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(54) CONTINUOUS PROCESS FOR BLEACHING ACID α-SULPHO-FATTY ACID ESTERS

(71) We, HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN, a German Company of 67 Henkelstrasse, 4000 Düsseldorf-Holthausen, Federal Republic of Germany do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to a continuous bleaching provess for raw, acid α-sulpho-fatty acid esters with the addition of alkylbenzene sulphonic acid and the use of an aqueous solution of hydrogen peroxide as a bleaching agent.

Austrian Patent Specification No. 239,770 describes a process for the bleaching of sulpho-fatty acid esters which comprises using hydrogen peroxide, compounds forming hydrogen peroxide, or other inorganic bleaching agents having an oxidative action, to bleach, under specific working conditions, the acid sulphonic acids obtained, in the absence of solvents, by treating the fatty acid esters with gaseous sulphur trioxide diluted with inert gas. However, when attempting to put the process into practice, technical difficulties arose when the proportion of sulpho-fatty acid esters having 16 or more carbon atoms in the fatty acid component amounted to more than 70% in the mixture to be bleached. This is the case, for example, with the sulpho-fatty acid esters of hydrogenated tallow fatty acid.

Owing to their melting or softening points, α-sulpho-fatty acid ester mixtures of this type must be maintained at temperatures of at least 40°C for the purpose of processing in continuous plant, in order to ensure the flowability of the sulphonic acids. If the quantity of hydrogen peroxide required for bleaching is now added in the form of an aqueous solution, the originally viscous but flowable and substantially homogeneous mass is converted into an inhomogeneous highly viscous product which is difficult to mix and which is virtually incapable of being pumped. Owing to the exothermic bleaching reaction which takes place, the inhomogeneous distribution of the hydrogen peroxide causes local overheating and thus the formation of coloured impurities.

In order to overcome this difficulty, German Patent Specification No. 1,234,709 proposes a continuous multi-stage bleaching process for acid products of sulphonation, namely raw α-sulpho-fatty acid esters, at least 70% of whose fatty acids have a chain length of 16 and/or 18 carbon atoms. In the first bleaching stage of this process, the products of sulphonation are partially bleached by adding thereto a quantity of bleaching agent less than the quantity required for complete bleaching, particularly an aqueous solution of hydrogen peroxide. After subsequent neutralization, the neutralized, partially bleached sulpho-fatty acid esters are completely bleached in the second bleaching stage with further bleaching agent, particularly with hypochlorous acid or salts thereof.

However, problems arise in the practical realization of this multi-stage bleaching process, since the quantity of bleaching agent to be metered in the first bleaching stage cannot be determined from the requirement for optimum bleaching, but is only limited by the viscosity of the bleaching mixture. Thus, a continuous mode of operation is no longer possible with a slight over-dosage of the bleaching agent. A further disadvantage arises when, in accordance with a technically preferred embodiment of the process described in German Patent Specification No. 1,234,709, sodium hypochlorite is used in the second bleaching stage as the bleaching agent having an oxidative action. The neutralized and bleached sulphonate pastes then contain an increased salt concentration of sodium chloride, so that the products have a very high paste viscosity and are therefore difficult to handle.

Therefore, the object of the invention was to develop a continuous process for the bleaching of raw acid α-sulpho-fatty acid esters, a method which could be put into practice without the aforesaid disadvantages.

According to the present invention there is provided a process for the bleaching of acid α-sulpho-fatty acid esters in which at least 70% of the fatty acids have a chain length of 16 to 24 carbon atoms, which process comprises bleaching the acid α-sulpho-fatty acid ester at a temperature of less than 90°C using 1 to 5 percent by weight of hydrogen peroxide calculated as 100% hydrogen peroxide and relative to the raw α-sulpho-fatty acid ester and used in the form of a 20 to 75% aqueous solution; a quantity of 2 to 50 percent by weight of an alkylbenzene sulphonic acid, whose side chain comprises 6 to 18 carbon atoms, being added at a temperature of from 40° to 65°C to the raw, acid α-sulpho-fatty acid ester before and/or during addition of the bleaching agent to said ester.

The alcoholic ester component of the acid α-sulpho-fatty acid esters preferably comprise monovalent or polyvalent alcohols having 1 to 3 carbon atoms, all the hydroxy groups having to be esterified in the case of the polyvalent alcohols.

The minimum temperatures to be observed during the addition, in accordance with the present invention, of alkylbenzene sulphonic acid are dependent upon the fatty acid composition of the fatty acid esters used as a starting material. If fatty acids having a maximum of 14 carbon atoms, particularly fatty acids having 10 and 12 carbon atoms, are present in quantities of approximately 30 percent by weight, the product of sulphonation softens at approximately 40°C and can be continuously processed at this temperature. The minimum temperatures increase as the C number of the fatty acid increases. Advantageously, alkylbenzene sulphonic acid is added at temperatures of at least 50°C to a sulphonic acid, 90% of whose fatty acids comprise C_{16}- and/or C_{18} fatty acids, such as a sulphonic acid of the type comprising hydrogenated tallow fatty acid ester. Before adding the bleaching agent, an aqueous solution of hydrogen peroxide, the temperature (of the sulphonic acid mixture) should, as far as possible, not exceed 70°C and, preferably should not exceed 65°C.

The alkylbenzene sulphonic acids suitable for the bleaching process in accordance with the present invention include those which are produced by reacting an excess of benzene with an alkylation agent in the presence of a Friedel-Craft catalyst and subsequent sulphonation. Suitable alkylation agents are olefins, alcohols or halides which contain linear or branched chains having 6 to 18 carbon atoms. Preferably, the alkylbenzene sulphonic acids used in accordance with the present invention contain a linear alkyl chain. However, a technical alkylbenzene sulphonic acid mixture having linear side chains of 10 to 13 carbon atoms is preferred.

The quantity of alkylbenzene sulphonic acid added is from 2 to 50 percent by weight, preferably between 3 and 25 percent by weight, relative to the sulphonated fatty acid ester. It will be appreciated that the quantity of alkylbenzene sulphonic acid suitable for reducing viscosity depends upon the nature, particularly the chain length distribution, of the fatty acid components of the raw α-sulpho-fatty acid ester.

The concentration of the aqueous solution of the hydrogen peroxide used as a bleaching agent has to be chosen such that, considered mathematically, the sulphuric acid, formed from the surplus sulphur trioxide present in the sulphonic acid and the water to which the bleaching agent is added, is no more dilute than a 60 percent by weight sulphuric acid. Products of sulphonation have a degree of sulphonation of at least 90%, preferaby at least 96%, are obtained if, during the sulphonation of the fatty acid esters, the entire quantity of SO_3 required for sulphonation, which can lie in the range of 1.2 to 1.5 mol of SO_3 per mol of fatty acid radical, is allowed to act upon the fatty acid ester at least for a time at temperatures above 70°C. As a result of this, the concentration of the aqueous solution of bleaching agent is from 20 to 75 percent by weight, preferably between 30 and 40 percent by weight. During the bleaching process, care has to be taken that the heat of reaction which occurs is dissipated by cooling and a bleaching temperature of less than 90°C, preferably 55°C to 75°C, is maintained.

It will be appreciated that the duration of the bleaching process depends upon the nature of the starting material, the quantity of the bleaching agent used and the bleaching temperature. It can vary within wide limits, although it generally lies between 5 minutes and 1 hour, preferably between 10 and 20 minutes.

After the bleaching process, the acid products can be neutralized in a known manner and converted to their salts. In addition to caustic soda, all other conventionally used inorganic or organic bases or basic salts can be used for neutralization, such as potassium hydroxide, alkali metal carbonate or -bicarbonate, ammonia and primary, secondary or tertiary amines with lower alkyl- or alkylol radicals.

The bleaching process in accordance with the present invention is particularly suitable for a continuous mode of operation, since troublesome increases in viscosity during the bleaching operation are avoided by adding alkylbenzene sulphonic acid to the raw α-sulpho-fatty acid ester product, and the products remain capable of being pumped.

By way of example, the process in accordance with the present invention can be carried out continuously in an apparatus as shown in the accompanying drawing. The reservoirs 1, 2 and 3 contain the α-sulpho-fatty acid ester product to be bleached, the alkylbenzene sulphonic acid to be added, and the bleaching agent. The three components are fed to a mixer 5 by means of a metering pump unit 4. The bleaching mixture comprising a raw acid product of sulphonation, added alkylbenzene sulphonic acid and an aqueous solution of hydrogen peroxide reacts in a heat exchanger 6 from where it is fed for neutralization 8. Advantageously, for improved dissipation of the heat of reaction, a portion of the bleached product is returned to the mixer 5 by means of a feed pump 7, wherein the ratio of bleached returned matter to unbleached sulphonic acid mixture can lie in the range of from 10:1 to 1:1.

The present invention will now be further illustrated by way of the following examples without, however, it being limited thereto:

Examples

If not stated otherwise, the bleaching tests described in the Examples were carried out in accordance with the following directions:

The required quantities of technical dodecylbenzene sulphonic acid (side chain length distribution of approximately 5 percent by weight of C_{10}, approximately 42 percent by weight of C_{11}, approximately 37 percent by weight of C_{12} and approximately 16 percent by weight of C_{13}) and 35% aqueous hydrogen peroxide solution were added to the raw product of sulphonation at temperatures of from 55 to 65°C. The bleaching temperature was maintained between 55 and 65°C by external cooling. 5 minutes after adding the bleaching agent, the viscosity of the bleaching mixture at the bleaching temperature was determined in a rotary viscosimeter according to Brookfield. The bleached products were neutralized with aqueous caustic soda after a total bleaching time of from 10 to 20 minutes. The colour values of the neutralized products in a 5 percent by weight aqueous solution were subsequently determined by means of a "Lovibond tintometer" manufactured by Tintometer Ltd., Salisbury (England), in vessels having a layer thickness of 4". "Lovibond" is a Trade Mark.

Example 1

The starting material for the bleaching operation was the product of sulphonation of an hydrogenated tallow fatty acid methyl ester (chain length distribution of the fatty acids: approximately 32% C_{16}, approximately 65% C_{18}). The degree of sulphonation of the product was 98%. The viscosity values of the bleaching mixtures at 63°C and the colour values of the bleached products are given in Table 1 for various quantities of bleaching agent (calculated as 100% hydrogen peroxide and related to the sulphonated ester) and technical dodecylbenzene sulphonic acid. It will be seen from the table that the viscosity of the bleaching mixture is reduced to a considerable extent by adding only 3 percent by weight of alkylbenzene sulphonic acid (ABS). Furthermore, the viscosity is greatly dependent upon the quantity of bleaching agent (H_2O_2) added.

Table 1

Results of the bleaching tests with sulphonated hardened tallow fatty acid methylester

ABS (percent by weight)	H_2O_2 (percent by weight)	Viscosity (cP, 63°C)	Colour values		
			yellow	red	blue
0	1.7	950	22	6	0
3	1.7	150	23	6.5	0
5	1.7	145	24	7	0
10	1.7	155	25	8	0
15	1.7	140	26	9	0
0	2.0	1400	11	3	0
3	2.0	260	12	3.2	0
5	2.0	170	12.5	3.4	0
10	2.0	160	14	3.8	0
15	2.0	165	17	4.4	0
0	2.5	> 10000	7	1.6	0
3	2.5	300	7.5	1.8	0
5	2.5	250	8	2.1	0
10	2.5	180	9	2.4	0
15	2.5	170	11	2.8	0

Example 2

In another series of bleaching tests, the product of sulphonation of the stearic acid methylester with a degree of sulphonation of 95.5% was bleached for approximately 15 minutes with the addition of technical dodecylbenzene sulphonic acid (A) and n-octylbenzene sulphonic acid (B) of uniform chain length, each with 2 percent by weight of hydrogen peroxide calculated as 100% H_2O_2 and related to the sulphonated ester. The viscosity and colour values of the products bleached at 65°C are given in Table 2.

Table 2

Results of the bleaching tests with sulphonated stearic acid methylester

ABS (percent by weight)	Viscosity (cP, 65°C)	Colour values		
		yellow	red	blue
0	> 10 000	13	3.5	0
5 A	450	15	3.8	0
10 A	250	14	4.0	0
15 A	150	20	5.0	0
5 B	500	14	3.7	0
10 B	300	15	3.9	0
15 B	200	19	5.2	0
20 B	190	25	8	0
30 B	185	27	12	0

Example 3

Table 3 gives the results of the bleaching tests with the product of sulphonation of hardened rape oil fatty acid methylester, the hydrogenated rape oil fatty acids having a chain length distribution of approximately 10% C_{16}-, approximately 40% C_{18}-, approximately 10% C_{20}- and approximately 40% C_{22} fatty acids. Different quantities of technical dodecylbenzene sulphonic acid (ABS) were added as alkylbenzene sulphonic acid to the raw product of sulphonation (degree of sulphonation 98%) as well as 2 percent by weight of hydrogen peroxide calculated as 100% hydrogen peroxide and relative to the sulphonated ester.

Table 3

Bleaching the product of sulphonation of a hardened rape oil fatty acid ester

ABS (percent by weight)	Viscosity (cP, 65°C)	Colour values		
		yellow	red	blue
0	not measurable	8	2.0	0
5	> 10 000	10	2.4	0
10	420	12	2.5	0
15	180	13	2.8	0

Example 4

The bleaching mixtures of the product of sulphonation of hardened tallow fatty acid ethylester were also tested in addition to the α-sulpho-fatty acid methylester products. The product (degree of sulphonation 93.4%) was bleached with different additional quantities of technical dodecylbenzene sulphonic acid with the use of 3.5 percent by weight of H_2O_2 (calculated as 100% H_2O_2 and related to the sulphonated fatty acid ester in the form of a 40% aqueous solution. The bleaching temperature was 55°C. The results of the measurements are given in Table 4.

Table 4

Bleaching tests on raw α-sulphohydrogenated tallow fatty acid ethylester

ABS (percent by weight)	Viscosity (cP, 55°C)	Colour values		
		yellow	red	blue
0	3 300	6	1.7	0
3	450	7	1.8	0
5	380	7	1.8	0
10	220	9	2.3	0
15	190	12	2.8	0

Example 5

43.2 kg (150 mol) /hour of hydrogenated tallow fatty acid methylester were continuously reacted with 13.8 kg (172.5 mol)/hour of SO_3 in the form of an approximately 5 percent by volume mixture with air at a circulating water temperature of 90°C. After passing through a secondary reaction container heated to 90°C (average dwell time: 20 min) and a cooling bath, the 57 kg products of sulphonation (degree of sulphonation 95.6%) yielded hourly were continuously mixed in a mixer with 4.07 kg = 3.5 l/hour and 3.5 percent by weight H_2O_2 (2.5 percent by weight of 100% H_2O_2, relative to sulphonated ester) at a temperature of 50 to 55°C and, for the purpose of bleaching, were subsequently pumped through a serpentine pipe provided with a cooling jacket. The serpentine pipe was dimensioned such that a dwell time of approximately 15 minutes resulted. The bleaching temperature was kept at 60 to 65°C by cooling with 50 to 55°C hot water. The pressure increased rapidly in excess of 10 atmospheres gauge pressure a short time after mixing the first sulphonated ester with the aqueous H_2O_2, so that the test had to be terminated. The bleaching mixture in the bleaching pipe had solidified to a highly viscous pulpy mass which was no longer capable of being pumped.

The test was repeated, although, in addition to the above-mentioned quantity of H_2O_2, 4 kg/hour of technical dodecylbenzene sulphonic acid (7 percent by weight relative to sulphonated ester) was continuously mixed in the mixer. A pressure of approximately 1.5 atmospheres gauge pressure was established in the bleaching pipe at a bleaching temperature of 63°C. The bleaching mixture was highly fluid and could be pumped through the serpentine pipe without difficulty. A viscosity of 200 cP was measured in a sample of the bleaching mixture in the rotary viscosimeter according to Brookfield. The bleached product was subsequently continuously neutralized with 7.5 percent by weight of aqueous caustic soda at 40 to 45°C, resulting in a 28 percent by weight aqueous paste of sodiumhydrogenated tallow fatty acid methylester sulphonate and sodiumdodecylbenzene sulphonate. The colour values of a 5 percent by weight solution, measured in the Lovibond tintometer were:
yellow 6, red 1,4 and blue 0.

WHAT WE CLAIM IS:

1. A process for the bleaching of acid α-sulpho fatty acid esters in which at least 70% of the fatty acids have a chain length of 16 to 24 carbon atoms, which process comprises bleaching the acid α-sulpho-fatty acid ester at a temperature of less than 90°C using 1 to 5 percent by weight of hydrogen peroxide calculated as 100% hydrogen peroxide and relative to the raw α-sulpho-fatty acid ester and used in the form of a 20 to 75% aqueous solution; a quantity of 2 to 50 percent by weight of an alkylbenzene sulphonic acid, whose side chain comprises 6 to 18 carbon atoms, being added at a temperature of from 40° to 65°C to the raw, acid α-sulpho-fatty acid ester before and/or during addition of the bleaching agent to said ester.

2. A process as claimed in Claim 1, in which the alcoholic ester component of the acid α-sulpho-fatty acid esters comprise monovalent or polyvalent alcohols having 1 to 3 carbon atoms, all the hydroxy groups having to be esterified in the case of the polyvalent alcohols.

3. A process as claimed in Claim 1 or Claim 2, in which the quantity of alkylbenzene sulphonic acid added is between 3 and 25 percent by weight relative to the raw acid α-sulpho-fatty acid ester.

4. A process as claimed in any of Claims 1 to 3, in which the alkylbenzene sulphonic acid is produced by reacting an excess of benzene with an alkylation agent in the presence of a Friedel-Craft catalyst and subsequent sulphonation.

5. A process as claime din any of Claims 1 to 4, in which the alkylbenzene sulphonic acid has a linear alkyl chain.

6. A process as claimed in any of Claims 1 to 5, in which the alkylbenzene sulphonic acid contains a linear side chain having 10 to 13 carbon atoms.

7. A process as claimed in any of Claims 1 to 6, in which the bleaching temperature is maintained at from 55° to 75°.

8. A process as claimed in any of Claims 1 to 7, which is continuous.

9. A process as claimed in any of Claims 1 to 8, in which the duration of the bleaching process is between 5 minutes and 1 hour.

10. A process as claimed in Claim 9, in which the duration of the bleaching process is between 10 and 20 minutes.

11. A process for the bleaching of acid α-sulpho-fatty acid esters substantially as hereinbefore described and with reference to any one of the Examples.

12. An α-sulpho-fatty acid ester whenever bleached by a process as claimed in any one of Claims 1 to 11.

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1565704 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*