

METHOD OF TREATING WASTEWATER CONTAINING FLUORIDE ION

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates to a method for treating a wastewater containing fluoride ion, and more particularly, to a method of an advanced treatment of various types of wastewater such as industrial wastewaters from semiconductor production apparatuses, surface treatment processes in the
10 production of electronic parts, smoke-desulfurizers of thermal power plants, stainless steel production processes, glass production processes, etc.

2. Description of the Prior Art

In electronic industries for the production of semiconductors such as LSI, various chemicals have been used in the production processes. Therefore, the
15 wastewater from the production processes must be treated to remove these chemicals. For instance, the wastewater often contains fluoride ion derived from hydrofluoric acid that is frequently used as an etchant for silicon wafers. Therefore, the fluoride ion must be removed from the wastewater. The current effluent standard for fluorine is 15 mg/L or lower. However, many
20 self-governing bodies are going to set a much stricter effluent standard, likely to 8 mg/L or lower.

The removal of fluoride ion is generally made by the addition of a calcium ion-generating substance such as calcium chloride and calcium hydroxide thereby to allow fluoride ion to crystallize out as calcium fluoride for
25 separation. Usually, after the crystallized calcium fluoride is flocculated and precipitated, fluoride ion still remaining in the wastewater is removed with the addition of an aluminum-based inorganic flocculant such as aluminum sulfate or an iron-based inorganic flocculant such as iron (III) chloride to ensure solid-liquid separation. However, it has been difficult to reduce the

concentration of fluoride ion of the wastewater to 8 mg/L or lower by the addition of such chemicals. Therefore, at present, the concentration of fluoride ion should be reduced by dilution with a fluorine-free waste water, etc.

One of alternative approaches is to remove fluoride ion from wastewater using a reaction column packed with granular calcium carbonate such as calcite (JP 5-170435 A). In this method, however, the granular calcium carbonate is dissolved away when the wastewater has a low pH. When the wastewater has a high alkalinity due to ammonia, etc., the pH becomes high and the elution of calcium ion from the granular calcium carbonate is inhibited, thereby making the reaction between calcium ion and fluoride ion insufficient. Therefore, the proposed method needs a control system for accurately measuring and controlling the acidity and the fluoride ion concentration of the wastewater. Another proposed approach is to treat the dissociated fluoride ion with ion exchange resins or chelate resins. Although these proposed methods are effective for reducing the fluoride ion concentration in the wastewater to several milligrams per liter, the facility costs and treating costs are high. Therefore, at present, these methods must be used in combination with the chemical addition methods described above.

SUMMARY OF THE INVENTION

In view of the above circumstances, an object of the present invention is to provide a method for treating a wastewater containing fluoride ion, which method can be performed in inexpensive facilities and surely meets strict effluent standards.

As a result of extensive study in view of the above object, the inventors have found that the concentration of fluoride ion of a wastewater can be surely reduced to 8 mg/L or lower in inexpensive facilities without using expensive ion exchange resins and chelate resins by adding a calcium-containing compound to a wastewater containing fluoride ion, and then, adding a specific

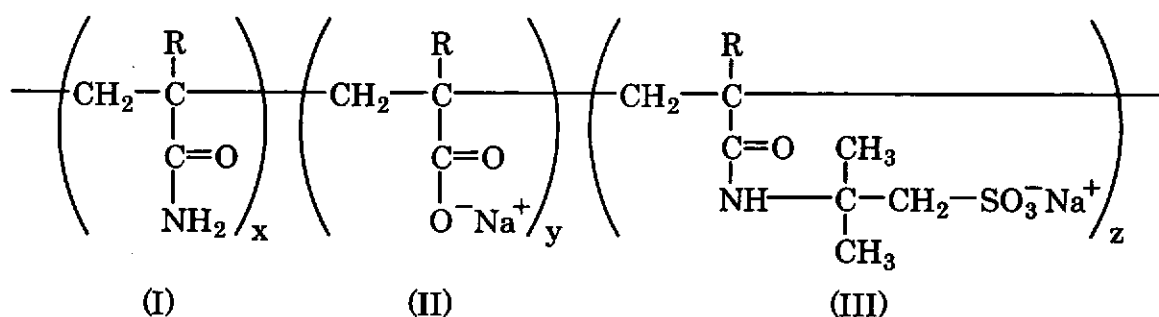
water-soluble polymer optionally together with a water-soluble organic polyelectrolyte having constitutional units derived from at least one organic acid selected from the group consisting of mannuronic acid, glucuronic acid and cellulose glycolic acid. The present invention has been accomplished on the basis of this finding.

Thus, the present invention provides a method for treating a wastewater containing fluoride ion, comprising:

adding a calcium-containing compound to the wastewater; and then

adding a water-soluble terpolymer comprising constitutional units

represented by the following formulas I, II and III:



wherein R is hydrogen or methyl, and x:y:z is 99.8:0.1:0.1 to 60:30:10.

In a preferred embodiment of the invention, a water-soluble organic polyelectrolyte having constitutional units derived from at least one organic acid selected from the group consisting of mannuronic acid, glucuronic acid and cellulose glycolic acid may be further added.

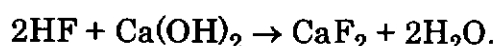
By treating a wastewater with a specific water-soluble polymer after treating fluoride ion with a calcium-containing compound, the concentration of fluoride ion in the wastewater is surely reduced to 8 mg/L or lower using facilities without using expensive ion exchange resins and chelate resins.

DETAILED DESCRIPTION OF THE INVENTION

In the method of the present invention, a wastewater containing fluoride ion is first treated by adding a calcium-containing compound. The treatment with the calcium-containing compound is conducted by known methods using

calcium chloride, calcium hydroxide, etc. The pH of the wastewater is adjusted to 7 or higher, more preferably 9 to about 14 by the addition of the calcium-containing compound. After the addition of the calcium-containing compound, the wastewater is preferably stirred at 15 to 35°C for 10 to 30 min to ensure the conversion of fluoride ion into calcium fluoride.

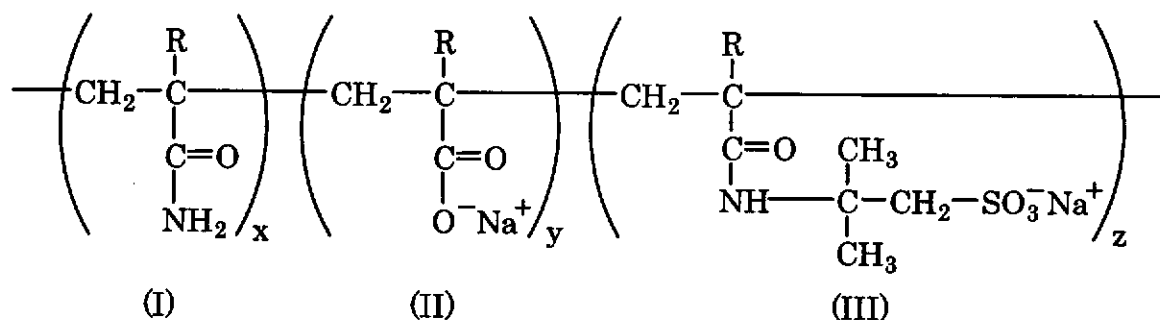
The amount of the calcium-containing compound to be added is preferably a stoichiometric equivalent amount or larger with respect to the amount of fluoride ion in the wastewater to be treated. For example, when the fluoride ion source is hydrofluoric acid, the stoichiometric equivalent amount of calcium hydroxide is calculated according to the following reaction formula:



The amount of the calcium-containing compound to be added is preferably 1 to 10 times the stoichiometric equivalent amount.

If a required amount of calcium is already present in the wastewater, the wastewater may be, in place of adding the calcium-containing compound, merely added with an alkali agent such as sodium hydroxide to adjust the pH to the range described above. Such a treatment of adding the alkali agent to the wastewater is one of the embodiments of the present invention. However, with only the treatment of adding an excessive amount of calcium-containing compound or the treatment by adjusting the pH with the alkali agent, it is difficult to reduce the concentration of fluoride ion to 8 mg/L or lower.

According to the present invention, the concentration of fluoride ion is reduced to 8 mg/L or lower by further treating the wastewater with the specific terpolymer represented by the following formula:



after the treatment with the calcium-containing compound.

In the above formula, R is hydrogen or methyl. As shown by the formula, the terpolymer is a water-soluble polymer comprising constitutional units (I) derived from acrylamide or methacrylamide, constitutional units (II) derived from acrylic acid or methacrylic acid and constitutional units (III) derived from 2-acrylamido-2-methylpropanesulfonic acid or 2-methacrylamido-2-methylpropanesulfonic acid. Letting the sum of the molar ratios of (I), (II) and (III) be 100, the molar ratio of the units, (I):(II):(III), is 99.8:0.1:0.1 to 60:30:10, preferably 98:1:1 to 80:15:5. If the molar ratio of the unit (II) exceeds 30, the fluorine treating performance of the terpolymer is lowered. Even if the molar ratio of the unit (III) exceeds 10, the fluorine treating performance of the terpolymer is no longer enhanced, rather resulting in increased production costs.

The terpolymer mentioned above has been already produced and marketed, and therefore, commercially easily available. The terpolymer may be produced by the methods described in JP 51-27228 B and JP 56-41285 B. Examples of the commercially available terpolymers include "Aron Flocc N-202", "Aron Flocc N-208", "Aron Flocc A-218" and "Aron Flocc A-268" all available from Toagosei Co., Ltd.

In the treatment of wastewater containing fluoride ion by adding calcium hydroxide, a polymer flocculant is generally used in addition to an inorganic flocculant such as aluminum sulfate to flocculate precipitated sludge for easiness of solid-liquid separation. The polymer flocculant usually used for this purpose is a copolymer comprising units derived from acrylamide or

methacrylamide and units derived from acrylic acid or methacrylic acid.

However, according to the inventors' experience, such a copolymer has no effect on treating fluorine, whereas, the terpolymer mentioned above is found to particularly enhance the fluorine treating performance.

5 The amount of the terpolymer to be added to the wastewater is 1 to 100 mg/L, preferably 1 to 20 mg/L. No additional effect is obtained even if the amount exceeds 100 mg/L to make the process less economical.

 When the terpolymer is used in combination with a water-soluble organic polyelectrolyte comprising constitutional units derived from at least
10 one organic acid selected from the group consisting of mannuronic acid, glucuronic acid and cellulose glycolic acid, the fluorine treating performance is surprisingly improved.

 Specific examples of the water-soluble organic polyelectrolyte include compounds produced by substituting sodium for the carboxyl hydrogen of
15 compounds comprising units derived from at least one organic acid selected from the group consisting of mannuronic acid, glucuronic acid and cellulose glycolic acid, i.e., sodium alginate and a sodium salt of carboxymethyl cellulose, with sodium alginate being preferred. Although sodium alginate and the sodium salt of carboxymethyl cellulose have been known as flocculating
20 assistants, functions thereof on the removal of fluoride ion from the wastewater are not known.

 The amount of the organic polyelectrolyte to be added to the wastewater is 1 to 100 mg/L, preferably 1 to 20 mg/L. No additional effect is obtained even if the amount exceeds 100 mg/L to make the process less economical.

25 The water-soluble polymer (terpolymer) is added to the wastewater treated with the calcium-containing compound either all at once or gradually in small portions. If the aluminum- or iron-based inorganic flocculant is optionally used, the water-soluble polymer may be added after or simultaneously with the addition of the inorganic flocculant. Alternatively, a

portion of the water-soluble polymer is first added to the wastewater treated with the calcium-containing compound, and then, the rest is added after or simultaneously with the addition of the inorganic flocculant.

The organic polyelectrolyte, if used in combination with the water-soluble polymer, may be added to the wastewater separately from the water-soluble polymer, i.e., either before or after the addition of the water-soluble polymer. Alternatively, the water-soluble polymer and the organic polyelectrolyte are mixed with each other prior to the addition, and then, the mixture is added to the wastewater treated with the calcium-containing compound. If the inorganic flocculant is optionally used, the mixture may be added after or simultaneously with the addition of the inorganic flocculant. Alternatively, a portion of the mixture is first added to the wastewater treated with the calcium-containing compound, and then, the rest is added after or simultaneously with the addition of the inorganic flocculant.

The weight ratio of the water-soluble polymer and the organic polyelectrolyte is preferably 1:5 to 1:0.2, more preferably 1:2 to 1:0.2 for either the separate addition or the simultaneous addition as a mixture.

The water-soluble polymer, the optional organic polyelectrolyte and the optional inorganic flocculant are added to the wastewater preferably at 15 to 35°C under stirring. After completing the addition, the wastewater is preferably stirred for 5 to 30 min at 15 to 35°C. After finishing the stirring, the wastewater is allowed to stand and the floc formed is removed by separation, thereby obtaining a treated wastewater having a concentration of fluoride ion of 8 mg/L or lower.

It has been confirmed that the concentration of fluoride ion in the wastewater is surely reduced to 8 mg/L or lower by the method described above. Thus, the concentration of fluoride ion in the wastewater is reduced to the intended level by the method of the present invention using inexpensive

facilities without using expensive ion exchange resins and chelate resins.

The concentration of fluoride ion of the wastewater is sufficiently reduced by the method of the present invention. If necessary, the wastewater treated by the method of the present invention may be further treated with a cationic organic polymer flocculant such as, but not limited thereto, copolymers of a quaternary compound of dimethylaminoethyl methacrylate or dimethylaminoethyl acrylate with acrylamide or methacrylamide, Mannich modified products of polyacrylamide or polymethacrylamide, and quaternary compounds thereof.

The present invention will be described in more detail by reference to the following examples, but it should be noted that the examples are not intended to limit the scope of the invention thereto.

EXAMPLES 1-4

A wastewater of pH 3.0 having a concentration of fluoride ion of 320 mg/L which was discharged from a semiconductor factory was treated. Into 150 mL of the wastewater, 2.5 equivalents (1550 mg/L) of calcium hydroxide with respect to fluoride ion were added under stirring, and the treatment was continued for 30 min. After adding aluminum sulfate in an amount of 200 mg/L (anhydride basis), each of the terpolymers having different ratios of constitutional units was added in an amount of 10 mg/L. The treatment was continued for 15 min. Thereafter, the treated wastewater was allowed to stand for 10 min. The supernatant was measured for the concentration of fluoride ion by a lanthanum-alizarin complexone absorption spectrophotometry according to JIS K0102. The terpolymers used were acrylic polymers in which R in the formula was hydrogen. The results are shown in Table 1.

Table 1

Terpolymer		Molar ratio of constitutional units (I):(II):(III)	Concentration of fluoride ion after treatment (mg/L)
Examples			
1	A	94.4:4.7:0.9	7.5
2	B	87.6:11.4:1.0	6.5
3	C	93.2:4.4:2.4	5.9
4	D	90.7:4.8:4.5	6.8

EXAMPLES 5-9

- The procedure of Example 1 was repeated to examine the effect of the combined use of the water-soluble polymer (terpolymer) and the water-soluble organic polyelectrolyte. As the water-soluble polymer, the terpolymer C was used. As the water-soluble organic polyelectrolyte, sodium alginate (block copolymer having a mannuronic acid/ glucuronic acid molar ratio of 1.5 or less) and sodium salt of carboxymethyl cellulose (esterification degree of 1.1) were used. The water-soluble polymer and the water-soluble organic polyelectrolyte were added at once after the addition of aluminum sulfate, or added in two portions after the addition of calcium hydroxide and after the addition of aluminum sulfate. The results are shown in Table 2.

Table 2

Examples	Amounts added after addition of calcium hydroxide (mg/L)		
	Terpolymer C	Sodium alginate	Sodium salt of carboxymethyl cellulose
5	—	—	—
6	—	—	—
7	5	5	—
8	5	—	5
9	5	5	—

Table 2 (contd.)

Examples	Amounts added after addition of aluminum sulfate (mg/L)			Concentration of fluoride ion after treatment (mg/L)
	Terpolymer C	Sodium alginate	Sodium salt of carboxymethyl cellulose	
5	10	10	—	3.0
6	10	—	10	4.6
7	5	5	—	1.9
8	5	—	5	4.6
9	5	—	—	2.5

COMPARATIVE EXAMPLES 1-3

The procedure of Example 1 was repeated except for omitting the use of the water-soluble polymer. In Comparative Example 2, a copolymer E (polymer flocculant) comprising 93.5 mol% of acrylamide units and 6.5 mol% of acrylic acid units was added after the addition of aluminum sulfate. In Comparative Example 3, the addition amounts of calcium hydroxide and aluminum sulfate were increased. The results are shown in Table 3.

Table 3

Comparative Examples	Calcium hydroxide (mg/L)	Aluminum sulfate (mg/L)	Copolymer E (mg/L)	Concentration of fluoride ion after treatment (mg/L)
1	1550	200	0	12.4
2	1550	200	10	12.0
3	3100	400	0	10.6

10

The results of Tables 1, 2 and 3 show that the concentration of fluoride ion of the wastewater is difficult to be reduced to 8 mg/L or lower by the known treatments using only calcium hydroxide, aluminum sulfate and optionally an acrylamide/acrylic acid copolymer, but, surely reduced to 8 mg/L or lower by the method of the present invention.

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EXAMPLES 10-13

The wastewater of pH 4.1 having a concentration of fluoride ion of 1140

mg/L which was discharged from a plating factory for the production of electronic parts was treated. Into 150 mL of the wastewater, 2.5 equivalents (5550 mg/L) of calcium hydroxide with respect to fluoride ion were added under stirring, and the treatment was continued for 30 min. After adding the

5 terpolymer B (Example 10) or adding the terpolymer B and sodium alginate used in Example 5 (Examples 11–13), the treatment was continued for 15 min. Thereafter, the treated wastewater was allowed to stand for 10 min. The supernatant was measured for the concentration of fluoride ion by ion chromatography. The results are shown in Table 4.

10 COMPARATIVE EXAMPLES 4–5

The procedure of Examples 10–13 was repeated by omitting the use of the terpolymer B and sodium alginate or by using only the copolymer E used in Comparative Example 2 in place of the terpolymer B and sodium alginate. The results are shown in Table 4.

15

Table 4

	Terpolymer B (mg/L)	Sodium alginate (mg/L)	Copolymer E (mg/L)	Concentration of fluoride ion after treatment (mg/L)
Examples				
10	10	0	0	7.4
11	5	5	0	4.0
12	5	10	0	3.3
13	10	5	0	3.8
Comparative Examples				
4	0	0	0	11.0
5	0	0	10	11.2

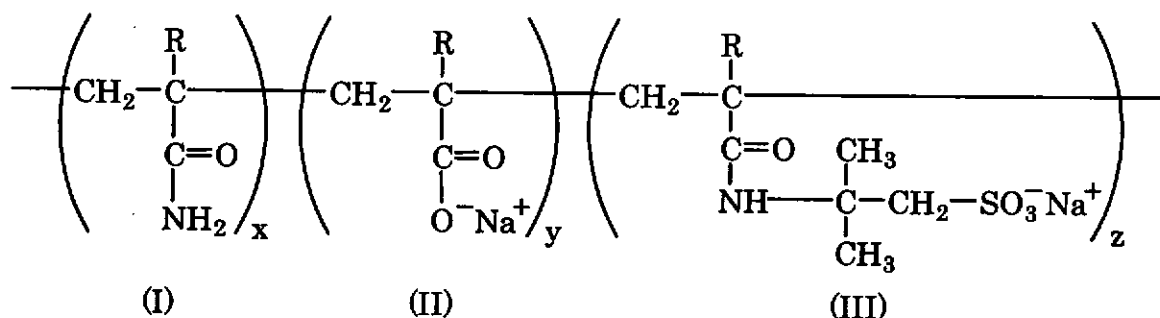
The results of Table 4 show that the concentration of fluoride ion is reduced to 8 mg/L or lower by the treating method of the present invention without adding aluminum sulfate after the treatment with calcium hydroxide.

WHAT IS CLAIMED IS:

1. A method for treating a wastewater containing fluoride ion, comprising:

adding a calcium-containing compound to the wastewater; and then

5 adding a water-soluble terpolymer comprising constitutional units represented by the following formulas I, II and III:



wherein R is hydrogen or methyl, and x:y:z is 99.8:0.1:0.1 to 60:30:10.

2. The method according to claim 1, wherein the amount of the
10 calcium-containing compound added to the wastewater is a stoichiometric equivalent amount with respect to the amount of fluoride ion or larger.

3. The method according to claim 1 or 2, wherein the amount of the water-soluble terpolymer added to the wastewater is 1 to 100 mg/L.

4. The method according to claim 1 or 2, wherein a water-soluble
15 organic polyelectrolyte comprising constitutional units derived from at least one organic acid selected from the group consisting of mannuronic acid, glucuronic acid and cellulose glycolic acid is added to the wastewater after adding the calcium-containing compound.

5. The method according to claim 4, wherein the amount of the
20 water-soluble organic polyelectrolyte added to the wastewater is 1 to 100 mg/L.

6. The method according to claim 4 or 5, wherein the weight ratio of the water-soluble terpolymer and the water-soluble organic polyelectrolyte is 1:5 to 1:0.2.

7. The method according to claim 1 or 2, wherein a concentration of
25 fluoride ion after the treatment is 8 mg/L or lower.