

The invention relates to a process for the preparation of storage stable aqueous sodium peroxymonosulphate solutions containing 5 to 50% by wt. of sodium peroxymonosulphate ( $\text{NaHSO}_5$ ) by partial neutralisation, with sodium hydroxide or sodium carbonate, of an aqueous solution containing Caro's acid ( $\text{H}_2\text{SO}_5$ ) and sulphuric acid.

Peroxymonosulphuric acid (Caro's acid) and salts thereof (peroxymonosulphates) are becoming increasingly important as oxidising agents in the oxidative removal of pollutants from waste water. Although Caro's acid is effective in such processes, it has to be produced in situ or directly prior to its use because of its limited storage stability. The etching solutions containing Caro's acid for the production of printed circuits, as have been described, for example, in EP-A 0 256 284, have a limited stability with regard to the active oxygen; under the given test conditions - 5 hours, 70 °C - the loss is about 15% if the solution used contains about 4.6% by wt. of peroxymonosulphuric acid. Such solutions are not, therefore, marketable.

Although peroxymonosulphates of alkali metals and alkaline earth metals and of some other metals and of ammonium are known in themselves - see DE-PS 10 80 083 - , only potassium peroxymonosulphate in the form of the storage stable triple salt  $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$  and ammonium peroxymonosulphate in the form of a solution known as "ammonium-stabilised Caro's acid" have found acceptance in practice. As the potassium-containing triple salt mentioned generally has to be dissolved in a dissolution plant prior to use, however, and the ammonium ion of the Caro's acid stabilised therewith must itself be regarded as a critical waste water constituent, there is a demand for easy to handle and ecotoxicologically safe, storage stable peroxymonosulphate solutions. Solutions containing sodium peroxy-monosulphate could be expected to be ecotoxicologically safe.

According to the processes described in DE-PS 10 80 083, metal monopersulphates are prepared by reaction of Caro's acid or mixtures of Caro's acid and sulphuric acid with the hydroxides or carbonates of the metals concerned up to a pH value of the reaction mixture of not more than 3. The reaction mixture initially obtained is converted immediately after its preparation, by means of vacuum or spray drying, to a salt mixture containing the corresponding peroxymonosulphate. In order to obtain sufficiently storage stable products, diluents with a stabilising effect are added preferably before or during drying.

In the process of DE-PS 10 80 083, solutions containing Caro's acid and sulphuric acid may be used, obtained either by electrolysis of a sulphuric acid containing preferably 35 to 50% by wt. followed by hydrolysis of the peroxydisulphuric acid formed or by reaction of a 50 to 88% by wt. aqueous hydrogen peroxide with concentrated or fuming sulphuric acid (oleum). For the preparation of sodium peroxymonosulphate, such  $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$  solutions are neutralised with a soda solution to a pH of 2.9, freed from precipitated Glauber's salt and subsequently dried.

An unsatisfactory aspect of the process considered above for the preparation of solutions containing  $\text{NaHSO}_5$  proved to be the fact that a substantial active oxygen loss was observed during neutralisation - even in the example concerned of DE-PS 10 80 083 the  $\text{NaHSO}_5$  yield in the solution is given as only 85% of the theoretical. In addition, the storage stability of the solution was unsatisfactory: the active oxygen content fell in an intolerable manner and at the same time the solution repeatedly became cloudy due to precipitating Glauber's salt. Evidently, the problems discovered when reworking the process were also the reason why no reference was made at any place of DE-PS 10 80 083 to the usability of the solution, but said solution was always concentrated by evaporation. The drying of the solution

containing  $\text{NaHSO}_5$  in order to obtain a storage stable solid product is associated, however, with a further loss of active oxygen and is moreover technically expensive, as a result of which the profitability is reduced.

The object of the invention is to demonstrate a process for the preparation of storage stable, aqueous sodium peroxymonosulphate solutions which does not have the disadvantages of the process known from DE-PS 10 80 083. The process was, therefore, to lead to storage stable solutions and to be characterised by a low active oxygen loss during neutralisation of the  $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$  solutions.

The object is achieved by a process for the preparation of storage stable, aqueous sodium peroxymonosulphate solutions containing 5 to 50% by wt. of sodium peroxymonosulphate by partial neutralisation, with sodium hydroxide or sodium carbonate at a temperature below 50 °C, of a solution containing Caro's acid ( $\text{H}_2\text{SO}_5$ ) and sulphuric acid obtained by reaction of sulphuric acid or oleum with an at least 50% by wt. aqueous hydrogen peroxide or by electrolysis of an at least 30% by wt. aqueous sulphuric acid followed by hydrolysis of the resulting peroxydisulphuric acid, which is characterised in that the solution containing Caro's acid and sulphuric used is one which contains less than 3 parts by weight of hydrogen peroxide per 100 parts by weight of Caro's acid ( $\text{H}_2\text{SO}_5$ ), and the partial neutralisation is carried out up to an equivalent ratio of total  $\text{SO}_3$  to sodium ions in the region of 1:1 to 1:1.3 and, if desired, the  $\text{NaHSO}_5$  content is adjusted by dilution with water or by removing water by distillation under reduced pressure during or after the partial neutralisation.

It was found that both the active oxygen yield during the partial neutralisation of a sulphuric acid-containing Caro's acid and the storage stability of the resulting solution containing sodium peroxymonosulphate with regard to the active

oxygen content depend to a considerable extent on the hydrogen peroxide content in the sulphuric acid-containing Caro's acid solution used or in the sodium peroxymonosulphate solution. The lower the  $\text{H}_2\text{O}_2$  content in the  $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$  solution and in the  $\text{NaHSO}_5/\text{NaHSO}_4$  solution, the lower the active oxygen losses during partial neutralisation and during storage. This behaviour could not have been expected before. It is assumed on the basis of the analytical investigations into the process according to the invention that hydrogen peroxide reacts with  $\text{H}_2\text{SO}_5$  and  $\text{NaHSO}_5$  immediately in some cases during the neutralisation stage and somewhat more slowly during storage, with decomposition, where an equimolar decomposition reaction must be assumed.

If the equivalent ratio of total  $\text{SO}_3$  to sodium ions of 1.1 to 1:1.3 according to the invention is adhered to, moreover,  $\text{NaHSO}_5$  solutions with a pH value of about 1 or below 1 are obtained, from which practically no solid is precipitated during several weeks' storage. The solutions prepared according to the invention are therefore economic, i.e., can be prepared with a high active oxygen yield and are marketable on account of their good storage stability. The user of aqueous solutions containing peroxymonosulphate, for example, for treating waste water for the purpose of oxidative removal of toxic waste water constituents, no longer needs to prepare such solutions himself directly before use or to use ammonium-containing solutions, but may use the solutions according to the invention, which are sufficiently storage stable. In order to increase further the storage stability, inherently known stabilisers for peroxymonosulphates, for example, dipicolinic acid, stannates and chelating complexing agents, particularly from the series of phosphonates such as hydroxyalkylidene diphosphonates, ethylenediaminetetra(methylene phosphonic acid), and diethylenetri-aminepenta(methylene phosphonic acid), may be added in an effective quantity to the sodium peroxymonosulphate solutions prepared according to the

invention, during or after the preparation of the solutions. The solutions prepared according to the invention, even in the absence of such stabilisers, are, however, much more stable than peroxymonosulphuric acid solutions with a comparable active oxygen content.

Solutions with an equivalent ratio of total  $\text{SO}_3$  to sodium ions of 1 to more than 1.3 have pH values above 1 and are no longer sufficiently storage stable because solid precipitates - see examples 12 to 14. "Total  $\text{SO}_3$ " means that molar quantity which is bound in the sulphuric acid-containing Caro's acid used in the form of  $\text{H}_2\text{SO}_5$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{S}_2\text{O}_8$ . In an equivalent ratio of 1 to less than 1, the stability with regard to the active oxygen content falls because the low stability of Caro's acid becomes increasingly apparent in this case - see example 1.

The solutions containing Caro's acid and sulphuric acid to be used in the process according to the invention are obtainable in an inherently known way - see e.g., DE-PS 10 80 083. Essentially, two process principles are possible, namely (1) the reaction of concentrated sulphuric acid or oleum (solutions of  $\text{SO}_3$  in sulphuric acid) with aqueous hydrogen peroxide and (2) the hydrolysis of an electrolytically produced peroxydisulphuric acid-containing solution containing aqueous sulphuric acid. It is important that the solutions that undergo partial neutralisation according to the invention should be only those whose hydrogen peroxide content is less than 3 parts by weight, preferably less than 2.5 and in particular less than 2 parts by weight per 100 parts by weight of Caro's acid. Depending on the planned application of the solution containing  $\text{NaHSO}_5$ , it may be expedient to use those  $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$  solutions which not only have as low an  $\text{H}_2\text{O}_2$  content as possible, but at the same time have as low a peroxydisulphate content as possible, preferably below 5 parts by weight of  $\text{H}_2\text{S}_2\text{O}_8$  per 100 parts by weight of Caro's acid. The selection of the suitable solution requires a knowledge of the

active oxygen bound as  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_5$  and  $\text{H}_2\text{S}_2\text{O}_8$ . The individual components can be determined easily, consecutively in the same sample, by potentiometry using a cerium (IV) sulphate solution and sodium arsenite solution: the  $\text{H}_2\text{O}_2$  content is determined initially by titration of a sample with a  $\text{Ce}(\text{SO}_4)_2$  solution; after the addition of an excess of  $\text{NaAsO}_2$  solution to the titrated sample as described above and back titration with the  $\text{Ce}(\text{SO}_4)_2$  solution, the value of the  $\text{H}_2\text{SO}_5$  content is obtained; after renewed addition of an  $\text{NaAsO}_2$  solution in excess, 15 minutes' boiling and back titration with the  $\text{Ce}(\text{SO}_4)_2$  solution, the  $\text{H}_2\text{S}_2\text{O}_8$  content is obtained. The same method of determination is also suitable for determining the content of the partially neutralised solutions.

By hydrolysis of an electrolytically produced  $\text{H}_2\text{S}_2\text{O}_8$ -containing solution, it is possible to obtain  $\text{H}_2\text{SO}_5$  solutions with a low  $\text{H}_2\text{O}_2$  content, but the  $\text{H}_2\text{S}_2\text{O}_8$  content is generally clearly above 5, usually above 10 parts by weight per 100 parts by weight of  $\text{H}_2\text{SO}_5$ . If hydrolysis is continued, however, there is a risk of an increase in the  $\text{H}_2\text{O}_2$  content and in addition a reduction in the active oxygen content.

The reaction of hydrogen peroxide with sulphuric acid or oleum is an equilibrium reaction. Depending on the concentration of the reactants and the molar ratio chosen, it is possible to obtain solutions with a different  $\text{H}_2\text{SO}_5$  content and  $\text{H}_2\text{O}_2$  residual content. In order to prepare solutions containing  $\text{H}_2\text{SO}_5$  and  $\text{H}_2\text{SO}_4$  with an  $\text{H}_2\text{O}_2$  content below 3 parts by weight per 100 parts by weight of  $\text{H}_2\text{SO}_5$ , aqueous  $\text{H}_2\text{O}_2$  solutions with an  $\text{H}_2\text{O}_2$  content of at least 50% by wt., particularly 70 to about 85% by wt., and fuming sulphuric acid, also known as oleum, with an  $\text{SO}_3$  content of at least 20% by wt., preferably above 50% by wt., particularly about 65% by wt., are used. The molar ratio of hydrogen peroxide to total  $\text{SO}_3$  - sum of  $\text{SO}_3$  and  $\text{SO}_3$  bound as  $\text{H}_2\text{SO}_4$  - is 1:1.1 to 1:1.6. The concentration of  $\text{H}_2\text{O}_2$  in the aqueous hydrogen peroxide, the concentration of  $\text{SO}_3$  in the oleum and the molar ratio must be matched such that the

molar ratio of the water brought into the reaction system with the aqueous hydrogen peroxide to the sulphur trioxide brought in with the oleum is less than 1; a molar ratio in the region of 0.8 is highly suitable. Under the conditions mentioned it is possible to obtain the solutions to be used in preference with an  $\text{H}_2\text{SO}_5$  content of 50-65% by wt., an  $\text{H}_2\text{SO}_4$  content of 20 to 40% by wt. and  $\text{H}_2\text{O}_2$  content of less than 1.5% by wt., particularly less than 1% by wt., in high yield, which may undergo partial neutralisation directly or after partial dilution with water.

Sodium hydroxide solution or a soda solution are suitable for partial neutralisation. A sodium hydroxide solution containing 10-50% by wt. is preferred; if highly concentrated  $\text{NaHSO}_5$  solutions are desired, a sodium hydroxide solution in the upper concentration range will be used. The heat of neutralisation is generally removed by cooling, so a reaction temperature below 50 °C is adhered to, preferably below 35 °C. Cooling may be brought about by customary cooling of the reactor, for example, by means of heat exchangers or by evaporative cooling.

The process of the invention may be carried out batchwise or continuously. In continuous execution, the reaction is carried out preferably in a reaction loop. The loop contains a reactor, preferably a tubular reactor, which is equipped preferably with mixing devices, for example, one or more static mixers, at least one dosing point in each case for the sodium hydroxide solution or soda solution and the solution containing Caro's acid, and an effective cooling device; further components of the loop are a circulation line equipped with a delivery device and a discharge point for the partially neutralised sodium peroxymonosulphate solution. In the first part of the reactor, the sulphuric acid-containing Caro's acid is introduced into the partially neutralised solution, circulating in the loop, of the desired concentration of  $\text{NaHSO}_5$  and  $\text{NaHSO}_4$ , and mixed with the circulating solution; at

a point removed from the dosing point mentioned for obtaining a sufficiently homogeneous mixture, sodium hydroxide solution is introduced and mixed. The reactor contents are kept at a temperature below 35 °C by external cooling or by an integral vacuum evaporative cooler. By drawing off the partially neutralised solution in front of the reactor, the volume of the reaction loop is kept constant.

An important advantage of the process according to the invention consists in the fact that it is possible to provide, in an economic manner, storage stable and hence marketable solutions containing 5 to 50% by wt., preferably 10 to 40% by wt. and particularly 15 to 35% by wt. of sodium peroxy-monosulphate. Whilst with the previously known preparation of solutions containing  $\text{NaHSO}_5$  for the purpose of drying said solutions, the active oxygen yield fell considerably even during partial neutralisation of the sulphuric acid-containing Caro's acid used, it is possible with the process of the invention to obtain the desired solutions with an active oxygen yield of generally more than 90%. In the particularly preferred embodiment, in which an  $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$  solution obtainable from a 70 to 85% by wt. hydrogen peroxide and a 50 to 70% by wt. oleum is partially neutralised, it is possible, particularly with the continuous method of operating described, to keep the active oxygen yield, based on hydrogen peroxide used, at above 90%. The satisfactory storage stability with regard to the active oxygen content and also the absence of turbidity substances of the solutions prepared according to the invention makes it possible to dispense with the expensive and yield-reducing drying of the solutions in order to obtain a storage stable  $\text{NaHSO}_5$  product; in addition, there is no need for a dissolution plant at the place of use.

The invention and its advantages are disclosed in more detail by the examples and comparative examples.

**Examples 1 to 7**

A charge of the aqueous hydrogen peroxide solution is placed in a flask provided with stirrer, thermometer and external cooling. Sulphuric acid or oleum is added dropwise with intense cooling - reaction temperature 0 to 10 °C. The molar ratio of  $\text{H}_2\text{O}_2$  to total  $\text{SO}_3$ , the concentrations of the reactants, the yield and the analyses of the  $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$  solution obtained follow from Table 1a.

For partial neutralisation, sodium hydroxide solution (37% by wt.) and the  $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$  solution produced above are fed in the given molar ratio into a flask equipped as above by means of two dropping funnels, a small quantity of  $\text{NaHSO}_5/\text{NaHSO}_4$  solution from a comparable previous batch or water being provided for the purpose of improved temperature control and thorough mixing. The reaction temperature is kept at 25 to 35 °C. The molar ratio of total  $\text{SO}_3$  to  $\text{NaOH}$ , the analysis of the solution and yield follow from Table 1b.

Examples 3 and 7 are according to the invention; examples 1, 2, 5, and 6 lie in some cases outside the molar ratios according to the invention and/or contain too much  $\text{H}_2\text{O}_2$  in the  $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$  solution, which leads to low yields during partial neutralisation and/or inadequate storage stability.

Example 4 is based on the molar ratios according to the invention but precipitation of essentially sodium sulphate occurred due to excessive concentration by evaporation; example 4 thus shows that limits are set to concentration by evaporation with increasing Na excess with respect to the total  $\text{SO}_3$ .

Table 1a: Preparation and analysis of the  $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$  solution

| Example No. | Aqu. $\text{H}_2\text{O}_2$<br>(% by wt. $\text{H}_2\text{O}_2$ ) | Starting material                  |                                                            | Analysis                              |                                       |                                                |                                      | Yield                                                        |
|-------------|-------------------------------------------------------------------|------------------------------------|------------------------------------------------------------|---------------------------------------|---------------------------------------|------------------------------------------------|--------------------------------------|--------------------------------------------------------------|
|             |                                                                   | Oleum<br>(% by wt. $\text{SO}_3$ ) | Molar ratio<br>$\text{H}_2\text{O}_2$ :Total $\text{SO}_3$ | $\text{H}_2\text{SO}_5$<br>(% by wt.) | $\text{H}_2\text{SO}_4$<br>(% by wt.) | $\text{H}_2\text{S}_2\text{O}_8$<br>(% by wt.) | $\text{H}_2\text{O}_2$<br>(% by wt.) | % $\text{H}_2\text{SO}_5$<br>based on $\text{H}_2\text{O}_2$ |
| 1           | 70                                                                | 65                                 | 1 : 1                                                      | 65                                    | 16                                    | 1.2                                            | 6                                    | 77                                                           |
| 2           | as example 1                                                      |                                    |                                                            |                                       |                                       |                                                |                                      |                                                              |
| 3           | 70                                                                | 65                                 | 1 : 1.5                                                    | 58                                    | 32                                    | 2.8                                            | 1.2                                  | 92                                                           |
| 4           | as example 3                                                      |                                    |                                                            |                                       |                                       |                                                |                                      |                                                              |
| 5           | 70                                                                | 20                                 | 1 : 1.3                                                    | 49                                    | 30                                    | 1                                              | 5                                    | 74                                                           |
| 6           | 85                                                                | 0 ( $=\text{H}_2\text{SO}_4$ )     | 1 : 1.3                                                    | 49                                    | 30                                    | 1                                              | 5.5                                  | 74                                                           |
| 7           | 70                                                                | 65                                 | 1 : 1.54                                                   | 56                                    | 33                                    | 2.8                                            | 1.0                                  | 92                                                           |

Table 1b: Partial neutralisation of the solutions according to Table 1a

| Example<br>No. | Molar ratio<br>Total SO <sub>3</sub> :NaOH | Analysis (% by wt.) |                    |                               | Yield<br>% NaHSO <sub>5</sub> based on<br>H <sub>2</sub> SO <sub>5</sub> used |
|----------------|--------------------------------------------|---------------------|--------------------|-------------------------------|-------------------------------------------------------------------------------|
|                |                                            | NaHSO <sub>5</sub>  | NaHSO <sub>4</sub> | H <sub>2</sub> O <sub>2</sub> |                                                                               |
| 1              | 1 : 0.5                                    | 22                  | 21                 | 3.2                           | 96 *)                                                                         |
| 2              | 1 : 1.0                                    | 33                  | 16                 | 2.2                           | 86                                                                            |
| 3              | 1 : 1.0                                    | 30                  | 21                 | 0.5                           | 98                                                                            |
| 4              | 1 : 1.27                                   | 44                  | nc                 | 0.3                           | 96 **)                                                                        |
| 5              | 1 : 1                                      | 25                  | 20                 | 2.0                           | 85                                                                            |
| 6              | 1 : 1                                      | 28                  | 20                 | 2.5                           | 87                                                                            |
| 7              | 1 : 1                                      | 30.5                | 22                 | 0                             | 95                                                                            |

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\*) The solution additionally contains 18% by wt. of H<sub>2</sub>SO<sub>5</sub> and 9% by wt. of H<sub>2</sub>SO<sub>4</sub>; in spite of the high H<sub>2</sub>O<sub>2</sub> content, the yield was high but the solution was not sufficiently storage stable - loss of HSO<sub>5</sub><sup>-</sup> within one week at 20 °C 41.5% of the starting value.

\*\*) Partial neutralisation took place under reduced pressure and with evaporation of water, whereby some solid precipitated (the analysis relates to the filtrate).

**Examples 8 and 9**

In order to illustrate the effect of the hydrogen peroxide content on the yield during partial neutralisation and the storage stability, 4.5% by wt. of hydrogen peroxide were added to the starting material of example 7 directly before partial neutralisation (example 8).

After partial neutralisation had ended, 3% by wt. of hydrogen peroxide were added to the solution of example 7 (example 9). The results,  $\text{NaHSO}_5$  and  $\text{H}_2\text{O}_2$  content directly after the preparation of the solutions including the additional  $\text{H}_2\text{O}_2$  addition and after 1 week's storage at room temperature, and yield or residual value of  $\text{NaHSO}_5$ , based on  $\text{H}_2\text{SO}_5$  used in partial neutralisation, follow from Table 2.

Table 2

| Example<br>No. |                   | NaHSO <sub>5</sub><br>(% by wt.) | H <sub>2</sub> O <sub>2</sub><br>(% by wt.) | NaHSO <sub>5</sub> yield<br>(% based on H <sub>2</sub> SO <sub>5</sub> used) |
|----------------|-------------------|----------------------------------|---------------------------------------------|------------------------------------------------------------------------------|
| 7              | after preparation | 30.5                             | 0                                           | 95                                                                           |
|                | after 1 week      | 30.0                             | 0                                           | 94                                                                           |
| 8              | after preparation | 24.5                             | 2.2                                         | 81                                                                           |
|                | after 1 week      | 16.0                             | 0                                           | 53                                                                           |
| 9              | after preparation | 28.6                             | 3.1                                         | 94                                                                           |
|                | after 1 week      | 21.7                             | 1.5                                         | 71                                                                           |

**Examples 10 and 11**

The test apparatus for partial neutralisation comprised a multiple-neck flask with an internal thermometer, stirrer, distillation bridge with receiver, vacuum pump and two pumps for precision dosing of the reaction components into the multiple-neck flask.

An aqueous  $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$  solution - prepared according to the details in example 1 - and a 37% by wt. sodium hydroxide solution are fed continuously in the desired quantity ratio into a charge of 100 ml of water in the flask. A reaction temperature of 25 to 35 °C at a pressure in the region of about 10 to 30 mbar is adjusted by means of the vacuum apparatus; at the same time, the water introduced with the raw materials and produced during neutralisation may be removed in order to obtain the desired  $\text{NaHSO}_5$  concentration. A partial stream may be drawn off from the flask in order to keep the volume of reaction mixture constant - but this was dispensed with in examples 10 and 11. The starting material quantities and analyses and yields can be derived from Table 3.

The active oxygen loss during the storage at room temperature of the solution of example 10 containing sodium peroxymonosulphate prepared according to the invention is approx. 1.7% in each case, based on the starting content, per 10 days, within 40 days.

Table 3

|                                                                                     | Example 10 | Example 11 |
|-------------------------------------------------------------------------------------|------------|------------|
| <hr/>                                                                               |            |            |
| <u>Starting material</u> for $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$ solution |            |            |
| Conc. $\text{H}_2\text{O}_2$ (% by wt.)                                             | 69         | 69         |
| Conc. oleum (% by wt.)                                                              | 65         | 65         |
| Molar ratio $\text{H}_2\text{O}_2$ : total $\text{SO}_3$                            | 1 : 1.54   | 1 : 1.54   |
| <u>Analysis</u> of $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$ solution           |            |            |
| $\text{H}_2\text{SO}_5$ (% by wt.)                                                  | 55.5       | 56.3       |
| $\text{H}_2\text{O}_2$ (% by wt.)                                                   | 0.95       | 0.96       |
| $\text{H}_2\text{S}_2\text{O}_8$ (% by wt.)                                         | 3.2        | 3.4        |
| <hr/>                                                                               |            |            |
| <u>Partial neutralisation</u>                                                       |            |            |
| Molar ratio total $\text{SO}_3$ :NaOH                                               | 1 : 1.23   | 1 : 1      |
| Quantity $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$ solution (g/h)               | 100        | 100        |
| Sodium hydroxide solution (g/h)                                                     | 110.5      | 89.6       |
| <hr/>                                                                               |            |            |
| <u>Analysis</u> of $\text{NaHSO}_5/\text{NaHSO}_4$ solution                         |            |            |
| $\text{NaHSO}_5$ (% by wt.)                                                         | 26.97      | 30.45      |
| $\text{NaHSO}_4$ (% by wt.)                                                         | 10.11      | 22.18      |
| $\text{H}_2\text{O}_2$ (% by wt.)                                                   | 0.02       | 0.02       |
| <hr/>                                                                               |            |            |
| <u>Yield</u> of $\text{NaHSO}_5$                                                    |            |            |
| based on $\text{H}_2\text{SO}_5$ used                                               | 94.3       | 95.0       |

**Examples 12 to 14**

According to the method of operating of examples 1 to 7, an aqueous  $\text{H}_2\text{SO}_5/\text{H}_2\text{SO}_4$  solution was partially neutralised. A 70% by wt.  $\text{H}_2\text{O}_2$  and a 65% by wt. oleum were used; the molar ratio of  $\text{H}_2\text{O}_2$  to total  $\text{SO}_3$  was 1 to 1.16. Partial neutralisation with a 37% by wt. sodium hydroxide solution took place up to the pH values given in the table (measured by means of a glass electrode and pH meter). The resulting molar ratios of total  $\text{SO}_3$  to  $\text{NaOH}$  and the yields of  $\text{NaHSO}_5$ , based on  $\text{H}_2\text{SO}_5$  used, follow from Table 4.

Table 4

| Example No. | Molar ratio<br>Total $\text{SO}_3$ : $\text{NaOH}$ | pH value | Yield<br>% $\text{NaHSO}_5$ based on $\text{H}_2\text{SO}_5$ |
|-------------|----------------------------------------------------|----------|--------------------------------------------------------------|
| 12          | 1 : 1.30                                           | 1        | 96.80                                                        |
| 13          | 1 : 1.36                                           | 2        | 93.40                                                        |
| 14          | 1 : 1.39                                           | 3        | 85.68                                                        |

Example 12 lies inside, examples 13 and 14 outside the limits according to the invention. In examples 13 and 14, solid precipitates even during partial neutralisation and during storage.

**Example 15**

An  $\text{NaHSO}_5$  solution, prepared in a similar manner to example 11 but with a higher concentration, was diluted by the addition of water to various  $\text{NaHSO}_5$  concentrations. The storage stability was determined by 5 hours' storage at 70 °C. The concentration of the  $\text{NaHSO}_5$  solutions and the loss of active oxygen (AO loss) in % of the starting value are given in the table.

Table

| $\text{NaHSO}_5$<br>concentration (% by wt.) | AO loss<br>(%) |
|----------------------------------------------|----------------|
| 5                                            | 1.5            |
| 10                                           | 4.2            |
| 15                                           | 5.0            |
| 20                                           | 7.7            |
| 25                                           | 10.8           |
| 30                                           | 14.0           |
| 35                                           | 21.5           |

Claims

1. A process for the preparation of storage stable aqueous sodium peroxymonosulphate solutions containing from 5 to 50% by weight of sodium peroxymonosulphate by partial neutralisation, by means of sodium hydroxide or sodium carbonate at a temperature below 50°C, of a solution containing Caro's acid and sulphuric acid obtained by the reaction of sulphuric acid or oleum with an at least 50% by weight aqueous hydrogen peroxide or by electrolysis of an at least 30% by weight aqueous sulphuric acid followed by hydrolysis of the resulting peroxydisulphuric acid, characterised in that the solution containing Caro's acid ( $\text{H}_2\text{SO}_5$ ) and sulphuric acid used is one which contains less than 3 parts by weight of hydrogen peroxide per 100 parts by weight of Caro's acid ( $\text{H}_2\text{SO}_5$ ) and the partial neutralisation is carried out up to an equivalent ratio of total  $\text{SO}_3$  to sodium ions in the range of from 1 : 1 to 1 : 1.3 and, if desired, the  $\text{NaHSO}_5$  content is adjusted by dilution with water or by removal of water by distillation at reduced pressure during or after the partial neutralisation.
2. A process according to Claim 1, characterised in that the solution containing Caro's acid and sulphuric acid used is one which has been obtained by the reaction of an about 70 to about 85% by weight aqueous hydrogen peroxide with oleum having an  $\text{SO}_3$  content of at least 20% by weight, preferably above 50% by weight, of  $\text{SO}_3$  in a molar ratio of hydrogen peroxide to total  $\text{SO}_3$  of from 1 : 1.1 to 1 : 1.6.
3. A process according to Claim 2, characterised in that the solution which is subjected to partial neutralisation is one which contains from 50 to 65% by weight of Caro's acid and from 20 to 40% by weight of sulphuric acid and less than 1.5% by weight of hydrogen peroxide.



4. A process according to one of Claims 1 to 3, characterised in that the partial neutralisation is carried out with a 10 to 50% by weight sodium hydroxide solution at a temperature of at most 35°C.
5. A process according to one of Claims 1 to 4, characterised in that the partial neutralisation is carried out continuously in a reaction loop whose reactor is equipped with an efficient cooling device, at least one dosing point for the solution containing Caro's acid and at least one dosing point for sodium hydroxide solution and the loop is equipped with a delivery device and a discharge point for the sodium peroxymonosulphate-containing reaction solution circulating in the reaction loop, the dosing points for sodium hydroxide solution being arranged at such a distance from the dosing points for the solution containing Caro's acid that the Caro's acid introduced becomes substantially homogenously mixed with the reaction solution in the loop before the sodium hydroxide solution is added.

