts to 70 to 90%-wt, relative to the total mixture.

6. The process according to any one of claims 1 to 5 wherein the optionally desalinated ester sulfate mixture is mixed with 10 to 50%-wt, relative to the non-hydrolyzed ester sulfate, of an already hydrolyzed ester sulfate and subsequently subjected to further hydrolysis.

7. The process according to any one of claims 1 to 6 wherein the hydrolysis of the ester sulfate is carried out under pressure.

8. The process according to any one of claims 1 to 7 wherein the used fatty acid esters or fatty acid ester derivatives, respectively, are esters of low-molecular, water-soluble, mono- or bivalent alcohols.

9. The process according to any one of claims 1 to 8 wherein the unsaturated fatty acid esters are used in admixture with saturated fatty acid esters.

10. The process according to any one of claims 1 to 9 wherein in case of using a mixture of different esters



in the sulfatation reaction and/or in the hydrolysis, the esters may be the same or different with respect to the fatty acid base and/or sulfatation degree.

11. The process according to any one of claims 1 to 10 wherein the fatty acid esters used are substantially free from fatty acids.

12. The process according to any one of claims 1 to 11 wherein the sulfated fatty acid esters used in the stage of hydrolysis are substantially free from cleavage products.

13. The process according to any one of claims 1 to 12 wherein the hydrolysis is carried out with strong and/or weak bases.