

Pumpable, highly concentrated aqueous pastes of alkali metal salts of α -sulfonated fatty acid alkyl esters and a process for their production.

This invention relates to aqueous pastes of alkali metal salts of α -sulfonated fatty acid alkyl esters.

It is known that α -sulfofatty acid ester salts may be obtained in the form of aqueous pastes by neutralizing α -sulfofatty acid esters, in particular with aqueous alkali metal hydroxide. The starting materials used are natural fats and/or oils obtained by ester cleavage and subsequent esterification with lower (C_1 - C_4) alkanols, more especially methanol, or by transesterifying the natural triglycerides with the lower (C_1 - C_4) alkanols. Depending on the origin of the natural starting material, the fatty acid ester mixtures obtained contain a comparatively broad range of fatty acids which is normally covered by C_{10} to C_{24} . The sulfonation of these fatty acid ester mixtures, in particular with gaseous SO_3 , leads to more or less heavily discolored, acidic crude sulfonates which have to be bleached and converted into ester sulfonate pastes by neutralization to a pH-value in the range from about 6 to 7. In this form, they are now acquiring increasing practical significance as surfactants and wetting agents for detergents and cleaners based on renewable raw materials of natural origin.

One particular difficulty involved in handling pastes of alkali metal salts of α -sulfonated fatty acid alkyl esters (hereinafter referred to as ester sulfonate salts) is their concentration/viscosity behaviour. It is only at comparatively low solids concentrations (for example up to solids contents of

1 approximately 35% by weight) that ester sulfonate salts pro-
duced on an industrial scale form, in aqueous mixture,
sufficiently fluid solutions or suspensions to guarantee the
uninterrupted operation of industrial processes. At higher
5 ester sulfonate salt contents (solids contents of around 40%
by weight or higher), the viscosity of the aqueous preparation
increases to such an extent that it no longer flows freely.
This gives rise to serious limitations namely:

Attempts to produce highly concentrated ester sulfonate
10 salt pastes directly by neutralizing the crude sulfonic acid
mixture with concentrated alkali^{metal}/hydroxide solution fail
because the stirrability and, hence, uniform miscibility of
the reaction mixture is lost. At the same time, it becomes
impossible to dissipate the heat of neutralization. Local
15 concentration and temperature peaks give rise to undesirable
secondary reactions, including in particular the formation of
disalts of the α -sulfofatty acids in large quantities through
ester cleavage. Another disadvantage is that, understandably,
ester sulfonate pastes immobilized by an increase in viscosity
20 can no longer be pumped on an industrial scale. Pipes become
blocked and the plant as a whole is brought to a prolonged
standstill.

The prior art on ester sulfonate salt pastes of the
type in question here is greatly concerned with these part-
25 icular problems. In particular, it has been proposed to use
flow aids and viscosity regulators to improve the flow behavior
of aqueous, commercial concentrates of α -sulfofatty acid ester
salts. Thus, DE-OS 33 05 430 forexample describes the use
of C_8 - C_{40} alcohols which, in addition, may contain one or more
30 hydroxyl groups as substituents and to which up to 20 moles
of ethylene oxide and/or propylene oxide per mole of alkanol
may be added. These viscosity regulators are added to the
ester sulfonate paste in quantities of from 1 to 15% by weight,
based on the quantity of surfactant, adjusting the viscosity
35 of the surfactant concentrate to at most 10,000 mPas at 70°C.

(12)

1 According to DE-OS 33 34 517, aqueous suspensions containing
from 40 to 65% by weight of α -sulfofatty acid ester salt,
from 2 to 10% by weight of a lower alcohol sulfate and,
optionally, at most 2% by weight of a lower alcohol are said
5 to be sufficiently fluid. These aqueous multicomponent
mixtures are obtained by initially preparing aqueous suspen-
sions containing from 30 to 55% by weight of the α -sulfofatty
acid ester salt in admixture with from 5 to 15% by weight of
a lower alcohol sulfate and from 8 to 40% by weight of a
10 lower alcohol and then concentrating the aqueous suspension
to the above-mentioned concentration values. According to
DE-OS 31 23 681, a highly concentrated aqueous solution of a
salt of an α -sulfofatty acid ester may be prepared by
neutralizing the crude sulfonic acid in a first stage to
15 pH 2.5-4 with a 15 to 50% by weight aqueous caustic alkali
solution in the presence of from 5 to 20% by weight of an
alcohol containing up to 4 carbon atoms, adding an aqueous
solution diluted to 1 - 5% by weight of alkali hydroxide to
the still acidic partially neutralized product in a following
20 stage and adjusting the pH-value to 6 - 7.

All these known proposals relate to the usual starting
materials of natural origin with the comparatively broad
range of chain lengths, for example from C_{10} to C_{24} , in the
fatty acid mixture. The present invention is based on the
25 surprising observation that, providing certain chain lengths
are selected for the fatty acid component of the ester
sulfonate salts, anomalies occur in the viscosity behavior of
highly concentrated salt pastes in the sense that, after the
usual increase in viscosity when the solids content rises
30 beyond about 40% by weight, a solids content is ultimately
obtained at which the viscosity values of the highly concen-
trated, aqueous ester sulfonate salt pastes fall again so
drastically that their free flow and, in particular their
pumpability at normal processing temperatures are guaranteed.

In a first embodiment, therefore, the present invention relates to aqueous pastes pumpable at temperatures of at least 60°C and having high contents of alkali metal salts of α -sulfonated fatty acid alkyl esters (ester sulfonate salts) surfactant, characterized in that they essentially contain ester sulfonate salts based on C₁₆ and/or C₁₈ fatty acids, have ester sulfonate salt solids contents of at least 6% by weight and substantially free from viscosity regulators.

The ester sulfonate salt solids content of the aqueous paste is preferably at least 65% by weight. Apart from being substantially free from viscosity regulators they are also preferably free of other viscosity-reducing additives.

Accordingly, the teaching of the present invention is based on the surprising discovery that, providing the chain length of the fatty acid component of the ester sulfonate salt is limited to C₁₆-C₁₈, aqueous suspensions having a particularly high concentration range of, in particular, from about 60 to 80% by weight and, preferably, from about 65 to 80% by weight are guaranteed free pumpability and miscibility at only moderately elevated temperatures of, for example, from 40 to 70°C, whereas if the solids content of the same ester sulfonate salts is reduced to a concentration range of around 40 to 60% by weight, the corresponding aqueous suspensions revert to their familiar concentration-viscosity behaviour, i.e. are no longer free-flowing or pumpable. The same applies when the limitation according to the invention with regard to the chain length of the fatty acid component of the ester sulfonate salts is not observed and, for example, the usual starting materials based on fatty acids mixtures having chain lengths of from C₁₂ to C₁₈ are

(15)

- 5 -

used. For ester sulfonate salt pastes of the type in question, there is no reduction in viscosity in the high solids range of 60 to 80% by weight which enables them to be freely and safely handled without the addition of viscosity regulators or other known measures.

The alkyl portion of the α -sulfonated fatty acid alkyl ester is derived from the lower alkanol (C_1 - C_4), in particular methanol used in the esterification or transesterification referred to above.

The presence in small quantities of fatty acids or fatty acid esters having chain lengths outside the desired range, of the type which can accumulate in the working up of natural fatty acid mixtures on an industrial scale, need not necessarily be troublesome. However, ester sulfonate salt pastes suitable for use in accordance with the invention contain those fatty acids outside the C_{16} - C_{18} range and, in particular, fatty acid esters of shorter chain length in quantities of at most up to about 10 mole % and preferably in quantities of distinctly less than 10 mole %. The mixing ratios discussed herein are ratios by weight. The mixing ratios of C_{16} - C_{18} fatty acids are preferably from about 3:2 to 0:1 and, more preferably, from about 3:2 to 1:2. A particularly important starting material for obtaining the highly concentrated and yet pumpable ester sulfonate salt pastes according to the invention are fatty acid esters, particularly fatty acid methyl esters, in which the mixing ratio of C_{16} to C_{18} is of the order of 1:1.

Industrial starting materials with the requisite mixing ratios for the number of carbon atoms in the fatty acid component accumulate in certain processes for working up natural fats and/or oils.

5

10

15

20

25

30

Thus, the production of oleic acid by splitting tallow using the so-called preferential wetting process of the working-up of palm oil leads to a product which contains the C_{16} and C_{18} fatty acids in a ratio of approximately 1:1 by weight. Accordingly, this product is a particularly suitable starting material for the purposes of the present invention. The production of so-called palm stearin from palm oil leads to fatty acid or fatty acid ester mixtures having a C_{16} to C_{18} ratio of about 60:40. The fatty acid cuts which accumulate in the working up of tallow frequently have a $C_{16}:C_{18}$ ratio of 1:2 with only slight impurities in the form of other fatty acids. Hardened soya oil has a $C_{16}:C_{18}$ mixing ratio of about 8:92. These starting materials are also suitable for the purposes of the present invention. By contrast, other standard fats and oils containing fatty acid mixtures, for example having chain lengths of from C_{12} to C_{18} , and at the same time only limited quantities of fatty acids within the $C_{16}-C_{18}$ range do not produce _____

lower viscosities when converted into ester sulfonate salt pastes having a solids content of 50% by weight and higher.

The pH-value of the highly concentrated aqueous ester sulfonate salt pastes according to the invention is preferably in the range from about 6 to 7. The viscosity of the pastes as determined by rotational viscosimeter generally does not exceed about 10,000 mPas at 70°C. The content of disalts is determined primarily by the mixing ratios selected for the ester sulfonation stage. The ester sulfonation stage is normally carried with an approximately 20% excess of SO₃ which, after neutralization with no other measures, leads to a disalt content of from about 20 to 25% by weight, based on washing-active substance (WAS). Disalt contents of this order do not affect the desired viscosity behavior of the highly concentrated ester sulfonate salt pastes. If desired, however, the disalt content may even be limited in known manner and, more particularly, in accordance with our copending Application No. 8522650 (Publication No. 2180233).

Referring to the accompanying drawings, Figure 1 shows the dependence of the viscosity behavior of an ester sulfonate salt paste according to the invention on the solids content (% WAS), the temperature dependence in the range from 60 to 90°C also being clearly apparent. The ester sulfonate salt in question here contains α-sulfonated fatty acid methyl ester with a mixing ratio of C₁₆ to C₁₈ of about 1:1, of the type which accumulates as co-product in the splitting of tallow by the preferential wetting process. Figure 1 shows that, beginning at a solids content of 40% WAS, there is a steep increase in viscosity - shear viscosity (D = 100 s⁻¹) - which reaches its maximum at about 50% WAS. When the solids content of the paste is further increased, viscosity falls and, between 60 and 75%, reaches WAS values which substantially correspond to the viscosity

behavior of a 30 to 40% ester sulfonate salt paste. By contrast, Figure 2 of the accompanying drawings illustrates the dependence of the viscosity behavior of an ester sulfonate salt paste derived from a commercial palm kernel oil containing a C_{12} - C_{18} fatty acid cut, the C_{12} - C_{14} fatty acid component making up at least about 70%. Starting at about 40% WAS, there is again a steep increase in viscosity, although no reduction in viscosity occurs when the solids content limits of 50% and 60% WAS are exceeded.

The discovery on which the present invention is based not only enables selected ester sulfonate salt pastes of higher solid concentrations to be safely handled, the teaching of the invention is particularly important for the production of highly concentrated ester sulfonate salt pastes. The difficulties arising out of the neutralization reaction and the undesirable thickening occurring as a result (producing inconsistencies in the reaction and also secondary reactions), which were hitherto regarded as unavoidable, may be safely eliminated in accordance with the invention. In the embodiment of the invention described hereinafter, it is possible directly to obtain ester sulfonate pastes of high solids content by neutralizing the crude sulfonic acids with highly concentrated alkali metal hydroxide, particularly sodium hydroxide, solutions. In this further embodiment, therefore, the present invention relates to the process for producing the highly concentrated ester sulfonate salt pastes which is characterized in that, optionally after acidic bleaching in known manner, more especially with H_2O_2 , the crude ester sulfonates are neutralized with intensive cooling at temperature below $90^{\circ}C$ to a pH-value of from about 6 to 7 using concentrated aqueous alkali^{metal}/hydroxide solution to form ester sulfonate salt pastes having a solids content of at least about 60% by weight and, if desired, are subjected to another bleaching treatment, more especially with $NaOCl$. To this end, the crude ester sulfonates and the concentrated aqueous alkali^{metal}/hydroxide solution are preferably fed into an intensively stirred and cooled

1 ester sulfonate paste of high solids content, preferably at least about 60% by weight WAS, so that neutralization takes place with salt formation within the desired, comparatively low viscosity aqueous ester sulfonate salt paste.

5 In the practical application of this neutralization process, it is important that the reaction mixture should be sufficiently cooled to dissipate the heat of neutralization so that the temperature does not exceed or significantly exceed an upper limit of the order of 90°C. Neutralization
10 temperatures of from about 60 to 90°C are particularly suitable. It is also preferred to limit the residence time (in continuous processes, the average residence time) of the reaction medium at temperatures in the above-mentioned range. The residence time or average residence time is preferably
15 not more than 30 minutes and, more particularly, less than about 20 minutes. By maintaining the above-mentioned temperatures and residence times, coupled with the intensive mixing of the suspension which is made possible by its low viscosity, the alkali/^{metal}hydroxide and crude sulfonic acid may
20 be uniformly mixed into the ester sulfonate paste, thus precluding any local differences in concentration and/or temperature. In addition, problems arising out of immobilization of the reaction mixture through excessive viscosity are ruled out by the fact that the WAS solids content of the
25 reaction medium is adjusted from the outset to such high concentrations that the low viscosity required prevails.

Using the process according to the invention, optionally prebleached crude sulfonates may be directly converted into free-flowing, fully neutralized ester sulfonate salt pastes
30 having a pH-value of from 6 to 7 with aqueous alkali/^{metal}hydroxide solutions having a concentration in the range of, for example, from 15 to 70% by weight and, preferably, from 30 to 55% by weight. The process according to the invention lends itself to modification in various ways. In one preferred embodiment,
35 neutralization is carried out continuously in a reaction loop

through which a C_{16} - C_{18} ester sulfonate salt paste according to the invention with solids contents of at least 60% by weight is circulated and cooled. On the one hand, α -sulfonated fatty acid esters within the above-mentioned chain-length range and aqueous neutralizing agent are introduced into this reaction loop whilst, on the other hand, a corresponding proportion of ester sulfonate paste is removed therefrom. The temperature in the neutralization loop is kept for example in the range from 80 to 90°C. If the crude sulfonic acid is subjected in known manner to acidic bleaching with H_2O_2 before neutralization, it may be advisable to place the neutralization circuit under pressure, for example under a pressure of up to 10 bars. If desired, the proportions of ester sulfonate paste removed from the neutralization circuit may be subjected to another bleaching treatment with NaOCl in the neutral range.

However, instead of reacting the alkali/^{metal}hydroxide and crude sulfonate in the neutralization cycle described above, neutralization may also be carried out in intensively stirred and cooled reactors already containing sufficient quantities of ester sulfonate paste. In this case, the process may be carried out in batches or even continuously.

Viscosity problems arising at the beginning of a continuous process may readily be overcome as follows:

At the beginning of the neutralization reaction, a viscosity regulator is added to the reaction mixture and, at the same time, sufficiently dilute reaction solutions are used, so that undesirable immobilization is safely prevented. Low-solids and/or viscosity-regulated ester sulfonate salt pastes such as these are concentrated in their ester sulfonate salt content while more viscosity regulator is continuously introduced. The viscosity of the pastes is best always kept at values of at most about 10,000 mPas at 70°C. After the

27

11

1 viscosity of the paste has reached its maximum at a solids
content of about 50% by weight WAS, it falls as the solids
content continuous to increase. The addition of viscosity
5 regulator may now be reduced until, in the desired concen-
tration range of the ester sulfonate salt paste, there is no
longer any need for viscosity regulation. At the same time,
provision is made by the introduction of highly concentrated
reactants (above all highly concentrated aqueous alkali hydroxide
solution), to ensure that the solids content of the reaction
10 medium remains in the desired range.

EXAMPLE

In a continuous sulfonation reactor, 42.5 kg/h (= 150
moles/h) of hardened tallow fatty acid methyl ester ($C_{16}:C_{18}$
15 1:1), from which the oleic acid had been removed before
hardening by separation using the preferential wetting process,
were reacted with 14.4 kg/h (= 180 moles/h) of SO_3 diluted
to 5% by volume with dry air to form α -sulfonated tallow fatty
acid methyl ester.

20 This sulfonation mixture was delivered at 80°C to a
continuous neutralization stage initially filled with water.
At the same time, 50% sodium hydroxide solution was introduced
to give a pH-value of from 5 to 7. The temperature is kept
at 80 to 90°C by cooling. The neutralized product is recir-
25 culated and thus concentrated. Beyond an active substance
(AS) content of about 25% by weight in the neutralized product,
from 5 to 8.5 kg/h of C_{28} Guerbet alcohol (10 to 15%, based on
AS) were introduced to reduce viscosity until the solids
concentration reached 55 to 60% AS. Thereafter, the addition
30 of the Guerbet alcohol was reduced in stages to 0% and the
neutralized product adjusted to a solids concentration of
approximately 70% AS. The highly concentrated paste may be
pumped without difficulty at temperatures in the range from
60 to 90°C.



22

12

CLAIMS:

1. Aqueous pastes pumpable at temperatures of at least 60°C and having high contents of alkali metal salts of α -sulfonated fatty acid alkyl ester (ester sulfonate salts) surfactant, characterised in that they essentially contain ester sulfonate salts based on C₁₆ and/or C₁₈ fatty acids, have ester sulfonate salt solids contents of at least 60% by weight and are substantially free from viscosity regulators.
2. Ester sulfonate salt pastes as claimed in claim 1, characterised in that their content of ester sulfonate salts of fatty acids containing less than 16 carbon atoms amounts to less than 10 mole %.
3. Ester sulfonate salt pastes as claimed in claims 1 and 2, characterised in that the ratio of C₁₆ to C₁₈ fatty acids therein is from 3:2 to 0:1.
4. Ester sulfonate salt pastes as claimed in claim 3 characterised in that the said ratio is between 3:2 and 1:2.
5. Ester sulfonate salt pastes as claimed in any of claims 1 to 4 characterised in that they are derived from commercial fats of natural origin and at least for the most part, contain α -sulfonated fatty acid methyl ester salts.
6. Ester sulfonate salt pastes as claimed in any of claims 1 to 5, characterised in that they have viscosities not exceeding 10,000 mPas at pH-values of from 6 to 7 and at temperatures of from 60 to 70°C.
7. Ester sulfonate salts pastes as claimed in claim 6 which contain no more than 25% by weight, based on wash active substance, of disalts.
8. Ester sulfonate salt pastes substantially as herein described with reference to the Example.
9. A process for producing ester sulfonate salt pastes as claimed in any of claims 1 to 8, characterised in that, optionally after acidic

2

13



bleaching in known manner with H_2O_2 , the crude ester sulfonates are neutralized with intensive cooling at temperatures not exceeding $90^\circ C$ to a pH-value of from 6 to 7 using concentrated aqueous alkali metal hydroxide solution to form ester sulfonate salt pastes having a solids content of at least 60% by weight and, if desired, are subjected to another bleaching treatment.

10. A process as claimed in claim 9 characterised in that the ester sulfonate salt paste formed has a solids content of from 65 to 80% by weight.

11. A process as claimed in claim 9 or claim 10, in which the further bleaching treatment is effected with $NaOCl$.

12. A process as claimed in any of claims 9 to 11 characterised in that the crude ester sulfonates and concentrated aqueous alkali metal hydroxide solution are introduced into an intensively stirred and cooled ester sulfonate salt paste having a solids content of at least 60% by weight.

13. A process as claimed in claim 12 characterised in that the average residence time of the reaction mixture under the temperature conditions of the neutralization reaction is no more than 20 minutes.

14. A process as claimed in any of claims 9 to 13 characterised in that aqueous alkali metal hydroxide solutions having a concentration of from 15 to 50% by weight are used.

15. A process as claimed in claim 14 characterised in that the alkali metal hydroxide is sodium hydroxide.

16. A process as claimed in any of claims 9 to 15, characterised in that neutralization is carried out continuously in a reaction loop through which the ester sulfonate salt paste having solids contents of at least 60% by weight is circulated and cooled, whilst on the one hand α -sulfonated fatty acid esters and aqueous



24

14

neutralizing agent are introduced into the loop and, on the other hand, a corresponding proportion of ester sulfonate salt paste is removed therefrom.

5 17. A process as claimed in any of claims 9 to 16 characterised in that, where it is carried out continuously, a viscosity reducing agent and water are added to the reaction mixture at the beginning of the neutralization reaction, viscosity-reduced aqueous
10 concentrates containing less than 60% by weight of α -sulfofatty acid ester salts and having a viscosity of at most 10,000 mPas at 70°C initially being obtained, after which the addition of viscosity-reducing agent and water is gradually reduced with cooling and
15 circulation until a paste containing from 60 to 80% by weight of α -sulfofatty acid ester salt is obtained as the reaction product without the addition of viscosity-reducing agent and water.

20 18. A process as claimed in claim 9 substantially as herein described with reference to the Example.

19. Ester sulfonate salt pastes when prepared by a process as claimed in any of claims 9 to 18.
