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(54) **PROCEDE POUR PRODUIRE DES SOLUTIONS AQUEUSES
D'HYDROXYLAMINE, PRATIQUEMENT EXEMPTES D'ION
METALLIQUE**

(54) **METHOD FOR PRODUCING AQUEOUS HYDROXYLAMINE
SOLUTIONS WHICH ARE SUBSTANTIALLY FREE OF
METAL IONS**

(57) L'invention concerne un procédé pour produire une solution aqueuse d'hydroxylamine, pratiquement exempte d'ion métallique. Ce procédé consiste à soumettre la solution d'hydroxylamine à au moins un traitement avec un échangeur de cations acide.

(57) The invention relates to a method for producing an aqueous hydroxylamine solution which is substantially free of metal ions. According to said method the hydroxylamine solution is subjected to at least one treatment with an acid cation exchanger.



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<p>(21) Internationales Aktenzeichen: PCT/EP99/00993</p> <p>(22) Internationales Anmeldedatum: 16. Februar 1999 (16.02.99)</p> <p>(30) Prioritätsdaten: 198 06 578.7 17. Februar 1998 (17.02.98) DE</p> <p>(71) Anmelder (für alle Bestimmungsstaaten ausser US): BASF AKTIENGESELLSCHAFT [DE/DE]; D-67056 Ludwigshafen (DE).</p> <p>(72) Erfinder; und (75) Erfinder/Anmelder (nur für US): WATZENBERGER, Otto [DE/DE]; Sedanstrasse 15, D-68199 Mannheim (DE). SCHNEIDER, Hans-Michael [DE/DE]; Zum Mersch 7, D-67549 Worms (DE).</p> <p>(74) Anwälte: KINZEBACH, Werner usw.; Reitsstötter, Kinzebach & Partner, Ludwigsplatz 4, D-67059 Ludwigshafen (DE).</p>		<p>(81) Bestimmungsstaaten: AL, AU, BG, BR, BY, CA, CN, CZ, GE, HU, ID, IL, IN, JP, KR, KZ, LT, LV, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, UA, US, eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Veröffentlicht <i>Ohne internationalen Recherchenbericht und erneut zu veröffentlichen nach Erhalt des Berichts.</i></p>
<p>(54) Title: METHOD FOR PRODUCING AQUEOUS HYDROXYLAMINE SOLUTIONS WHICH ARE SUBSTANTIALLY FREE OF METAL IONS</p> <p>(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG WÄSSRIGER, IM WESENTLICHEN METALLIONENFREIER HYDROXYLAMINLÖSUNGEN</p> <p>(57) Abstract</p> <p>The invention relates to a method for producing an aqueous hydroxylamine solution which is substantially free of metal ions. According to said method the hydroxylamine solution is subjected to at least one treatment with an acid cation exchanger.</p> <p>(57) Zusammenfassung</p> <p>Die vorliegende Erfindung betrifft ein Verfahren zur Herstellung einer wässrigen Hydroxylaminlösung, die im wesentlichen metallionenfrem ist, wobei man die Hydroxylaminlösung mindestens einer Behandlung mit einem sauren Kationenaustauscher unterwirft.</p>		

METHOD FOR PRODUCING AQUEOUS HYDROXYLAMINE SOLUTIONS
WHICH ARE SUBSTANTIALLY FREE OF METAL IONS

The present invention relates to a process for the preparation of aqueous hydroxylamine solutions which are essentially free of metal ions.

10 Highly pure, concentrated, aqueous hydroxylamine solutions are used, inter alia, in the electronics industry, for example together with other substances for the preliminary cleaning of the boards. For use in the electronics industry, an impurity content of well below 1 ppm, in general even in the ppb range, is usually required (i.e. electronic grade product). However, the hydroxyl-amine solutions now commercially available contain impurities in the ppm range, for example sodium sulfate or other metal compounds, resulting from the preparation of said solutions.

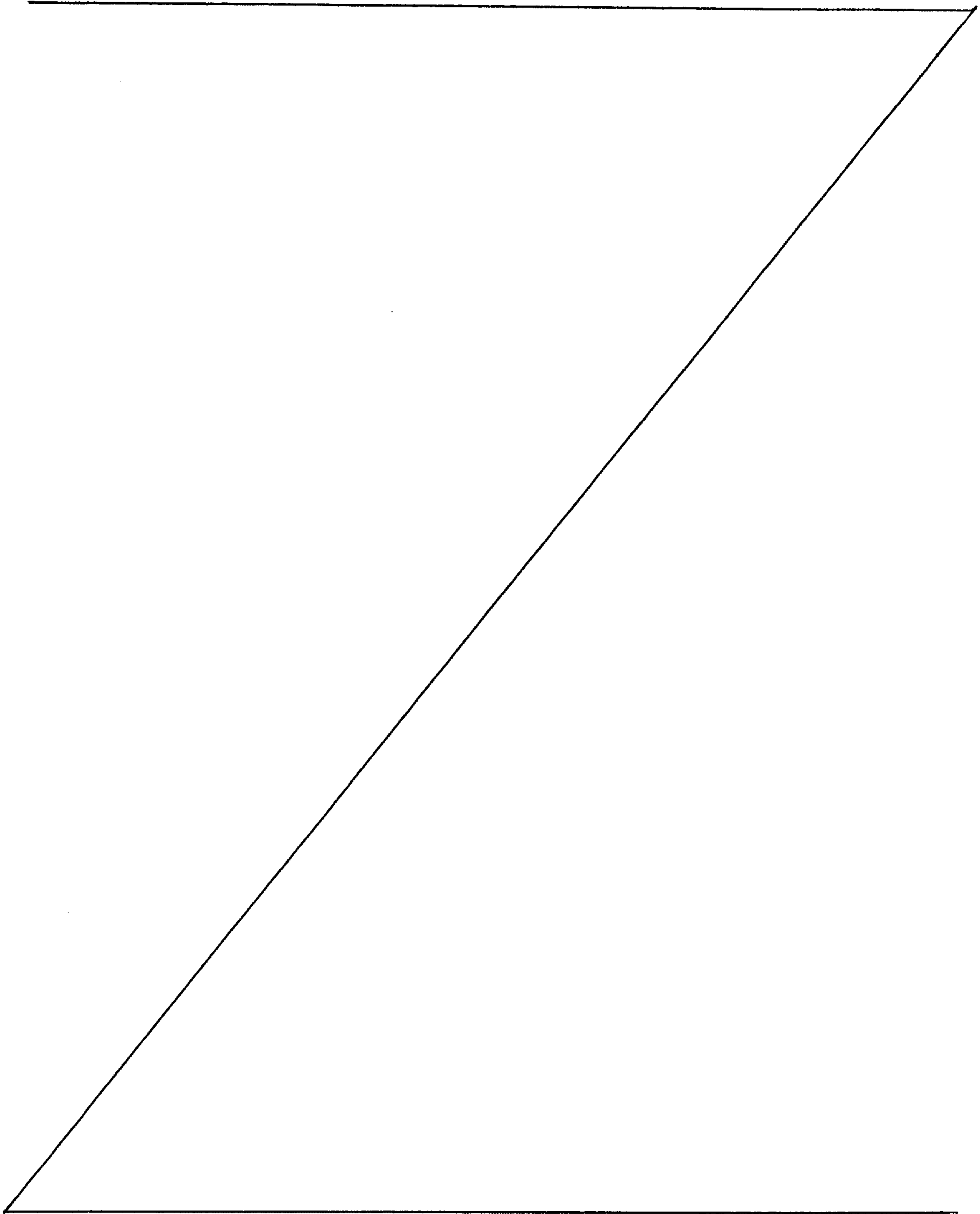
20 One possibility for purification is working up by distillation, as described in US-A-5,472,679. However, it must be ensured that the temperature of 65°C is not exceeded during the distillation since the onset temperature, i.e. the temperature at which detectable decomposition begins, is about 70°C for 50% strength by weight hydroxylamine solution. To permit the isolation of hydroxylamine as a top product, distillation is usually carried out on a small scale and in vacuo at very low temperatures. Such a distillation is very expensive and time-consuming.

The working up by distillation, described in WO 97/22551, avoids the disadvantages of the process described in the stated U.S. patent. Nevertheless, it is true that the process of WO 97/22551, too, is relatively expensive. Accordingly, salt-free aqueous electronic grade hydroxylamine solutions are correspondingly expensive, so that their use is limited by economics to a few applications.

30 It is an object of the present invention to provide a process for the preparation of hydroxylamine solutions which are essentially free of metal ions, in particular sodium ions, the process being simple and economical to carry out.

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The use of cation exchangers for separating metal ions from aqueous solutions is known. Typical applications are in the area of water purification, metal ions generally being separated off unselectively. The object is usually the preparation of a



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solution essentially free of metal ions. Cation exchangers capable of separating polyvalent metal ions which readily form complexes, for example Fe^{3+} or Ni^{2+} , selectively from aqueous solutions are also known. This is based on the fact that these
5 metal ions form complexes with the ion exchanger which has chelate-forming groups as is reported, for example, in The Many Faces of Ion-Exchange Resins, Chemical Engineering, June 1997, 94-100. There, the table on page 98 indicates that the affinity of Fe^{3+} ions to the ion exchanger described is 350,000 times
10 higher than that of the comparative substance Ca^{2+} , and that of the Ni ions is 3200 times higher. In the presence of about 50 g/l of ammonium ions (corresponding to 200 g/l of ammonium sulfate), the affinity values decrease sharply, the affinity of nickel ions to, for example, 30.

15 Alkali metal cations are not included in this table. They have a much lower affinity than even the calcium ions used in the table for comparison.

In addition to the metal present as an impurity, aqueous
20 hydroxylamine solutions also contain the hydroxylammonium cation formed by acceptance of a proton. In a 50% strength by weight hydroxylamine solution, 15.14 mol of hydroxylamine/l are present in addition to from 1 to 10 ppm of metal ions (corresponding to from 0.4 to 1.7×10^{-5} mol/l, based on Na^+ ions). There is a
25 deficiency of cations to be separated off relative to the hydroxyl-ammonium cations. Under these conditions, a person skilled in the art expects that a further decrease in the concentration of the metal ions contained in these small amounts, and in particular alkali metal ions, is no longer possible by
30 treatment with an ion exchanger.

We have found, surprisingly, that this object is achieved and that the metal ions can be separated off selectively by treating the hydroxylamine solutions with an acidic cation exchanger.

35 The present invention therefore relates to a process for the preparation of an aqueous hydroxylamine solution, in particular a highly pure one, which is essentially free of metal ions, wherein the hydroxylamine solution is subjected to at least one treatment
40 with an acidic cation exchanger.

A weakly acidic cation exchanger, i.e. a cation exchanger having a pH in the acid form of from 2 to 6, in particular from 3 to 6, is preferably used for this purpose. Furthermore, a cation

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exchanger which has chelate-forming groups, such as iminodiacetic acid groups, is preferably used.

Suitable cation exchangers are, for example, the Lewatit TP types 5 from Bayer, such as Lewatit TP 207, the Amberlite IRC types, Duolite C 433, etc., Dowex CCR or MWC and the like. The cation exchangers are used in the acid form. If required, they are for this purpose treated with an acid, for example sulfuric acid, in order to remove the cation. They are then usually washed 10 acid-free with high-purity water.

The treatment of the hydroxylamine solution can also be effected using a strongly acidic cation exchanger in the acid form, i.e. a cation exchanger in the acid form having a pH of from 0 to 2, in 15 particular from 0 to 1. Usable strongly acidic cation exchangers are, for example, the resins Amberlite IR-120, IR-122 and IRC-50 and Amberjet 1500H from Rohm & Haas, Dowex 88 from Dow Chemical, Duolite C-200, C-26, C-280 from Rohm and Haas and Purolite C-100, C-105 and C-150. The acid form can be produced using conventional 20 strong acids, such as hydrochloric acid.

The treatment of the hydroxylamine solution with the cation exchanger is carried out in the usual manner, for example by treatment in a reaction vessel with stirring. Preferably, 25 however, the hydroxylamine solution is poured over a bed of cation exchanger, for example a column loaded with the cation exchanger.

On the cation exchanger, hydroxylamine undergoes slight 30 decomposition, inter alia into N_2 and NH_3 . The gas bubbles formed can impair the uniformity of the liquid stream and lead to undesired axial back-mixing. It is therefore particularly preferred to pass the hydroxylamine solution opposite to the direction of gravitational force over a bed comprising the cation 35 exchanger. Thus, the treatment of the hydroxylamine solution can be expediently carried out in a column loaded with the cation exchanger and fed from below. Preferably, the feed is effected at a high flow rate, preferably a flow rate ≥ 10 m/h, in particular ≥ 15 m/h (the flow rate is the volume of hydroxylamine solution 40 throughput per hour, based on the cross section of the empty column). Expediently, a retaining element, for example a perforated plate or a knitted fabric, which prevents the discharge of the cation exchanger, is present at the upper end of the column. As a result of these measures, gas bubbles formed are 45 continuously discharged from the column and the ion exchanger is

present as a cohesive bed. Undesired back-mixing of the solution to be purified is thus avoided.

The temperature at which the treatment is carried out is not
5 critical. However, because of the decomposability of the hydroxylamine, higher temperatures are avoided. In general, a temperature of from 0 to about 50°C, preferably 20 - 30°C, is employed.

10 The ratio of hydroxylamine solution to be purified to cation exchanger depends on the amount of cations to be removed. A person skilled in the art can determine the suitable amount in a simple manner by monitoring the purification effect.

15 The novel process can be carried out continuously or batchwise. The continuous procedure is preferred.

The novel process makes it possible to purify hydroxylamine solutions which contain up to about 50 ppm, in particular up to
20 30 ppm, in general from 1 to 10 ppm, of metal ions. The metal ions are in general alkali metal ions, in particular sodium ions.

The hydroxylamine solutions obtained by the novel process are essentially free of metal ions, i.e. they contain less than
25 1 ppm, in particular less than 0.5 ppm, of metal ions. Repeating the treatment with a cation exchanger one or more times makes it possible further to reduce the metal ion content, for example to <0.1 ppm. Said solutions are therefore suitable for use in the electronics industry.

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The novel treatment of the hydroxylamine solution with an acidic cation exchanger can be combined with an anion exchanger treatment. The aqueous hydroxylamine solutions to be treated according to the invention contain, as a rule, a stabilizer which
35 prevents or retards decomposition of the hydroxylamines. The stabilizers are generally anionic complexing agents which are capable of complexing and deactivating heavy metal ions which, in uncomplexed form, are potent catalysts of the hydroxylamine decomposition. In the treatment of stabilized hydroxylamine
40 solutions with an anion exchanger, the stabilizer is bound to the anion exchanger. There is therefore the danger that the hydroxylamine solution treated with an anion exchanger is no longer sufficiently stable. Although stabilizer can again be added to the hydroxylamine solution after the treatment with an
45 anion exchanger, the conventional stabilizers contain, as a result of their preparation, a larger or smaller amount of alkali

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metal ions, in particular sodium ions, so that the success of the purification by a preceding cation exchanger treatment is substantially canceled out by the subsequent addition of stabilizer. As a rule, it is therefore preferable if the novel
5 process does not include any treatment of the hydroxylamine solution with an anion exchanger, in particular a strongly basic anion exchanger.

It has proven particularly preferable to subject the
10 hydroxylamine solution, after the treatment with the acidic cation exchanger, to a treatment with an anion exchanger and in particular a strongly basic anion exchanger in the hydroxyl form, in order to remove undesired anions.

15 For removing undesired anions in a hydroxylamine solution to be treated, it is also possible to use a process in which the hydroxylamine solution is subjected to at least one treatment with an anion exchanger in hydroxyl form, a stabilizer, preferably an anion complexing agent, is added to the treated
20 hydroxylamine solution, and the hydroxylamine solution is then subjected to at least one treatment with an acidic cation exchanger. An alternative, preferred process is one in which the hydroxylamine solution is subjected to at least one treatment with an anion exchanger in hydroxyl form, the hydroxylamine
25 solution is then subjected to at least one treatment with an acidic cation exchanger, and an aqueous solution of a stabilizer, in particular of an anionic complexing agent, which was subjected beforehand to a treatment with an acidic cation exchanger to remove metal ions, in particular alkali metal ions, is added to
30 the hydroxylamine solution.

Usable basic anion exchangers are, for example, the resins Amberlite IRA-400, IRA-402, IRA-904, IRA-92, IRA-93 and Duolite
35 A-109 from Rohm & Haas, Dowex 66 and Dowex II from Dow Chemical and Purolite A-600, A-400, A-300, A-850 and A-87 and Lewatit types from Bayer AG. The base form of the anion exchanger can be produced using conventional bases, such as sodium hydroxide or potassium hydroxide. The treatment with the anion exchanger is effected analogously to the treatment with the cation exchanger.

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The examples which follow illustrate the invention without restricting it.

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Example 1

The Na form of the weakly acidic, macroporous ion exchanger Lewatit TP 207 (from Bayer) which contains iminodiacetic acid groups and has a very low selectivity with respect to Na was washed Na-free with 0.5 molar sulfuric acid at 5 (ml/h)/ml of ion exchanger resin. Said ion exchanger was then washed sulfuric acid-free with demineralized water until a pH of 6.5 was reached.

140 g/h of 50% strength by weight of hydroxylamine solution containing 10 ppm of Na ions were passed at room temperature over a 19.5 ml bed of said ion exchanger. The ratio of hydroxylamine solution feed to ion exchanger volume was 7 (ml/h)/ml. After specified times, fractions of the purified solutions were collected and the residual Na content was determined. The resulting fractions of purified solution had the following Na contents:

	Amount in g	Na content in mg/l
20 Fraction 1	29.3	not determined
Fraction 2	29.6	2
Fraction 3	32.7	0.2
Fraction 4	33.9	0.2

3.4 g of hydroxylamine solution were thus purified per ml of ion exchanger.

Example 2

The hydroxylamine solution obtained according to Example 1 had a sulfate content of 30 ppm (30mg/l). To reduce the sulfate content, the solution was passed over an anion exchange column containing about 40 ml of anion exchanger in the hydroxyl form (7 ml/h hydroxylamine solution per ml of anion exchanger).

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The following ion exchangers were used:

Amberlite IRA-92

Lewatit M 511

Amberlite IRA-900

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In all cases, the sulfate content was reduced to 10 ppm (limit of detection).

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We claim:

1. A process for the preparation of an aqueous hydroxylamine
5 solution which is essentially free of metal ions, wherein the
hydroxylamine solution is subjected to at least one treatment
with an anion exchanger in hydroxyl form, a stabilizer is
added to the treated hydroxylamine solution, and the
hydroxylamine solution is then subjected to at least one
10 treatment with an acidic cation exchanger.
2. A process for the preparation of an aqueous hydroxylamine
solution which is essentially free of metal ions, wherein the
hydroxylamine solution is subjected to at least one treatment
15 with an anion exchanger in hydroxyl form, the hydroxylamine
solution is then subjected to at least one treatment with an
acidic cation exchanger, and an aqueous solution of a
stabilizer, which was subjected beforehand to a treatment
with a cation exchanger to remove metal ions, is added to the
20 hydroxylamine solution.
3. A process as claimed in claim 1 or 2, wherein a weakly acidic
cation exchanger is used.
- 25 4. A process as claimed in any of the preceding claims, wherein
a cation exchanger having chelate-forming groups is used.
5. A process as claimed in any of the preceding claims, wherein
the hydroxylamine solution is passed over a bed of the cation
30 exchanger.
6. A process as claimed in claim 5, wherein the hydroxylamine
solution is passed opposite to the direction of gravitational
force over the bed of the cation exchanger.

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