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(54) Title: STABILIZER FOR HYDROXYLAMINE, METHOD FOR STABILIZING HYDROXYLAMINE, AND STABILIZED HYDROXYLAMINE SOLUTION

(57) Abstract: Provided are a method for stabilizing hydroxylamine at high temperatures and high concentration and/or in the presence of metal impurities such as Fe, and a stabilized hydroxylamine solution. The method for stabilizing hydroxylamine includes adding 3,4-dihydroxybenzoic acid as storage stabilizer, and optionally an antioxidant.



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DESCRIPTION

STABILIZER FOR HYDROXYLAMINE, METHOD FOR STABILIZING
HYDROXYLAMINE, AND STABILIZED HYDROXYLAMINE SOLUTION

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Cross reference of the related application

This application is an application filed under 35 U.S.C.
§ 111(a) claiming pursuant to 35 U.S.C. § 119(e) of the filing
date of Provisional Application 60/636,547 on December 17,
10 2004, pursuant to 35 U.S.C. § 111(b).

FIELD OF THE INVENTION

The present invention relates to a stabilizer for
hydroxylamine, a method for stabilizing hydroxylamine, and a
15 stabilized hydroxylamine solution.

BACKGROUND OF THE INVENTION

Hydroxylamine and its derivatives have widespread
industrial uses as raw materials of medical and agricultural
20 chemical intermediates, reducing agents and metal
surface-treating agents, and also for fiber treatment and
dyeing. However, free hydroxylamine is very unstable and is
easily decomposed at high temperatures or high concentration
in the presence of, for example, metal ions (particularly heavy

metal ions). Consequently, hydroxylamine is generally produced and handled in the form of salts that are relatively stable.

However, hydroxylamine is more suited in many uses than hydroxylamine salts, and it is frequently necessary to handle an aqueous hydroxylamine solution at high temperatures or high concentration. Therefore, attempts have been made to stabilize hydroxylamine at high temperatures or high concentration and in the presence of metal impurities such as Fe.

As an example, Patent Document 1 (JP-B-S52-48118) discloses a stabilizing method in which a stabilizer is added to a crystal of hydroxylamine and/or a salt thereof, or a hydroxylamine solution, wherein the stabilizer is an aromatic compound in which two or more consecutive carbon atoms in the aromatic ring are each substituted with a hydroxyl group.

However, hydroxylamine solutions containing such stabilizers as pyrogallol, catechol, 4-tert-butylcatechol, 2,3-dihydroxynaphthalene and 2,3-dihydroxybenzoic acid have a problem that the decomposition of hydroxylamine cannot be prevented sufficiently at high temperatures or high concentration and in the event that metal impurities such as Fe are mixed.

Furthermore, hydroxylamine solutions containing the

stabilizers described in Patent Document 1 are colored at high temperatures or high concentration.

[Patent Document 1] JP-B-S52-48118

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DISCLOSURE OF THE INVENTION

It is an object of the present invention to provide a stabilizer for hydroxylamine, a method for stabilizing hydroxylamine, and a stabilized hydroxylamine solution.

The present inventors have made intensive studies to solve the aforesaid problems and have found that 3,4-dihydroxybenzoic acid can stabilize a hydroxylamine solution.

The present inventors have also found that the use of 3,4-dihydroxybenzoic acid in combination with an antioxidant can stabilize a hydroxylamine solution at a higher level. The present invention has been accomplished based on these novel findings. These findings are discovered by the inventors at the first time.

The present invention is based on the above findings and concerns to the following (1) to (7):

(1) A method for stabilizing hydroxylamine comprising adding 3,4-dihydroxybenzoic acid as storage stabilizer to a hydroxylamine solution.

(2) The method for stabilizing hydroxylamine as

described in (1), further comprising adding an antioxidant.

(3) The method for stabilizing hydroxylamine as described in (2), wherein the antioxidant is at least one compound selected from the group consisting of alcohols, phenol derivatives, compounds having an ethylenic double bond, compounds having an acetylenic triple bond, nitrile compounds, sulfur-containing compounds, nitrogen-containing compounds and phosphorous-containing compounds.

(4) A stabilized hydroxylamine solution comprising hydroxylamine and 3,4-dihydroxybenzoic acid.

(5) The stabilized hydroxylamine solution as described in (4), further comprising an antioxidant.

(6) The stabilized hydroxylamine solution as described in (5), wherein the antioxidant is at least one compound selected from the group consisting of alcohols, phenol derivatives, compounds having an ethylenic double bond, compounds having an acetylenic triple bond, nitrile compounds, sulfur-containing compounds, nitrogen-containing compounds and phosphorous-containing compounds.

(7) A stabilizer for hydroxylamine comprising 3,4-dihydroxybenzoic acid as active ingredient.

The present invention enables stabilization of a hydroxylamine solution, and can provide a stabilized hydroxylamine solution.

PREFERRED EMBODIMENTS OF THE INVENTION

Hereinbelow, the stabilizer and stabilizing method for a hydroxylamine solution, and the stabilized hydroxylamine solution according to the present invention will be described in detail.

The method for stabilizing hydroxylamine of the invention stabilizes hydroxylamine by adding 3,4-dihydroxybenzoic acid as storage stabilizer to a hydroxylamine solution.

The stabilized hydroxylamine solution of the invention includes hydroxylamine and 3,4-dihydroxybenzoic acid.

The stabilizer for hydroxylamine of the invention includes 3,4-dihydroxybenzoic acid as active ingredient.

In the hydroxylamine stabilizing method, 3,4-dihydroxybenzoic acid is added to a hydroxylamine solution and the decomposition of hydroxylamine can be prevented even at high temperatures or high concentration and/or in the event that metal impurities such as Fe are contained in the solution. Furthermore, the method can prevent the hydroxylamine solution from being colored at high temperatures or high concentration.

In the invention, 3,4-dihydroxybenzoic acid is not particularly limited as long as it is commercially or industrially available. Preferably, it has a low content of

metal impurities because otherwise the decomposition of hydroxylamine may be accelerated. High-purity hydroxylamine with little metal impurities is preferable for use in the electronics industry. A hydrate of 3,4-dihydroxybenzoic acid is also employable.

The mass ratio of 3,4-dihydroxybenzoic acid to hydroxylamine (3,4-dihydroxybenzoic acid/hydroxylamine) is suitably in the range of 1.0×10^{-9} to 1.0, preferably 1.0×10^{-8} to 0.1. When the mass ratio is smaller than 1.0×10^{-9} , the stabilizer may fail to prevent the decomposition of hydroxylamine. The mass ratio greater than 1.0 may entail removal or recovery of the excess 3,4-dihydroxybenzoic acid.

When 3,4-dihydroxybenzoic acid is added to hydroxylamine, it may be in the form of solid or in the form of solution or suspension in a solvent. The solvent used herein may be water and/or an organic solvent. The organic solvents include hydrocarbons, ethers, esters and alcohols capable of dissolving 3,4-dihydroxybenzoic acid, but are not limited thereto unless the use is adversely affected. Of the solvents, water and/or alcohol may be suitably used.

3,4-Dihydroxybenzoic acid may be added in the form of hydroxylamine solution. The solvent may be the same or different from that of the hydroxylamine solution depending on the condition or intended use, and is preferably the same.

The amount of the solvent may be determined appropriately.

In the hydroxylamine stabilizing method,
3,4-dihydroxybenzoic acid may be added in combination with an
antioxidant to a hydroxylamine solution to achieve a higher
5 level of prevention of the decomposition of hydroxylamine at
high temperatures or high concentration and/or in the presence
of metal impurities such as Fe.

This advantageous effect is probably explained by that
the antioxidant prevents oxidation and consequent
10 deterioration of 3,4-dihydroxybenzoic acid caused by
hydroxylamine or air.

The antioxidants for use in the hydroxylamine
stabilizing method include alcohols, phenol derivatives,
compounds having an ethylenic double bond, compounds having
15 an acetylenic triple bond, nitrile compounds,
sulfur-containing compounds, nitrogen-containing compounds
and phosphorous-containing compounds.

The stabilizing method may employ one or two or more kinds
of the antioxidants.

20 The antioxidant used in the invention is not particularly
limited as long as it is commercially or industrially available.
Preferably, it has a low content of metal impurities because
otherwise the decomposition of hydroxylamine can be
accelerated. High-purity hydroxylamine with little metal

impurities is preferable for use in the electronics industry.

The mass ratio of the antioxidant to hydroxylamine (antioxidant/hydroxylamine) is suitably in the range of 1.0×10^{-9} to 1.0, preferably 1.0×10^{-8} to 0.1. When the mass ratio is smaller than 1.0×10^{-9} , the stabilizer may fail to prevent the decomposition of hydroxylamine. The mass ratio greater than 1.0 may entail removal or recovery of the excess antioxidant. As already described, the alcohols are used as solvents capable of dissolving 3,4-dihydroxybenzoic acid as storage stabilizer, and therefore the mass ratio of the antioxidant being an alcohol to hydroxylamine is not limited to the above range when the solvent used is an alcohol.

The antioxidant may be added to hydroxylamine directly or in the form of solution or suspension in a solvent. The solvent used herein may be water and/or an organic solvent. The organic solvents include hydrocarbons, ethers, esters and alcohols capable of dissolving the antioxidant, but are not limited thereto unless the use is adversely affected. Of the solvents, water and/or alcohol may be suitably used. The antioxidant may be added in the form of hydroxylamine solution. The solvent may be the same or different from that of the hydroxylamine solution depending on the condition or intended use, and is preferably the same. Furthermore, the solvent may be the same or different from that for 3,4-dihydroxybenzoic

acid depending on the condition or intended use, and preferably 3,4-dihydroxybenzoic acid and the antioxidant are dissolved in the same solvent together. The amount of the solvent may be determined appropriately depending on the type and amount
5 of the antioxidant used.

The alcohols usable as antioxidant in the hydroxylamine stabilizing method of the invention include monohydric alcohols such as methanol, ethanol, propanol, butanol, pentanol, cyclohexyl alcohol, furfuryl alcohol,
10 tetrahydrofurfuryl alcohol, benzyl alcohol and glycolic acid; and polyhydric alcohols such as ethylene glycol, propylene glycol, butane diol, hexane diol, cyclohexane diol and glycerin. The polyhydric alcohols further include monosaccharides such as glyceraldehyde, erythrose, threose,
15 ribose, arabinose, xylose, lyxose, allose, altrose, glucose, mannose, gulose, idose, galactose, talose, dihydroxyacetone, erythrulose, ribulose, xylulose, psicose, fructose, sorbose and tagatose; disaccharides such as maltose, cellobiose, lactose, sucrose, trehalose and saccharose; and derivatives
20 of the monosaccharides and disaccharides such as erythritol, threitol, ribitol, arabinitol, xylitol, allitol, altritol, glucitol, mannitol, iditol and galactitol.

The phenol derivatives usable as antioxidant in the invention include phenol, 4-t-butylphenol, 4-methoxyphenol,

2,6-di-t-butyl-4-methylphenol, 2-t-butyl-4-methoxyphenol,
3-t-butyl-4-methoxyphenol, 2-t-butyl-4-methylphenol,
2,6-di-t-butylphenol, 2,4,6-trimethylphenol,
2-i-propyl-5-methylphenol,

5 n-octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate,
tetrakis(methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)
propionate)methane, tris(3,5-di-t-butyl-4-hydroxybenzyl)
isocyanurate, hydroquinone, 2,5-di-t-butylhydroquinone,
2,5-di-t-amylhydroquinone and tocopherol.

10 The ethylenic double bond-containing compounds include
styrene, o-nitrostyrene, m-nitrostyrene, p-nitrostyrene,
o-cyanostyrene, m-cyanostyrene, p-cyanostyrene,
divinylbenzene, p-styrenesulfonic acid, 2-vinylpyridine,
4-vinylpyridine, 2-vinyl-5-ethylpyridine,
15 2-methyl-5-vinylpyridine, acrylamide, methyl acrylate, ethyl
acrylate, methyl methacrylate, ethyl methacrylate, allyl
alcohol, allyl acetate and acrylonitrile.

The acetylenic triple bond-containing compounds include
propargyl alcohol, 1-butyne-1-ol, 2-butyne-1-ol,
20 3-butyne-1-ol, 3-butyne-2-ol, 2-butyne-1,4-diol and
2-butyne-1,4-diol diacetate.

The nitrile compounds include propionitrile,
butyronitrile, isobutyronitrile, 3-methoxypropionitrile,
malononitrile, adiponitrile, 1,6-dicyanohexane,

3-dimethylaminopropionitrile, benzonitrile, phthalonitrile, isophthalonitrile and terephthalonitrile.

The sulfur-containing compounds include phenothiazine, 2,2'-dibenzothiazolyl disulfide, 2-mercaptobenzothiazole, 5 2-mercaptobenzimidazole, sodium salt of 2-mercaptobenzothiazole, thiouric acid, bismuthiol, distearyl-3,3'-thiodipropionate, dilauryl-3,3'-thiodipropionate, dimyristyl-3,3'-thiodipropionate, cysteine, cystine, 10 dimercaptosuccinic acid, 2-aminoethanethiol, toluene-3,4-dithiol and furfuryl mercaptan.

The nitrogen-containing compounds include 1,1-diphenyl-2-picryl-hydrazyl, N-nitrosodiphenylamine, 4-nitrosodiphenylamine, 2-methyl-2-nitrosopropane, 15 α -phenyl(t-butyl)nitro, N-phenyl-N'-i-propyl phenylenediamine, 5,5-dimethyl-N-phenyl-N'-i-propyl phenylenediamine, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, nitrosobenzene and diphenylamine.

The phosphorous-containing compounds include 20 triethylphosphine, triphenylphosphine, trimethyl phosphite, triethyl phosphite, triphenyl phosphite, distearylpentaerythritol diphosphite, diphenyl-i-octyl phosphite and tris(2,4-di-t-butylphenyl)phosphite.

Hydroxylamine used in the invention is not particularly

limited as long as it is commercially or industrially available. Preferably, it has a low content of metal impurities because otherwise the decomposition of hydroxylamine can be accelerated. High-purity hydroxylamine with little metal
5 impurities is preferable for use in the electronics industry.

In the stabilizing method, hydroxylamine may be used in the form of solid or solution in a solvent. The solvent used herein may be water and/or an organic solvent. The organic solvents include hydrocarbons, ethers, esters and alcohols,
10 but are not limited thereto unless the use is adversely affected. Of the solvents, water and/or alcohol may be suitably used.

The hydroxylamine concentration in the hydroxylamine solution may be adjusted by appropriately selecting the amount of solvent and is not particularly limited. Preferably, the
15 concentration is in the range of 0.1 to 90% by mass, more preferably 1.0 to 70% by mass.

Hydroxylamine for use in the stabilizing method of the invention may be prepared by the following process as an example.

20 (Reaction Step)

The process for preparing hydroxylamine includes a reaction step of reacting a hydroxylamine salt with an alkali compound to obtain hydroxylamine.

Examples of the hydroxylamine salts include inorganic

acid salts of hydroxylamine, such as sulfate, hydrochloride, nitrate, phosphate, hydrobromide, sulfite, phosphite, perchlorate, carbonate and hydrogencarbonate; and organic acid salts such as formate, acetate and propionate. Of these, the invention preferably employs at least one salt selected from the group consisting of hydroxylamine sulfate ($\text{NH}_2\text{OH} \cdot 1/2\text{H}_2\text{SO}_4$), hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$), hydroxylamine nitrate ($\text{NH}_2\text{OH} \cdot \text{HNO}_3$) and hydroxylamine phosphate ($\text{NH}_2\text{OH} \cdot 1/3\text{H}_3\text{PO}_4$).

The hydroxylamine salt is not particularly limited as long as it is commercially or industrially available. Preferably, it has a low content of metal impurities because metal impurities can accelerate the decomposition of the hydroxylamine salt or hydroxylamine prepared. However, impurities may be present as long as they do not induce the decomposition of the hydroxylamine salt or hydroxylamine, can be removed by purification, and do not cause adverse effects in use of hydroxylamine.

The hydroxylamine salt may be used directly as solid or in the form of solution or suspension in a solvent. The solvent used herein may be water and/or an organic solvent. The organic solvents include hydrocarbons, ethers and alcohols, but are not limited thereto unless the reaction is adversely affected. Of the solvents, a solvent containing water and/or

alcohol may be suitably used. Insoluble salts and the like produced during the reaction may be filtered out and at least part of the filtrate may be used as the solvent.

The amount of solvent may be determined appropriately
5 depending on the amount of hydroxylamine salt used and conditions such as reaction temperature. The mass ratio of the solvent to the hydroxylamine salt (solvent/hydroxylamine salt) is generally in the range of 0.1 to 1000, preferably 1 to 100.

10 The alkali compound is preferably at least one compound selected from the group consisting of alkali metal-containing compounds, alkaline earth metal-containing compounds, ammonia and amines.

The alkali metal-containing compounds include oxides,
15 hydroxides and carbonates of lithium, sodium, potassium, rubidium and cesium, with hydroxides and carbonates of sodium and potassium being preferred.

The alkaline earth metal-containing compounds include oxides, hydroxides and carbonates of beryllium, magnesium,
20 calcium, strontium and barium, with oxides and hydroxides of magnesium, calcium, strontium and barium being preferred.

The ammonia may be in the form of gas or solution such as aqueous ammonia solution.

The amines include primary, secondary and tertiary

amines. The amines may be monoamines or polyamines such as diamines and triamines having two or more amino groups in the molecule, and may be cyclic amines.

The monoamines include methylamine, dimethylamine,
5 trimethylamine, ethylamine, diethylamine, triethylamine,
n-propylamine, di-n-propylamine, tri-n-propylamine,
i-propylamine, di-i-propylamine, tri-i-propylamine,
n-butylamine, di-n-butylamine, tri-n-butylamine,
i-butylamine, di-i-butylamine, tri-i-butylamine,
10 sec-butylamine, di-sec-butylamine, tri-sec-butylamine,
tert-butylamine, di-tert-butylamine, tri-tert-butylamine,
allylamine, diallylamine, triallylamine, cyclohexylamine,
dicyclohexylamine, tricyclohexylamine, n-octylamine,
di-n-octylamine, tri-n-octylamine, benzylamine,
15 dibenzylamine, tribenzylamine, diaminopropylamine,
2-ethylhexylamine, 3-(2-ethylhexyloxy)propylamine,
3-methoxypropylamine, 3-ethoxypropylamine,
3-(diethylamino)propylamine, bis(2-ethylhexyl)amine,
3-(dibutylamino)propylamine, α -phenylethylamine,
20 β -phenylethylamine, aniline, N-methylaniline,
N,N-dimethylaniline, diphenylamine, triphenylamine,
o-toluidine, m-toluidine, p-toluidine, o-anisidine,
m-anisidine, p-anisidine, o-chloroaniline, m-chloroaniline,
p-chloroaniline, o-bromoaniline, m-bromoaniline,

p-bromoaniline, o-nitroaniline, m-nitroaniline,
p-nitroaniline, 2,4-dinitroaniline, 2,4,6-trinitroaniline,
p-aminobenzoic acid, sulfanilic acid, sulfanilamide,
monoethanolamine, diethanolamine and triethanolamine.

5 The diamines include 1,2-diaminoethane,
N,N,N',N'-tetramethyl-1,2-diaminoethane,
N,N,N',N'-tetraethyl-1,2-diaminoethane, 1,3-diaminopropane,
N,N,N',N'-tetramethyl-1,2-diaminopropane,
N,N,N',N'-tetraethyl-1,2-diaminopropane, 1,4-diaminobutane,
10 N-methyl-1,4-diaminobutane, 1,2-diaminobutane,
N,N,N',N'-tetramethyl-1,2-diaminobutane,
3-aminopropyldimethylamine, 1,6-diaminohexane,
3,3-diamino-N-methyldipropylamine, 1,2-phenylenediamine,
1,3-phenylenediamine, 1,4-phenylenediamine and benzidine.

15 The triamines include 2,4,6-triaminophenol,
1,2,3-triaminopropane, 1,2,3-triaminobenzene,
1,2,4-triaminobenzene and 1,3,5-triaminobenzene.

The tetraamines include β, β', β'' -triaminotriethylamine.

The cyclic amines include pyrrole, pyridine, pyrimidine,
20 pyrrolidine, piperidine, purine, imidazole, oxazole, thiazole,
pyrazole, 3-pyrroline, quinoline, isoquinoline, carbazole,
piperazine, pyridazine, 1,2,3-triazine, 1,2,4-triazine,
1,3,5-triazine, 1,2,3-triazole, 1,2,5-triazole,
1,2,4-triazole, 1,3,4-triazole and morpholine.

The amines usable as the alkali compounds are not limited to the aforesaid compounds and further include asymmetric compounds having different substituent groups such as ethylmethylaniline. The amines may be used singly or in
5 combination of two or more kinds.

The alkali compound is not particularly limited as long as it is commercially or industrially available. Preferably, it has a low content of metal impurities, as is the case with hydroxylamine.

10 The equivalent ratio of the alkali compound to the hydroxylamine salt (alkali compound/hydroxylamine salt) is suitably in the range of 0.1 to 100, preferably 0.5 to 10, more preferably 1 to 2. With the equivalent weight of the hydroxylamine salt being 1, the equivalent weight is 1 for the
15 alkali metal-containing compound, 2 for the alkaline earth metal-containing compound, 1 for ammonia, 1 for the monoamine, and 2 for the diamine.

When the equivalent ratio is greater than 100, the excess alkali compound can induce the decomposition of hydroxylamine
20 and entail recovery of large amount of unreacted alkali compound. The equivalent ratio smaller than 0.1 may entail recovery of large amount of unreacted hydroxylamine salt.

The alkali compound may be used in the form of solution or suspension in a solvent. The solvent used herein may be

water and/or an organic solvent. The organic solvents include hydrocarbons, ethers and alcohols, but are not limited thereto unless the reaction is adversely affected. Of the solvents, water and/or alcohol may be suitably used. Insoluble salts and the like produced during the reaction may be filtered out and at least part of the filtrate may be used as the solvent.

The amount of solvent may be determined appropriately depending on the amount of alkali compound used and conditions such as reaction temperature. The mass ratio of the solvent to the alkali compound (solvent/alkali compound) is generally in the range of 0.5 to 1000, preferably 0.8 to 100.

In the process of preparing hydroxylamine, the reaction step of reacting the hydroxylamine salt and the alkali compound to obtain hydroxylamine, and later-described separation, purification and concentration steps may be performed in the presence of a stabilizing agent. The stabilizing agent may be conventional, with examples including 8-hydroxyquinoline, N-hydroxyethylethylenediamine-N,N,N'-triacetic acid, glycine, ethylenediaminetetraacetic acid, cis-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid, trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid, N,N'-di(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid, N-hydroxyethyliminodiacetic acid, N,N'-dihydroxyethylglycine, diethylenetriaminepentaacetic

acid, ethylenebis(oxyethylenenitrilo)tetraacetic acid,
bisexamethylenetriaminepentaacetic acid,
hexamethylenediaminetetraacetic acid,
triethylenetetraminehexaacetic acid,
5 tris(2-aminoethyl)aminehexaacetic acid, iminodiacetic acid,
polyethyleneimine, polypropyleneimine, o-aminoquinoline,
1,10-phenanthroline, 5-methyl-1,10-phenanthroline,
5-chloro-1,10-phenanthroline, 5-phenyl-1,10-phenanthroline,
hydroxyanthraquinone, 8-hydroxyquinoline-5-sulfonic acid,
10 8-hydroxymethylquinoline, thioglycolic acid, thiopropionic
acid, 1-amino-2-mercapto-propionic acid, 2,2-dipyridyl,
4,4-dimethyl-2,2-dipyridyl, ammonium thiosulfate,
benzotriazole, flavone, morin, quercetin, gossypetin,
robinetin, luteolin, fisetin, apigenin, galangin, chrysin,
15 flavonol, pyrogallol, oxyanthraquinone,
1,2-dioxyanthraquinone, 1,4-dioxyanthraquinone,
1,2,4-trioxyanthraquinone, 1,5-dioxyanthraquinone,
1,8-dioxyanthraquinone, 2,3-dioxyanthraquinone,
1,2,6-trioxyanthraquinone, 1,2,7-trioxyanthraquinone,
20 1,2,5,8-tetraoxyanthraquinone,
1,2,4,5,8-pentaoxyanthraquinone,
1,6,8-dioxy-3-methyl-6-methoxyanthraquinone, quinalizarin,
flavan, lactone, 2,3-dihydrohexono-1,4-lactone,
8-hydroxyquinaldine, 6-methyl-8-hydroxyquinaldine,

5,8-dihydroxyquinaldine, anthocyan, pelargonidin, cyanidin, delphinidin, peonidin, petunidin, malvidin, catechin, sodium thiosulfate, nitrilotriacetic acid, 2-hydroxyethyl disulfide, 1,4-dimercapto-2,3-butanediol, thiamine hydrochloride, 5 catechol, 4-t-butylcatechol, 2,3-dihydroxynaphthalene, 2,3-dihydroxybenzoic acid, 2-hydroxypyridine-N-oxide, 1,2-dimethyl-3-hydroxypyridine-4-one, 4-methylpyridine-N-oxide, 6-methylpyridine-N-oxide, 1-methyl-3-hydroxypyridine-2-one, 2-mercaptobenzothiazole, 10 2-mercaptocyclohexylthiazole, 2-mercapto-6-t-butylcyclohexylthiazole, 2-mercapto-4,5-dimethylthiazoline, 2-mercaptothiazoline, 2-mercapto-5-t-butylthiazoline, tetramethylthiuram disulfide, tetra-n-butylthiuram disulfide, 15 N,N'-diethylthiuram disulfide, tetraphenylthiuram disulfide, thiuram disulfide, thiourea, N,N'-diphenylthiourea, di-o-tolylthiourea, ethylenethiourea, thiocetamide, 2-thiouracil, thiocyanuric acid, thioformamide, thioacetamide, thiopropionamide, thiobenzamide, 20 thionicotinamide, thioacetanilide, thiobenzanilide, 1,3-dimethylthiourea, 1,3-diethyl-2-thiourea, 1-phenyl-2-thiourea, 1,3-diphenyl-2-thiourea, thiocarbazide, thiosemicarbazide, 4,4-dimethyl-3-thiosemicarbazide, 2-mercaptoimidazoline, 2-thiohydantoin, 3-thiourazole,

2-thiouramil, 4-thiouramil, thiopentanol, 2-thiobarbituric acid, thiocyanuric acid, 2-mercaptoquinoline, thiocoumazon, thiocoumothiazon, thiosaccharin, 2-mercaptobenzimidazole, trimethyl phosphite, triethyl phosphite, triphenyl phosphite, 5 trimethylphosphine, triethylphosphine and triphenylphosphine. 3,4-Dihydroxybenzoic acid may be used as the stabilizing agent too.

The above stabilizing agents may be used singly or in combination of two or more kinds. The stabilizing agents can 10 prevent the decomposition of the hydroxylamine salt or hydroxylamine by metal impurities or the like.

The stabilizing agent is not particularly limited as long as it is commercially or industrially available. Preferably, it has a low content of metal impurities, as is the case with 15 the hydroxylamine salt.

The mass ratio of the stabilizing agent to the hydroxylamine salt (stabilizing agent/hydroxylamine salt) is suitably in the range of 1.0×10^{-9} to 1.0, preferably 1.0×10^{-8} to 0.1. When the mass ratio is smaller than 1.0×10^{-9} , the 20 stabilizing agent may fail to prevent the decomposition of the hydroxylamine salt or hydroxylamine by metal impurities. The mass ratio greater than 1.0 may entail removal or recovery of the excess stabilizing agent.

The stabilizing agent may be used directly as solid or

in the form of solution in a solvent. The solvent used herein may be water and/or an organic solvent. The organic solvents include hydrocarbons, ethers, esters and alcohols, but are not limited thereto unless the reaction is adversely affected. Of 5 the solvents, water and/or alcohol may be suitably used. The amount of solvent may be determined appropriately depending on the type and amount of stabilizing agent used and conditions such as reaction temperature.

In the process of hydroxylamine production, the reaction 10 step is preferably performed by adding the hydroxylamine salt to a reaction solution or suspension of the alkali compound in the solvent, in which case hydroxylamine produced is less likely to form a complex with the by-product salt and is less prone to being adsorbed to or incorporated in the by-product 15 insoluble salt.

Also preferably, the hydroxylamine salt is added to a reaction liquid containing the alkali compound while the pH of the reaction liquid is maintained at 7 or above, more preferably 7.5 or above, still preferably 8 or above. This 20 pH of the reaction liquid can reduce the tendency of hydroxylamine produced to form a complex with the by-product salt and to being adsorbed to or incorporated in the by-product insoluble salt.

Alternatively, the reaction step may be performed by

adding the alkali compound to a reaction solution or suspension of the hydroxylamine salt in the solvent.

Still alternatively, the reaction step may be performed by simultaneously adding the hydroxylamine salt and the alkali compound to react them. In this case, the amounts of the hydroxylamine salt and the alkali compound are desirably controlled while the pH of the reaction liquid is preferably maintained at 7 or above, more preferably 7.5 or above, still preferably 8 or above. The hydroxylamine salt and the alkali compound may be added directly as solid or in the form of solution or suspension in the solvent. When the alkali compound is ammonia, it may be introduced in the form of gas.

In the reaction step for producing hydroxylamine, the stabilizing agent may be added by a known method without limitation. For example, the stabilizing agent may be introduced in a reactor before the reaction is started, or may be added during the reaction in accordance with necessity. Alternatively, the stabilizing agent may be dissolved or suspended in the solvent together with the alkali compound and the hydroxylamine salt.

The reaction step is preferably carried out at a reaction temperature of 0 to 80°C, more preferably 5 to 50°C. When the reaction temperature is above 80°C, problems such as decomposition of hydroxylamine may occur. On the other hand,

a reaction temperature below 0°C makes the reaction slow to cause problems such as lowered productivity.

The reaction heat generated by the reaction between the hydroxylamine salt and the alkali compound will be released
5 outside the system by means of water, warm water or heat transfer medium to keep the reaction temperature within a certain range. The heat released outside the system by means of water, warm water or heat transfer medium is preferably utilized as heat source for other facility.

10 The reaction step may be carried out in a known manner, for example batchwise, semi-batchwise or continuously.
(Separation Step)

The hydroxylamine production process may include a step of separating hydroxylamine from insoluble matters.

15 The insoluble matters are, for example, matters that are precipitated in the reaction liquid during the reaction step.

Examples of the insoluble matters include salts formed by the reaction between the hydroxylamine salt and the alkali compound in the reaction step, the hydroxylamine salts and the
20 alkali compounds.

Specifically, the separation step for separating the insoluble matters may be performed in the event that the salts formed by the reaction between the hydroxylamine salt and the alkali compound in the reaction step, the hydroxylamine salt,

the alkali compound and the like have increased their concentrations above the solubility to form insoluble matters precipitated.

The separation may be carried out by a known method such
5 as filtration, pressing, centrifugal separation, sedimentation separation and floatation separation. The separation by filtration may be performed by any of natural filtration, pressure filtration and vacuum filtration. The separation by sedimentation may be performed by any of
10 clarification separation and sedimentation concentration. The separation by floatation may be performed by any of pressure floatation and ionization floatation.

The insoluble matters separated in the separation step may be washed with a solvent to recover hydroxylamine adsorbed
15 to or incorporated in the insoluble matters.

The solvent for washing the insoluble matters may be the same or different from the solvent used in the reaction step. Water and/or an organic solvent may be used as the washing solvent. The organic solvents include hydrocarbons, ethers,
20 esters and alcohols, but are not limited thereto unless the recovery of hydroxylamine is adversely affected. Of the solvents, water and/or alcohol may be suitably used as the washing solvent. The amount of washing solvent may be determined appropriately depending on the type and amount of

insoluble matters and separation conditions.

In the separation step, the temperature at which the insoluble matters are separated is preferably in the range of 0 to 80°C, more preferably 5 to 50°C. When the separation
5 temperature is above 80°C, problems such as decomposition of hydroxylamine may occur. On the other hand, when the temperature of the reaction liquid is below 0°C, problems such as large amounts of energy required for cooling may arise. Part or all of the filtrate obtained by filtering out the
10 insoluble matters and/or the washings obtained by washing the insoluble matters may be used as solvent for dissolving or suspending the reaction material hydroxylamine salt and/or alkali compound.

The separation step is preferably performed in the
15 presence of a stabilizing agent for hydroxylamine, as is the case with the reaction step. The stabilizing agent may be newly added in the separation step, or the one used in the previous step may be continuously utilized.

The stabilizing agent may be the same or different from
20 that used in the reaction step depending on the condition or intended use. The stabilizing agent prevents side reactions such as hydroxylamine decomposition by metal impurities and improves the production yield of hydroxylamine.

The amount of stabilizing agent is suitably such that

the mass ratio of the stabilizing agent to hydroxylamine (stabilizing agent/hydroxylamine) is in the range of 1.0×10^{-9} to 1.0, preferably 1.0×10^{-8} to 0.1. When the mass ratio is smaller than 1.0×10^{-9} , the stabilizing agent may fail to prevent
5 the decomposition of hydroxylamine by metal impurities. The mass ratio greater than 1.0 may entail removal or recovery of the excess stabilizing agent.

The separation step may be carried out in a known manner, for example batchwise, semi-batchwise or continuously.

10 (Purification Step)

The hydroxylamine production process may include a purification step of purifying the above-obtained hydroxylamine solution by ion exchange.

The ion exchange method may be conventional, with
15 examples including cation exchange, anion exchange and chelate exchange.

The purification by cation exchange may be performed by known methods using strongly acidic cation exchange resins and weakly acidic cation exchange resins. Preferably, the cation
20 exchange resins are previously acid treated to become H type.

The purification by anion exchange may be performed by known methods using strongly basic anion exchange resins and weakly basic anion exchange resins. Preferably, the anion exchange resins are previously alkali treated to become OH

type.

The purification by chelate exchange may be performed by known methods using chelate exchange resins. Preferably, the chelate exchange resins are previously acid treated to
5 become H type.

The purification may be performed by cation exchange, anion exchange and chelate exchange in combination. As an example, cation exchange may be followed by anion exchange, or anion exchange may be followed by cation exchange. Further,
10 a monobed resin or mixed bed resin that is a mixture of a cation exchange resin and an anion exchange resin may be used.

The ion exchange temperature is preferably in the range of 0 to 70°C, more preferably 5 to 50°C. When the ion exchange temperature is above 70°C, problems such as decomposition of
15 hydroxylamine may occur. On the other hand, when the ion exchange temperature is below 0°C, problems such as large amounts of energy required for cooling may arise.

Part of the purified hydroxylamine solution may be used as solvent for dissolving or suspending the reaction material
20 hydroxylamine salt and/or alkali compound.

The purification step is preferably performed in the presence of a stabilizing agent for hydroxylamine, as is the case with the reaction step. The stabilizing agent may be newly added in the purification step, or the one used in the

previous step may be continuously utilized.

The stabilizing agent may be the same or different from that used in the reaction step depending on the condition or intended use. The stabilizing agent prevents side reactions
5 such as hydroxylamine decomposition by metal impurities and improves the production yield of hydroxylamine.

The amount of stabilizing agent is suitably such that the mass ratio of the stabilizing agent to hydroxylamine (stabilizing agent/hydroxylamine) is in the range of 1.0×10^{-9}
10 to 1.0, preferably 1.0×10^{-8} to 0.1. When the mass ratio is smaller than 1.0×10^{-9} , the stabilizing agent may fail to prevent the decomposition of hydroxylamine by metal impurities. The mass ratio greater than 1.0 may entail removal or recovery of the excess stabilizing agent.

15 The purification step by ion exchange may be carried out in a known manner, for example batchwise, semi-batchwise or continuously.

(Concentration Step)

The hydroxylamine production process may include a step
20 of concentrating hydroxylamine by distillation at the bottom of a distillation column.

The distillation method may be conventional, with examples including simple distillation, multistage distillation, steam distillation and flash distillation.

Simple or multistage distillation can provide a high-concentration hydroxylamine solution from the column bottom.

The distillation column may be a common plate column such as a bubble tray column or a sieve plate column and may be filled with common packings such as Raschig ring, pall ring and saddle.

The distillation temperature as measured in the column bottom is preferably in the range of 0 to 70°C, more preferably 5 to 60°C. When the temperature of the column bottom is above 70°C, problems such as decomposition of hydroxylamine may occur. On the other hand, when the column bottom temperature is below 0°C, problems such as large amounts of energy required for cooling may arise.

The distillation pressure, although dependent on the temperature, is preferably in the range of 0.5 to 60 kPa, more preferably 0.8 to 40 kPa in the column bottom.

Part of the concentrated hydroxylamine solution may be used as solvent for dissolving or suspending the reaction material hydroxylamine salt and/or alkali compound.

A low-concentration hydroxylamine solution often comes out from the top or side of the distillation column, and part or all of such solution may be used as solvent for dissolving or suspending the reaction material hydroxylamine salt and/or alkali compound.

The concentration step is preferably performed in the presence of a stabilizing agent for hydroxylamine, as is the case with the reaction step. The stabilizing agent may be newly added in the concentration step, or the one used in the
5 previous step may be continuously utilized.

The stabilizing agent may be the same or different from that used in the reaction step depending on the condition or intended use. The stabilizing agent prevents side reactions such as hydroxylamine decomposition by metal impurities and
10 improves the production yield of hydroxylamine.

The amount of stabilizing agent is suitably such that the mass ratio of the stabilizing agent to hydroxylamine (stabilizing agent/hydroxylamine) is in the range of 1.0×10^{-9} to 1.0, preferably 1.0×10^{-8} to 0.1. When the mass ratio is
15 smaller than 1.0×10^{-9} , the stabilizing agent may fail to prevent the decomposition of hydroxylamine by metal impurities. The mass ratio greater than 1.0 may entail removal or recovery of the excess stabilizing agent.

The concentration step for concentrating hydroxylamine
20 by distillation at the column bottom may be carried out in a known manner, for example batchwise, semi-batchwise or continuously.

The hydroxylamine production process may include a purification step of purifying concentrated hydroxylamine by

ion exchange.

The ion exchange method may be conventional, with examples including cation exchange, anion exchange and chelate exchange.

5 The purification by cation exchange may be performed by known methods using strongly acidic cation exchange resins and weakly acidic cation exchange resins. Preferably, the cation exchange resins are previously acid treated to become H type.

10 The purification by anion exchange may be performed by known methods using strongly basic anion exchange resins and weakly basic anion exchange resins. Preferably, the anion exchange resins are previously alkali treated to become OH type.

15 The purification by chelate exchange may be performed by known methods using chelate exchange resins. Preferably, the chelate exchange resins are previously acid treated to become H type.

20 The purification may be performed by cation exchange, anion exchange and chelate exchange in combination. As an example, cation exchange may be followed by anion exchange, or anion exchange may be followed by cation exchange.

Further, a monobed resin or mixed bed resin that is a mixture of a cation exchange resin and an anion exchange resin may be used.

The ion exchange temperature is preferably in the range of 0 to 70°C, more preferably 5 to 50°C. When the ion exchange temperature is above 70°C, problems such as decomposition of hydroxylamine may occur. On the other hand, when the ion
5 exchange temperature is below 0°C, problems such as large amounts of energy required for cooling may arise.

Part of the purified hydroxylamine solution may be used as solvent for dissolving or suspending the reaction material hydroxylamine salt and/or alkali compound.

10 The purification step is preferably performed in the presence of a stabilizing agent for hydroxylamine, as is the case with the reaction step. The stabilizing agent may be newly added in the purification step, or the one used in the previous step may be continuously utilized.

15 The stabilizing agent may be the same or different from that used in the reaction step depending on the condition or intended use. The stabilizing agent prevents side reactions such as hydroxylamine decomposition by metal impurities and improves the production yield of hydroxylamine.

20 The amount of stabilizing agent is suitably such that the mass ratio of the stabilizing agent to hydroxylamine (stabilizing agent/hydroxylamine) is in the range of 1.0×10^{-9} to 1.0, preferably 1.0×10^{-8} to 0.1. When the mass ratio is smaller than 1.0×10^{-9} , the stabilizing agent may fail to prevent

the decomposition of hydroxylamine by metal impurities. The mass ratio greater than 1.0 may entail removal or recovery of the excess stabilizing agent.

As described above, hydroxylamine for use in the
5 stabilizing method of the invention may be prepared by the process including:

(1) the reaction step for obtaining hydroxylamine by reacting the hydroxylamine salt and the alkali compound;

(2) the separation step for separating hydroxylamine and
10 insoluble matters;

(3) the purification step for purifying hydroxylamine by ion exchange; and

(4) the concentration step for concentrating hydroxylamine by distillation at the column bottom.

15 These steps are preferably carried out in the order of the reaction step, the separation step, the purification step and the concentration step. The steps (1) to (4) may be performed in an arbitrary order provided that the step (1) comes first, and the same step may be performed two or more times.

20 By the aforementioned process, hydroxylamine can be obtained at a concentration of 10% by mass or more, 20% by mass or more, or 40% by mass or more.

Hydroxylamine obtained by the above process has a metallic impurity content of not more than 1 ppm by mass, not

more than 0.1 ppm by mass, or not more than 0.01 ppm by mass with respect to each metal. The metals as impurities are, for example, alkali metals and alkaline earth metals derived from the alkali compounds used in the reaction step, and Fe which notably accelerates the decomposition of hydroxylamine.

Hydroxylamine obtained by the above process has an anion impurity content of not more than 100 ppm by mass, not more than 10 ppm by mass, or not more than 1 ppm by mass with respect to each anion. The anions as impurities are, for example, sulfate ions, chloride ions and nitrate ions derived from the raw material hydroxylamine salts.

When 3,4-dihydroxybenzoic acid is added in any of the steps (1) to (4), it is not needed to be removed or recovered and may be continuously used as storage stabilizer. In this case, the amount of 3,4-dihydroxybenzoic acid newly added as storage stabilizer is determined by including in the calculation the amount of 3,4-dihydroxybenzoic acid already present in the solution.

20

EXAMPLES

The present invention will be hereinafter described in greater detail by Examples, but it should be construed that the invention is in no way limited to such Examples.

(Examples 1-3)

Storage stabilizer 3,4-dihydroxybenzoic acid was added to a 50% by mass aqueous hydroxylamine solution having an Fe concentration of not more than 0.01 ppm by mass, in a predetermined concentration relative to the 50% by mass aqueous hydroxylamine solution.

100 g of the 50% by mass aqueous hydroxylamine solution obtained as described above was added to a 500 ml PFA container with a lid, and the container was covered and placed in a 50°C thermostatic chamber.

After 30 days, the aqueous hydroxylamine solution was visually observed for coloration, and the hydroxylamine concentration was titrated with hydrochloric acid. The hydroxylamine decomposition ratio was obtained by the following formula:

Hydroxylamine decomposition ratio (%) = $(50-A)/50 \times 100$
wherein A is the hydroxylamine concentration (% by mass) after 30 days.

The results are given in Table 1.

(Comparative Examples 1-6)

These Comparative Examples were performed in the same manner as in Examples 1 to 3, except that storage stabilizer 3,4-dihydroxybenzoic acid was replaced with the storage stabilizers shown in Table 1.

The results are given in Table 1.

Table 1

Example	Storage stabilizer	Storage stabilizer concentration (ppm by mass)	Antioxidant	Antioxidant concentration (ppm by mass)	Coloration	Hydroxylamine decomposition ratio (%)
Ex. 1	3,4-dihydroxy benzoic acid	500	None	0	No	1.4
Ex. 2	3,4-dihydroxy benzoic acid	700	None	0	No	1.2
Ex. 3	3,4-dihydroxy benzoic acid	1000	None	0	No	1.0
Comp. Ex. 1	None	0	None	0	No	2.9
Comp. Ex. 2	Pyrogallol	500	None	0	Yes (yellow)	2.3
Comp. Ex. 3	Catechol	500	None	0	Yes (yellow)	2.1
Comp. Ex. 4	4-tert-butylcatechol	500	None	0	Yes (yellow)	2.4
Comp. Ex. 5	2,3-dihydroxy naphthalene	500	None	0	Yes (yellow)	2.4
Comp. Ex. 6	2,3-dihydroxy benzoic acid	500	None	0	Yes (yellow)	2.6

The results of Examples and Comparative Examples above prove that 3,4-dihydroxybenzoic acid is effective as storage stabilizer for stabilizing the aqueous hydroxylamine solution without coloration.

5 (Examples 4-12)

Storage stabilizer 3,4-dihydroxybenzoic acid was added to a 50% by mass aqueous hydroxylamine solution having an Fe concentration of not more than 0.01 ppm by mass, in a predetermined concentration relative to the 50% by mass
10 aqueous hydroxylamine solution. Further, an antioxidant was added to the 50% by mass aqueous hydroxylamine solution in a predetermined concentration relative to the solution.

100 g of the 50% by mass aqueous hydroxylamine solution obtained as described above was added to a 500 ml PFA container
15 with a lid, and the container was covered and placed in a 50°C thermostatic chamber.

After 30 days, the aqueous hydroxylamine solution was visually observed for coloration, and the hydroxylamine concentration was titrated with hydrochloric acid. The
20 hydroxylamine decomposition ratio was obtained by the following formula:

Hydroxylamine decomposition ratio (%) = $(50-A)/50 \times 100$
wherein A is the hydroxylamine concentration (% by mass) after 30 days.

The results are given in Table 2.

Table 2

Example	Storage stabilizer	Storage stabilizer concentration (ppm by mass)	Antioxidant	Antioxidant concentration (ppm by mass)	Coloration	Hydroxylamine decomposition ratio (%)
Ex. 4	3,4-dihydroxy benzoic acid	500	Furfuryl alcohol	100	No	1.1
Ex. 5	3,4-dihydroxy benzoic acid	500	D(-)-fructose	100	No	1.1
Ex. 6	3,4-dihydroxy benzoic acid	500	2,4,6-trimethyl phenol	100	No	1.2
Ex. 7	3,4-dihydroxy benzoic acid	500	styrene	100	No	1.1
Ex. 8	3,4-dihydroxy benzoic acid	500	Propargyl alcohol	100	No	1.2
Ex. 9	3,4-dihydroxy benzoic acid	500	Benzonitrile	100	No	1.1
Ex. 10	3,4-dihydroxy benzoic acid	500	Bismuthiol	100	No	1.2
Ex. 11	3,4-dihydroxy benzoic acid	500	2-methyl-2-nitrosopropane	100	No	1.1
Ex. 12	3,4-dihydroxy benzoic acid	500	Triphenyl phosphite	100	No	1.2

The results of Examples above prove that the combined use of 3,4-dihydroxybenzoic acid and antioxidant is more effective for stabilizing the aqueous hydroxylamine solution without coloration.

5 (Examples 13-15)

Storage stabilizer 3,4-dihydroxybenzoic acid was added to a 50% by mass aqueous hydroxylamine solution having an Fe concentration of not more than 0.01 ppm by mass, in a predetermined concentration relative to the 50% by mass
10 aqueous hydroxylamine solution.

20 g of the 50% by mass aqueous hydroxylamine solution obtained as described above was added to a 500 ml PFA container with a lid.

Subsequently, a 1000 mg/L standard solution of Fe (III)
15 was added to the 50% by mass aqueous hydroxylamine solution in a predetermined Fe concentration, and the container was covered and placed in a 50°C thermostatic chamber.

After 7 days, the hydroxylamine concentration was titrated with hydrochloric acid. The hydroxylamine
20 decomposition ratio was obtained by the following formula:

$$\text{Hydroxylamine decomposition ratio (\%)} = (50-B)/50 \times 100$$

wherein B is the hydroxylamine concentration (% by mass) after 7 days.

The results are given in Table 3.

(Comparative Examples 7-12)

These Comparative Examples were performed in the same manner as in Examples 13 to 15, except that storage stabilizer 3,4-dihydroxybenzoic acid was replaced with the storage
5 stabilizers shown in Table 3.

The results are given in Table 3.

Table 3

Example	Storage stabilizer	Storage stabilizer concentration (ppm by mass)	Antioxidant	Antioxidant concentration (ppm by mass)	Fe (III) concentration (ppm by mass)	Hydroxylamine decomposition ratio (%)
Ex. 13	3,4-dihydroxy benzoic acid	500	None	0	10	8.7
Ex. 14	3,4-dihydroxy benzoic acid	700	None	0	10	6.2
Ex. 15	3,4-dihydroxy benzoic acid	1000	None	0	10	4.6
Comp. Ex. 7	None	0	None	0	1	100
Comp. Ex. 8	Pyrogallol	500	None	0	10	100
Comp. Ex. 9	Catechol	500	None	0	10	13
Comp. Ex. 10	4-tert-butylcatechol	500	None	0	10	43
Comp. Ex. 11	2,3-dihydroxy naphthalene	500	None	0	10	35
Comp. Ex. 12	2,3-dihydroxy benzoic acid	500	None	0	10	100

The results of Examples and Comparative Examples above prove that 3,4-dihydroxybenzoic acid is effective as storage stabilizer for stabilizing the aqueous hydroxylamine solution in the presence of Fe.

5 (Examples 16-24)

Storage stabilizer 3,4-dihydroxybenzoic acid was added to a 50% by mass aqueous hydroxylamine solution having an Fe concentration of not more than 0.01 ppm by mass, in a predetermined concentration relative to the 50% by mass
10 aqueous hydroxylamine solution. Further, an antioxidant was added to the 50% by mass aqueous hydroxylamine solution in a predetermined concentration relative to the solution.

20 g of the 50% by mass aqueous hydroxylamine solution obtained as described above was added to a 500 ml PFA container
15 with a lid.

Subsequently, a 1000 mg/L standard solution of Fe (III) was added to the 50% by mass aqueous hydroxylamine solution in a predetermined Fe concentration, and the container was covered and placed in a 50°C thermostatic chamber.

20 After 7 days, the hydroxylamine concentration was titrated with hydrochloric acid. The hydroxylamine decomposition ratio was obtained by the following formula:

Hydroxylamine decomposition ratio (%) = $(50-B)/50 \times 100$
wherein B is the hydroxylamine concentration (% by mass) after

7 days.

The results are given in Table 4.

Table 4

Example	Storage stabilizer	Storage stabilizer concentration (ppm by mass)	Antioxidant	Antioxidant concentration (ppm by mass)	Fe (III) concentration (ppm by mass)	Hydroxylamine decomposition ratio (%)
Ex. 16	3,4-dihydroxy benzoic acid	500	Furfuryl alcohol	100	10	7.9
Ex. 17	3,4-dihydroxy benzoic acid	500	D(-)-fructose	100	10	8.0
Ex. 18	3,4-dihydroxy benzoic acid	500	2,4,6-trimethyl phenol	100	10	8.0
Ex. 19	3,4-dihydroxy benzoic acid	500	styrene	100	10	7.9
Ex. 20	3,4-dihydroxy benzoic acid	500	Propargyl alcohol	100	10	8.2
Ex. 21	3,4-dihydroxy benzoic acid	500	Benzonitrile	100	10	7.9
Ex. 22	3,4-dihydroxy benzoic acid	500	Bismuthiol	100	10	7.8
Ex. 23	3,4-dihydroxy benzoic acid	500	2-methyl-2-nitrosopropane	100	10	7.9
Ex. 24	3,4-dihydroxy benzoic acid	500	Triphenyl phosphite	100	10	8.0

The results of Examples above prove that the combined use of 3,4-dihydroxybenzoic acid and antioxidant is more effective for stabilizing the aqueous hydroxylamine solution in the presence of Fe.

5

INDUSTRIAL APPLICABILITY

The present invention enables stabilization of a hydroxylamine solution, and provides a stabilized hydroxylamine solution. In particular, the invention
10 remarkably improves the stability of hydroxylamine at high temperatures and high concentration and/or in the presence of metal impurities. Consequently, a wider range of uses of hydroxylamine is enabled.

CLAIMS

1. A method for stabilizing hydroxylamine comprising adding 3,4-dihydroxybenzoic acid as storage stabilizer to a hydroxylamine solution.
2. The method for stabilizing hydroxylamine according to claim 1, further comprising adding an antioxidant.
3. The method for stabilizing hydroxylamine according to claim 2, wherein the antioxidant is at least one compound selected from the group consisting of alcohols, phenol derivatives, compounds having an ethylenic double bond, compounds having an acetylenic triple bond, nitrile compounds, sulfur-containing compounds, nitrogen-containing compounds and phosphorous-containing compounds.
4. A stabilized hydroxylamine solution comprising hydroxylamine and 3,4-dihydroxybenzoic acid.
5. The stabilized hydroxylamine solution according to claim 4, further comprising an antioxidant.

6. The stabilized hydroxylamine solution according to claim 5, wherein the antioxidant is at least one compound selected from the group consisting of alcohols, phenol derivatives, compounds having an ethylenic double bond, 5 compounds having an acetylenic triple bond, nitrile compounds, sulfur-containing compounds, nitrogen-containing compounds and phosphorous-containing compounds.

7. A stabilizer for hydroxylamine comprising 10 3,4-dihydroxybenzoic acid as active ingredient.