

PURIFICATION OF HYDROXYLAMINE

Field of the Invention

The present invention relates to a method for the purification of hydroxylamine. More particularly, there is provided a method of
5 purifying aqueous solutions of hydroxylamines by means of ion exchange.

Background of the Invention

Hydroxylamine has found many uses in a variety of industries. In the pharmaceutical industry and in connection with stripping
10 compositions for photoresists it has found wide use. In both the pharmaceutical industry and for photoresist treatment it is important that the product is free of impurities such as anions and cations.

U.S. Patent No. 4,147,623 of Koff et al., which is herein
15 incorporated by reference, discloses the purification of hydroxylamine by ion exclusion which includes use of anion exchange resin in which hydroxylammonium salts are passed. The ion exchange resin is primarily utilized as a reaction source rather than for separation.

20 U.S. Patent No. 4,202,765 to Koff et al., which is herein incorporated by reference, discloses the separation of hydroxylamine from a solution of hydroxylammonium salt through the use of a cation exchange resin. The process does not teach the exclusion of anions.

U.S. Patent No. 5,318,762 to Cawlfeld et al. discloses treating solutions of hydroxylammonium salts containing excess acid by passing the solutions through a weak base ion exchange resin.

U.S. Patent No. 4, 166,842 discloses a process of extracting
5 hydroxylammonium ions from a solution utilizing a cation exchange resin which included the further step of converting the hydroxylammium ions to hydroxylamine.

None of the prior art teach the removal of cations and anions from hydroxylamine so as to produce a highly purified
10 hydroxylamine.

Summary of the Invention

The present invention provides a method for the purification of hydroxylamine so that cations and anions which are normally present are greatly reduced. The process contains the steps which
15 comprise:

A. Passing an aqueous solution of hydroxylamine through at least one macroporous or gel, strong acid ion exchange resin bed which has been treated with a dilute hydrochloric acid solution, and then

20 B. Passing the solution from Step A through a strong base anion exchange resin bed.

Preferably, the hydrochloric acid solution is about 5 to 20% by weight hydrochloric acid.

Advantageously, there is utilized a plurality of cationic ion
25 exchange resin beds and a plurality of anionic ion exchange beds.

It is therefore an object of the invention to provide hydroxylamine solutions which are substantially free of undesirable cations and anions.

It is another object of the invention to purify hydroxylamine through the use of ion exchange resins.

Description of the Preferred Embodiments

According to the present invention, there is provided the purification of hydroxylamine whereby the resulting product is substantially free of undesirable cations and anions. The invention provides a process whereby an aqueous solution of hydroxylamine is passed through at least one bed of a cation strong acid ion exchange resin and at least one bed of a strong base anionic exchange resin. It is essential in the invention that the cationic exchange resin is pretreated with a dilute solution of hydrochloric acid. The hydrochloric acid treatment is with a 5-20% hydrochloric acid solution, preferably, about 5-10% hydrochloric acid solution.

The anionic strong base ion exchange resin is preferably treated with either a dilute potassium hydroxide or sodium hydroxide solution so as to remove any undesirable cations which may be present.

In accordance with the invention, it has been found that cation resins containing strong acid groups in the hydrogen form are capable of removing many of the undesirable trace metals. Also, using conventional methods of pretreatment such as with dilute sulfuric acid does not produce the same results as found

when dilute hydrochloric acid has been used to pretreat or regenerate the ion exchange resin. It is preferred to also pretreat or regenerate the cationic exchange resin with a dilute solution of hydroxylamine such as a 5-20% solution, preferably, about 5-10% by weight solution of hydroxylamine before passing a 50% by weight solution of hydroxylamine through one or more beds of the ion exchange resins.

An exothermic reaction is present when the hydroxylamine solution is added to the ion exchange bed so that it is preferable to utilize a dilute hydroxylamine solution to condition the ion exchange resin. The 50% aqueous hydroxylamine solution which is utilized reacts with a strong base cation exchange resin to produce the corresponding amine salt accompanied by a strong exothermic reaction. Once the amine salt has been formed and the exotherm subsides, the Na⁺, K⁺ and other cations exchange in the resin bed satisfactorily.

The flow rate of the pretreatment with the 5-20%, preferably 5-10% by weight of hydroxylamine solution can be used to control the exotherm reaction which initially takes place.

Most commercial ion exchange resins, both anionic and cationic, require additional cleaning or regeneration to take place prior to use. If the cleaning or regeneration is not performed, excessive decomposition of hydroxylamine take place. In the situation where the Na/K⁺ values go down but the CA²⁺ values go up, it has been found that regeneration of the cationic resin with

dilute hydrochloric acid and the regeneration of the anionic resin with a base is required prior to use.

Both gel type and macroporous type of ion exchange resins can be used in the present process. Preferred are the polystyrene and polyacrylic acid strong acid hydrogen form cationic exchanges and the strong base anion exchangers of the polystyrene or polyacrylic type and O^4 form.

The weak acid type cationic exchanges and the weak base anionic exchangers either alone or in combination with other exchangers have been found ineffective to reduce both the cationic and anionic trace materials found in the hydroxylamine compositions which are commercially produced.

The anion exchange resins which may be utilized in the present invention include the Purolite anion exchange resins A-600, A-400, A-300A-300E, A-400, A-850 and A-87, Rohm & Haas resins IRA-400, IRA-402, IRA-904 and IRA-93, Dow resins SBR, SAR, Dowex 66 and Dowex II, Ionac ASB-1, Duolite A-109 and the like in the OH^- form.

The cation exchange resins which may be utilized in the invention include Purolite resins CT-151, C-100, C-150, C-105 and NRW-100, Rohm & Haas resins IR-120, IR-122, 200, DP-1 and IRC-50, Dow resin MSC-1, Dowex 88 and CCR-2, Ionac resin CC and CNN, Duolite resin C-200, C-26, C-280 and the like in the H^+ form.

The following examples are provided to further illustrate the present invention and are not intended to limit the scope of the present invention.

Example 1

1. Into a 1 inch diameter glass column containing a stopcock was added 25ml of Purolite CT-151 cation exchange resin. The column was flushed with 1 liter of DI water. The resin was then
5 flushed with 1000ml of 10% hydrochloric acid. The column was tested to determine if all undesirable cations are removed by inductively coupled plasma (ICP) analysis. The column was then flushed with DI water until the chloride ion level was < 0.5ppm. The column was then dried with nitrogen.

10 A 5% hydroxylamine solution was poured through the column and there was an exothermic reaction. After the exotherm was complete a 50% hydroxylamine solution was passed through the column.

2. A glass column was prepared with Purolite anion exchange resin A-400 similar to Part I. 1000ml of 8% KOH was passed through
15 the column until an inductively coupled plasma analysis indicated removal of metal anions, particularly FeCl_4^- . The column was then flushed with 2 liters of DI water until the K^+ analysis by ICP was < 5ppb. The column was then dried with nitrogen and ready for use. The 50% hydroxylamine solution processed in Step 1 was then passed
20 through the cation exchange resin.

Preferably, the 50% hydroxylamine solution is passed through a plurality (about 5) of the prepared cation exchange beds and then through about 3 anion exchange beds.

The reduction of trace metals by use of the process of Example 1 is summarized as follows:

		Before ion exchanged (ppb)	After ion exchanged (ppb)
5	Al	536	< 5
	Ca	72	< 5
	Cr	70	< 5
	Fe	313	< 5
	Mg	15	< 5
10		Before ion exchanged (ppb)	After ion exchanged (ppb)
	Ni	29	9
	K	307	< 5
	Si	1687	< 5
15	Na	183	< 5

Comparative Example 1

The process of Example 1 was followed except that in lieu of 10% HCl, there was used 10% H₂SO₄ in Step 1 to condition the resin.

The resulting hydroxylamine after passage through the anion exchange resin contained an unacceptable amount of trace cations.

Comparative Example 2

The procedure of Example 1 was followed except that in Step 2 Purolite A-100 a polystyrene type weak base anion exchange resin was utilized.

The resulting hydroxylamine after passage through the anion exchange resin contained an unacceptable amount of trace anions.

Comparative Example 3

The procedure of Example 2 was followed except that in Step 2 Purolite A-830 a weak base polyacrylic anion resin having a free base ionic form was utilized as the anion exchange resin.

The resulting hydroxylamine after passage through the anion exchange resin contained an unacceptable amount of trace anions.



What Is Claimed Is:

1. A method for the purification of hydroxylamine which comprises the steps of:

A. passing an aqueous solution of hydroxylamine through at least one macroporous or gel strong acid ion exchange resin bed which has been treated with a dilute solution of hydrochloric acid, and then

B. passing the solution from Step A through at least one strong base anion exchange resin bed.

2. The method of claim 1 wherein about 5 to 20% hydrochloric acid solution is used in step in treating the resin of Step A.

3. The method of claim 1 wherein said resin of Step A is a strong acid polystyrene resin.

4. The method of claim 1 wherein said resin of Step B comprises polystyrene cross-linked with divinylbenzene.

5. The method of claim 1 wherein said hydroxylamine solution comprises about 5 to 10% by weight of hydroxylamine.

6. The method of claim 5 including the subsequent step of passing a 50% by weight hydroxylamine solution.



7. The method of claim 1 wherein said hydroxylamine solution is passed through a plurality of resin beds in Step A.

8. The method of claim 1 wherein said hydroxylamine solution from Step A is passed through a plurality of resin beds in Step B.

9. A method for the purification of hydroxylamine which comprises the steps of:

a) forming a plurality of strong acid ion exchange beds;

b) forming a plurality of strong base ion exchange beds;

c) treating the strong acid ion exchange beds with a dilute hydrochloric acid solution;

d) treating the strong base ion exchange beds with a solution of sodium hydroxide or potassium hydroxide;

e) passing an aqueous solution containing about 5 to 20% by weight of hydroxylamine through said strong acid and strong base ion exchange beds; and then

f) passing an aqueous solution containing about 50% by weight of hydroxylamine through said strong acid and strong base ion exchange beds.

10. An aqueous hydroxylamine solution prepared by the method of claim 1.

11. An aqueous hydroxylamine solution prepared by the method of claim 9.



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(21) International Application Number: PCT/US98/10445 (22) International Filing Date: 21 May 1998 (21.05.98) (30) Priority Data: 08/895,361 16 July 1997 (16.07.97) US (71) Applicant: ASHLAND INC. [US/US]; P.O. Box 2219, Columbus, OH 43216 (US). (72) Inventors: RIDDLE, Floyd, L.; 1020 Macuncie Avenue, Emmaus, PA 18049 (GB). MICHELOTTI, Francis, W.; 3560 Southwood Drive, Easton, PA 18042 (US). (74) Agents: CONNAUGHTON, Martin; Ashland Inc., P.O. Box 219, Columbus, OH 43216 (US) et al.		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PURIFICATION OF HYDROXYLAMINE (57) Abstract The invention provides a method for purification of hydroxylamine so as to have a substantial reduction of cations and anions. The method involves passing a solution of hydroxylamine through at least one strong acid ion exchange bed and then through at least one strong base anion exchange resin bed. The strong acid ion exchange bed is preconditioned with dilute hydrochloric acid.		