

Method for reducing the concentration of SO₃ in a reaction mixture comprising methane sulfonic acid and SO₃

The present invention refers to a method for reducing the concentration of SO₃ in a reaction mixture comprising methane sulfonic acid CH₃-SO₃H and SO₃. The method comprises a step of determining the amount of an additive needed to reduce the concentration of SO₃ by measuring density and/or conductivity of the mixture.

Alkane sulfonic acids are organic acids that can reach a similar acid strength as that of inorganic mineral acids, for example, sulfuric acid. However, in contrast to usual mineral acids such as sulfuric and nitric acids, the sulfonic acids are non-oxidizing and do not give off vapors that are harmful to health, as can be observed with hydrochloric and nitric acids. Further, many sulfonic acids, for example, methane sulfonic acid, are biologically degradable. The applications of sulfonic acids are many, for example, in cleaning agents, surfactants, as catalysts, and in organic synthesis, pharmaceutical chemistry, for example, as protective groups. The salts of sulfonic acids are employed, for example, as surfactants, for example, sodium dodecylsulfonate, or in the electroplating industry, especially as tin, zinc, silver, lead and indium, but also other metal alkylsulfonates. The very high solubility of alkyl sulfonates plays an important role, in particular. Further, no harmful gases are formed in electrolysis, and the use of toxic compounds, for example, cyanide, which is common in many cases, is dispensed with.

The structurally simplest representative of alkane sulfonic acids is methane sulfonic acid. Different methods for the synthesis are described in the prior art, for example in US 2,493,038, US 2005/0070614, WO 2007/136425 A2, EP 3071549 A1. In the prior art, methane and SO₃ are reacting with each other. The resulting reaction mixture comprises methane sulfonic acid as well as SO₃ as non-reacted educt. This SO₃ should be removed prior to distillation, as otherwise side products may occur (Robinson and Silberberg: "The reaction of methanesulfonic acid with sulfur trioxide", Canadian Journal of Chemistry, Vol. 44 (1966), 1437ff). Respective removal is for example disclosed in WO 2018/208701 A1 or European patent application 19176382.0. But even though there is the teaching that excess of SO₃ is to be removed, there is no teaching on how the amount of additive, needed to remove or at least significantly reduce the concentration of SO₃, is determined. Thus, there is the need for a method which enables the reduction of concentration of SO₃ in a liquid mixture in a fast and easy manner.

Surprisingly, it was found that conductivity and/or density of a mixture comprising methane sulfonic acid as well as SO₃ enables to determine the amount of an additive needed to significantly reduce the concentration of SO₃ in said mixture. The problem of the present disclosure is there

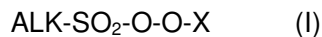
fore solved by a first aspect, in a method for reducing the SO₃ concentration in a mixture comprising methane sulfonic acid and SO₃, the method comprising:

- i. providing a mixture comprising methane sulfonic acid and SO₃,
- ii. determining the amount of an additive necessary to reduce the concentration of SO₃ in the mixture by forming a reaction product between the additive and SO₃,
- iii. introducing said predetermined amount of the additive into the mixture;
- iv. optionally repeating steps ii. and iii.,

wherein the determination of the amount of additive necessary to reduce the concentration of SO₃ in the mixture is performed by measuring conductivity and/or density of the reaction mixture, and wherein the additive preferably comprises water.

The mixture provided in step i. may be a reaction mixture resulting from a method of producing methane sulfonic acid from methane and SO₃ as described in the prior art. Preferably, it is a method as disclosed in EP 3071549 A1 and/or European patent application 19176382.0. In these cases, the mixture is a reaction mixture comprising methane sulfonic acid, methane and SO₃ as non-reacted educts, sulfuric acid as well as eventually occurring side products. In a preferred embodiment, providing of step i. comprises:

in a first step reacting methane sulfonic acid and hydrogen peroxide with each other to form a compound according to the following formula (I)



wherein ALK is methyl and X = hydrogen. This compound according to formula (I) is then provided in a reactor together with sulfur trioxide and methane. Due to the addition of the methane, a pressure within a range of from 1-200 bar is set. The reaction mixture is inside a high-pressure reactor and the temperature is controlled to be within a range of from 0° C to 100° C. Due to the reaction of the components to with each other, drop of the pressure can be monitored. This reaction mixture comprises the reaction product, namely the alkane sulfonic acid, as well as non-reacted educts, which are hydrocarbon and sulfur trioxide.

SO₃ may be provided as pure SO₃ or as oleum within the meaning of the present invention.

The additive is a compound which is able to react with SO₃ forming a compound preferably with a boiling point different from that of methane sulfonic acid. Preferably, the additive comprises water so that sulfuric acid is formed. The additive is a compound which is able to react with SO₃ forming a compound preferably with a boiling point different from that of the sulfonic acid. Preferably, the additive comprises water so that sulfuric acid is formed. If necessary, sulfuric acid or any other reaction product of SO₃ and the additive may be separated from the sulfuric acid in a

subsequent step. This may be performed via distillation, rectification or any other method known from the prior art.

The additive preferably comprises water, but the additive may further comprise hydrogen peroxide, sulfuric acid, methane sulfonic acid, $\text{ALK-SO}_2\text{-O-O-X}$ and/or $\text{ALK-SO}_2\text{-O-O-SO}_2\text{-O-X}$,
5 wherein ALK is methane and X is hydrogen, or mixtures of two or more of them. Usually, the additive always comprises water. Thus, if for example methane sulfonic acid is added as additive, the additive comprises water and the respective methane sulfonic acid. The concentration of water in the additive is preferably at least 2 % by weight or more or 5 % by weight or more,
10 alternatively it is 10 % by weight or more, especially at least 20% by weight or more, more preferably at least 25% by weight or more, especially preferred at least 30% by weight or more, always based on the total weight of the additive. The higher the concentration of water, the lower the amount of additive needed to reduce the concentration of SO_3 in the mixture.

15 It may also be the case that in a first step pure water is added and afterwards an additive with a low concentration of water to better control the complete concentration of water added into the mixture. Steps iii. and iv. of the method of the present invention may be repeated. It is also within the scope of the present invention that in a first step a first additive is added, wherein when repeating step ii another additive is added.

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It is of course also within the scope of the present invention, that not only one additive but mixtures of different additives are added. If for example $\text{ALK-SO}_2\text{-O-O-SO}_2\text{-OX}$ and/or $\text{ALK-SO}_2\text{-O-O-X}$ with H_2O_2 are added, the reaction between SO_3 and methane may be activated again, so that a higher yield can be obtained. Sulfuric acid or water can be added to destroy disulfuric acid. Water is less
25 preferred as additive, as the reaction between SO_3 or disulfuric acid and water is highly exotherm. If the temperature inside the reaction vessel is getting too high, side products may occur. Thus, by using an additive which comprises water not only the composition of the reaction mixture can be controlled leading to better distillation performance, but also the temperature can be better controlled, leading to less side products. Therefore, the concentration of water of the additive is preferably 90% by weight or less, especially 80% by weight or less, more preferred 75% by weight or
30 less, especially preferred 70% by weight or less.

A further advantage of the method of the present invention in a preferred embodiment is the use of the specific additive. When adding a preferred additive comprising water and hydrogen peroxide,
35 sulfuric acid, alkane sulfonic acid, $\text{ALK-SO}_2\text{-O-O-X}$, or $\text{ALK-SO}_2\text{-O-O-SO}_2\text{-O-X}$, it is possible to adapt the exact composition of the mixture. Thus, the concentration of methane sulfonic acid and sulfuric acid in the mixture can be controlled. This is of advantage if a distillation step shall be performed afterwards.

In a preferred embodiment, the method according to the present invention further comprises the step of

v. purification of the mixture, especially by distillation.

- 5 Purification is needed, if pure methane sulfonic acid shall be the reaction product or if the concentration of methane sulfonic acid should be increased. This may be performed by distillation and/or crystallization.

10 Preferably, the additive comprises methane sulfonic acid and water. It was found that the distillation step is more effective in cases where the concentration of the methane sulfonic acid in the mixture to be distilled is higher, the distillation is more effective. Preferably, the concentration of methane sulfonic acid in the mixture to be distilled is at least 30% by weight to 70 % by weight, especially 35 % by weight to 65 % by weight, preferably 40 % by weight to 60 % by weight or at about 50 % by weight.

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The mixture provided in step i. of the method of the present invention may also be obtained after using methane sulfonic acid in any process and it is intended to recycle the methane sulfonic acid after this process. In cases, where the mixture comprises SO_3 besides the methane sulfonic acid, the method of the present invention can be applied as well.

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In cases where the mixture comprises further sulfuric acid (H_2SO_4), SO_3 will react with the sulfuric acid leading to the formation of disulfuric acid. In the presence of methane, also the formation of a corresponding methyl disulfuric acid ($\text{CH}_3\text{-SO}_2\text{-O-SO}_3\text{H}$) is possible. If in the following disulfuric acid is mentioned, this always also means the corresponding methyl disulfuric acid. Nevertheless, the additive which comprises water will also react with disulfuric acid leading to the formation of twice the equivalence of sulfuric acid. Due to the high hygroscopic properties of disulfuric acid, it is not necessary to add pure water, but it is sufficient to add an additive which comprises water.

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30 The amount of additive needed has to be determined in order to impart the desired SO_3 content to the mixture. The concentration of SO_3 shall preferably be reduced by 50 % or more or 70% or more, advantageously by 90% or more, especially by 95% or more, preferably by 98% or more, especially preferred by at least 99%. If stoichiometric amounts of water are added, it can be assumed that SO_3 is completely removed. SO_3 reacts with water in a highly exothermic reaction to sulfuric acid. As long as the mixture is liquid, the equilibrium of the reaction is more or less completely on the side of the product. In a solution of SO_3 and water, comprising equivalent amounts of the compounds, no free SO_3 can be detected in the liquid. Thus, with the method of the present invention it is possible to remove SO_3 quasi completely from the mixture.

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To do so, the concentration of SO_3 in the mixture has to be determined. At the same time, the concentration of additive and especially of water in the mixture has to be determined, as the concentration of water in the mixture should usually be kept well below 3 % by weight, based on the total weight of the mixture. Usually, anhydrous methane sulfonic should be obtained in a process, where the method of the present invention is art of the purification. The desired water/additive content depends on the mixture provided in step i. and also on the overall process, of which the method of the present invention may be part of it.

To determine the amount of additive needed for imparting the desired SO_3 concentration, it is essential to know the relation between SO_3 concentration in the mixture, water concentration in the mixture and conductivity and density of the mixture respectively. Hence, for a specific mixture, a calibration curve has to be established. Fig. 1 shows exemplarily a calibration curve for a mixture comprising methane sulfonic acid, sulfuric acid and SO_3 and where water is added as additive.

In the X-direction, the concentration of SO_3 and water respectively are shown in weight percent. The Y-axis shows the conductivity in mS/cm. Starting from a concentration of sulfur trioxide of approximately 6 weight-% (based on the total weight of the composition, which is 100 % by weight), water was added. This results in an increase of the conductivity. At a certain point, essentially all sulfur trioxide was destroyed due to the reaction with water so that only sulfuric acid is present. Addition of excess of water results in a dramatic increase of conductivity, enabling to control the amount of additive to be added by measuring the conductivity. The content of sulfur trioxide and water in the mixture is thus relevant for the conductivity of a mixture provided in step i.

Preferably, the amount of water added is slightly above stoichiometric compared to the concentration of SO_3 present in the mixture. Preferably, the amount of water is slightly above this, which enables to reduce the formation of methane sulfonic acid anhydride. Nevertheless, the presence of water in the mixture should be kept as low as possible. The excess of water is therefore preferably no more than 3 % by weight, especially it is 2.5 % by weight or less, advantageously 2 % by weight or less or 1.5 % by weight or less compared to the concentration of SO_3 present in the mixture. The concentration of water in the mixture after addition of the additive is preferably within a range of from 0.1 % by weight to 2 % by weight, especially from 0.2 % by weight to 1 % by weight, preferred from 0.3 % by weight to 0.6 % by weight, especially preferred from 0.4 % by weight to 0.5 % by weight, where the concentration is based on the total weight of the composition as a whole. Surprisingly it was found that the formation of methane sulfonic acid anhydride in further purification steps, especially during distillation, can tremendously reduced in cases where the mixture comprises water in the above-mentioned concentrations.

With the method according to the invention, it is thus not only possible to determine the amount of additive to be added and to significantly reduce the concentration of SO₃ sulfur trioxide from the mixture, but also to control the concentration of water present in the mixture which helps to reduce the concentration of unwanted side products.

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Similar to the measurement of the conductivity, also the density of the mixture can be determined. Again, the density is dependent on the concentration of sulfur trioxide and water being present in the mixture. The addition of the additive comprising water results in a reduced concentration of sulfur trioxide. This leads to an increased density of the mixture. With excess of

10 water, the density of the mixture is decreasing again.

Thus, in a first aspect it is sufficient to determine either conductivity or density of the mixture to determine the amount of additive needed to react with SO₃ present in the mixture. In a preferred embodiment, both of density and conductivity are determined. This helps for a better determination of the amount of additive to be added and provides for a higher security of the measurement.

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For both of conductivity and density are temperature dependent, it is possible to provide measurements with a temperature correlation so that the shown values of a specific measurement can be compared with a baseline and an automatic control for the addition of the additive can be provided.

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Further advantage of conductivity and density measurements is that the measurement is fast so that the response, i.e. addition or non-addition of the additive is fast as well. This enables to provide a method not only in a batch (i.e., non-continuous) process but also in a continuous process.

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According to one embodiment, the method according to the present invention is thus performed in a batch process. In a preferred embodiment, the method according to the present invention is performed in a continuous process. Especially in a continuous process it is possible to determine the values for density and/or conductivity not only in one position of the continuous reactor but to perform it at several different positions. Usually, the continuous process is performed in a pipe. In this case, several measurements distributed over the pipe would be possible and preferred. The number of measure points would be two or more, preferably three or more, especially four or more, depending on the size and length of the continuous reactor. Especially in this case, it may be necessary to repeat steps iii. and iv. of the method of the present invention. But independently of a continuous or batch process, it is of course within the scope of the present

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invention that after addition of the additive for a first time, density and/or conductivity of the mixture are determined again, and further additive is added afterwards.

5 Destroying SO_3 with an additive comprising water results in the formation of heat, as the reaction is an exothermic one. This heat has to be removed, which can easily be performed by simply mixing the reaction mixture. The mixing can be performed by a static or a non-static mixer, i.e. a paddle mixer or others. It is also dependent on where the method is performed in a non-continuous batch process or a continuous process. In a continuous process, non-static mixers can be present through the continuous reactor, i.e. the pipe. In a non-continuous batch process,
10 it is preferred that non-static mixers are used.

Addition of the additive results in an exothermic reaction. Thus, the mixture should be cooled during and after the addition of the additive to keep the temperature constant, if needed. Of course, the increase of the temperature is dependent on the concentration of SO_3 and the concentration of SO_3 reacting with water. An increase in temperature may lead to the formation of
15 side products. Thus, the temperature should in the present case be kept well below 80°C , especially well below 70°C , preferably at 65°C or less, preferred at 60°C or less or at 55°C or less. Temperatures of 20°C or 25°C up to 35°C or up to 40°C are suitable for the mixture prior to addition of the additive. Cooling is necessary but can be performed with water cooling for
20 example. Stirring also helps to distribute the heat throughout the mixture and enable a more effective cooling of the system.

The method of the present invention enables thus a good control over the composition of the reaction mixture, after reaction between methane and SO_3 was performed prior to the further
25 purification of the remaining reaction mixture. This purification can be performed by any method known in the art. For example, distillation or melt crystallization are described in WO 2017/080994 A1, WO 2017/080991 A1, WO 2018/208701 A1 or EP 19176382.0. The purification is performed by distillation, excess of methane should be removed prior to the distillation. The excess of methane may be removed prior to the addition of the additive to the reaction
30 mixture or afterwards. Preferably, non-reacted methane is removed after SO_3 was destroyed. This is preferred as removal of methane is usually performed by simply reducing the pressure. If this is performed prior to destruction of sulfur trioxide, said sulfur trioxide may be released together with the methane, which is of course not preferred. Therefore, preferably first non-reacted sulfur trioxide which is present in the reaction mixture is destroyed, where the amount of
35 additive to be added is determined by measurement of conductivity and/or density of the reaction mixture. Afterwards, the methane, which is again non-reacted educt, is performed.

Measuring conductivity and/or density enable thus a high quality determination of additive which is needed to reduce or even remove SO_3 which is present in a mixture. Besides conductivity and density, it is also possible and preferred to determine the acoustic velocity of the mixture. The acoustic velocity especially enables the determination of the content of SO_3 in oleum. Also, the determination of the speed velocity enables thus to determine the amount of additive needed to reduce or even remove excess of SO_3 . Determination of the acoustic velocity improves the accuracy of the present method and increases the security. If one of the measurements shows wrong results, still there are two measure methods enabling determination in the amount of additive to be added. Further methods, such as RAMAN spectroscopy, IR spectroscopy, UV-Vis spectroscopy, viscosity, gravimetric measurements, refractive index, titration and thermal conductivity may be determined as well or alternatively. Density and conductivity are the preferred methods, as the measurement is fast and can easily be performed and can be performed inline. The other mentioned methods cannot be performed in-line thus they cannot be used in a continuous process but for a batch mood only. Nevertheless, also the above-mentioned methods enabling to determine the amount of additive to be added to destroy excess of SO_3 .

Conductivity in general is a parameter used to measure the ionic concentration and activity of a solution. The more salt, acid or alkali in a solution, the greater its conductivity. The unit of conductivity is S/m, often also S/cm.

Conductivity is measured by making a measurement of the electrical resistance. The simplest kind of measuring cell used consists of two similar electrodes. An alternating voltage applied to one of the electrodes causes the ions in the solution to migrate towards the electrodes. The more ions in the solution, the greater the current which flows between the electrodes. The instrument measures the current and uses Ohm's law to calculate first the conductance of the solution and then – by taken the cell data into account – the conductivity. The measurements described in this patent may be done using a Cond330i/SET device (by WTW, manufacturer of conductivity measurement devices) with a TetraCon 325/Pt electrode.

Conductivity may also be measured based on or analogous to DIN EN 27888 (Nov. 1993).

Density measurements may, for example, be done via oscillation-type density meters, as described e.g. in ISO 15212-1 (June 1999) and 15212-2 (July 2002). Alternative measurements of density are also possible. The sensors used in density meters are electrically or mechanically induced oscillating systems, whose oscillation frequencies or periodes are a function of the sample density. Depending on the sensor design, the fluid sample can either flow through the sensor (e.g. U-formed sensors, used in the aforementioned measurements) or the sensor can

be immersed in the liquid. Instrument constants of the adjusted density meter are used to calculate the sample density from the oscillation frequency or oscillation periode.

In the following paragraphs, several non-limiting experimental **examples** are reported, in order to illustrate some aspects of the present invention.

Example 1:

In a glass flask equipped with a magnetic stir bar, a conductivity probe (a Mettler Toledo conductivity probe 710) and a thermometer, 151,51g of a mixture of 143,03g sulfuric acid and 8,48g SO₃ are filled in and the temperature controlled to 20°C. Under inert gas atmosphere (N₂), water was added portionwise into the mixture and the conductivity was measured. During the addition, the conductivity drops from 26,8 mS/cm to 8,7 mS/cm upon addition of 1,9g H₂O, which represents an equimolar amount to the SO₃ amount in the starting mixture. Further addition up to a total of 6,4g H₂O increased the conductivity to 92,4 mS/cm, as seen in the figure 1 and table below. The kink in the conductivity curve represents the amount of additive needed to reduce the amount of SO₃ according to the application. Based on the SO₃ amount in the starting mixture, a conductivity of ~31mS/cm is obtained for ~0,5 wt% H₂O in the reaction mixture.

Table 1: conductivity of water addition to oleum 32

water addition m[g] / portion	Σ water m[g]	conductivity mS/cm
0	0,00	26,80
100	0,10	26,30
100	0,20	25,80
100	0,30	25,20
100	0,40	24,80
100	0,50	24,30
100	0,60	23,70
100	0,70	23,00
200	0,90	21,50
200	1,10	19,81
200	1,30	17,43
200	1,50	14,99
200	1,70	11,89
200	1,90	8,70
200	2,10	14,26
200	2,30	23,30
200	2,50	31,10
400	2,90	43,70
500	3,40	55,30
500	3,90	64,40
500	4,40	71,80
1000	5,40	83,60
1000	6,40	92,40

Example 2: Addition of water

315,11g of a mixture consisting of 48,78g Oleum 65 (with a SO₃ concentration of 62-65 wt%), 29,49g H₂SO₄ (100 %) and 236,84g MSA (100 %) is filled in a 250 ml 4-neck flask equipped with a magnetic stir bar, a conductivity probe (Cond330i/SET (WTW) with TetraCon 325/Pt electrode), a reflux condenser and a thermometer. The resulting mixture consists of ~9,5 wt% SO₃, ~15wt% H₂SO₄ and ~75,5 wt% MSA. Under stirring, small amounts of deionized water was added dportionwise and the conductivity measured at temperatures between 23-27°C, as seen in the table below. The conductivity decreases until an equimolar amount of water (i.e. ~6,9 g) is added. Further addition increases the conductivity again. The kink in the conductivity curve represents the amount of additive needed to reduce the amount of SO₃ according to the application.

Table 2: conductivity of water addition to a mixture of ~75,5 wt% MSA ~15 wt% H₂SO₄ and ~9,5% SO₃

Σ water m[g]	conductivity mS/cm	temperature °C
0,00	3,50	21,50
0,18	3,55	22,60
1,02	3,67	27,20
2,01	3,58	25,90
3,01	3,41	23,60
5,05	2,97	26,00
6,03	2,58	26,50
6,52	2,35	26,10
6,52	2,28	21,80
6,92	4,67	23,50
7,10	7,14	23,60
7,45	11,30	24,40
7,75	14,63	23,90
7,96	16,59	24,30
8,32	19,71	24,10
8,82	23,50	24,20
9,78	29,60	24,70
12,17	39,30	26,00

Example 3: Addition of water

191,57g of a mixture consisting of 18,01g Oleum 32 (with a SO₃ concentration of 30-32 wt%), 39,47g H₂SO₄ (100 %) and 134,08g MSA (100 %) is filled in a 250 ml 4-neck flask equipped with a magnetic stir bar, a conductivity probe (Cond330i/SET (WTW) with TetraCon 325/Pt electrode), a reflux condenser and a thermometer. The resulting mixture consists of ~3 wt% SO₃, ~27wt% H₂SO₄ and ~70 wt% MSA. Under stirring, small amounts of deionized water was added

portionwise and the conductivity measured at temperatures between 24-26°C, as seen in the table below. The conductivity decreases until an equimolar amount of water (i.e. ~1,2 g) is added. Further addition increases the conductivity again. The kink in the conductivity curve represents the amount of additive needed to reduce the amount of SO₃ according to the application.

- 5 Table 3: conductivity of water addition to a mixture of ~70 wt% MSA ~27 wt% H₂SO₄ and ~3% SO₃

Σ water m[g]	conductivity mS/cm	temperature °C
0,00	3,15	24,80
0,10	3,15	25,60
0,21	3,06	24,60
0,31	3,01	25,40
0,42	2,95	25,60
0,52	2,85	25,30
0,62	2,79	25,20
0,73	2,70	24,40
0,83	2,64	25,30
0,94	2,55	24,50
1,04	2,50	24,80
1,15	2,47	25,60
1,25	3,37	23,80
1,35	5,45	24,30
1,45	7,57	24,70
1,55	9,42	25,10
1,65	11,24	25,50
1,76	12,88	23,70
1,856	14,47	24,10
1,957	16,07	24,50
2,093	17,81	25,10
2,303	20,50	25,20
2,512	22,90	26,00
2,721	25,20	24,60
3,016	27,80	25,80
3,295	30,20	23,00

Example 4: Addition of MSA 70%

- 190,99g of a mixture consisting of 18,25g Oleum 32 (with a SO₃ concentration of 30-32 wt%),
 10 39,47g H₂SO₄ (100 %) and 133,27g MSA (100 %) is filled in a 250 ml 4-neck flask equipped with a magnetic stir bar, a conductivity probe (Cond330i/SET (WTW) with TetraCon 325/Pt electrode), a reflux condenser and a thermometer. The resulting mixture consists of ~3 wt% SO₃, ~27wt% H₂SO₄ and ~70 wt% MSA. Under stirring, small amounts of MSA 70% was added portionwise and the conductivity measured at temperatures between 22-26°C, as seen in the table
 15 below. The conductivity decreases until an equimolar amount of water (i.e. ~1,2 g, which equals ~4g MSA 70%) is added. Further addition increases the conductivity again. The kink in the conductivity curve represents the amount of additive needed to reduce the amount of SO₃ according to the application.

Table 4: conductivity of MSA 70% addition to a mixture of ~70 wt% MSA ~27 wt% H₂SO₄ and ~3% SO₃. The water amount is calculated based on 30wt% water in MSA.

Σ MSA 70%	Σ water	conductivity	temperature
m[g]	m[g]	mS/cm	°C
0,00	0,00	2,89	23,00
0,42	0,13	2,77	23,90
0,79	0,24	2,73	24,50
1,09	0,33	2,60	25,00
1,40	0,42	2,54	25,40
1,70	0,51	2,48	25,80
2,01	0,60	2,40	23,20
2,31	0,69	2,34	23,90
2,63	0,79	2,57	24,50
2,93	0,88	2,51	25,00
3,24	0,97	2,45	25,50
3,54	1,06	2,34	23,30
3,85	1,16	2,31	23,90
4,15	1,25	2,80	24,30
4,43	1,33	4,21	24,50
4,74	1,42	6,06	24,70
5,06	1,52	7,85	24,50
5,37	1,61	9,55	24,60
5,676	1,7028	11,06	24,80
5,973	1,7919	12,47	24,90
6,285	1,8855	13,88	25,00
6,597	1,9791	15,08	22,40
6,912	2,0736	16,31	22,60
7,448	2,2344	18,04	23,00
7,983	2,3949	19,22	23,30
8,524	2,5572	21,60	23,70
9,323	2,7969	23,90	24,20
10,128	3,0384	26,00	24,60
10,935	3,2805	27,80	25,10
11,744	3,5232	29,90	25,40
12,555	3,7665	31,10	25,80

The appended figures further illustrate some aspects of the invention and of the above experimental examples.

Claims

1. Method for reducing the SO₃ concentration in a mixture comprising methane sulfonic acid and SO₃, the method comprising:
 - 5 i. providing a mixture comprising methane sulfonic acid and SO₃,
 - ii. determining the amount of an additive necessary to reduce the concentration of SO₃ in the mixture by forming a reaction product between the additive and SO₃,
 - iii. introducing said predetermined amount of the additive into the mixture;
 - iv. optionally repeating steps ii. and iii.,
- 10 wherein the determination of the amount of additive necessary to reduce the concentration of SO₃ in the mixture is performed by measuring conductivity and/or density of the reaction mixture, and wherein the additive comprises water.
2. Method according to claim 1, wherein conductivity and density are measured.
- 15 3. Method according to claim 1 or 2, wherein further the acoustic velocity of the reaction mixture is determined.
4. Method according to any of claims 1 to 3, wherein the concentration of SO₃ is reduced by
 - 20 90% or more, especially by 95% or more, preferably by 98% or more, especially preferred by at least 99%.
5. Method according to any of claims 1 to 4, wherein in step ii) additionally RAMAN and/or IR and/or UV-Vis spectroscopy and/or viscosity and/or gravimetric measurements and/or re-
 - 25 fractive index and/or titration and/or thermal conductivity are determined.
6. Method according to any of claims 1 to 5, wherein the mixture further comprises methane and/or sulfuric acid.
- 30 7. Method according to claim 1, wherein the additive additionally comprises hydrogenperoxide, sulfuric acid, alkane sulfonic acid, ALK-SO₂-O-OX, and/or ALK-SO₂-O-O-SO₂-OX, wherein ALK is methane, and X is hydrogen, as well as mixtures of two or more of them.
8. Method according to any of claims 1 or 7, wherein the amount of additive added in step iii
 - 35 is at least stoichiometric compared to the concentration of SO₃ in the mixture.
9. Method according to any of claims 1 to 8, wherein the determination of the amount of additive needed in the process is performed at least in one position, preferably in at least two

different positions, preferably at three or more different positions of the reactor in which the method is performed.

10. Method according to any of claims 1 to 9, wherein addition of the additive in step iii. is performed under mixing.
11. Method according to any of claims 1 to 10, further comprising
 - v. purification of the obtained mixture, preferably by distillation.
12. Method according to any of claims 1 to 11, wherein the method is a continuous or a non-continuous process, preferably it is a continuous process.