

PROCESS FOR REMOVING SOLID PARTICLES, ESPECIALLY
SILICIA AND/OR ALUMINA PARTICLES, FROM AQUEOUS
EFFLUENTS

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The present invention relates to the treatment of effluents, in particular those coming from the microelectronics industry, for the purpose of discharging them or recycling them in another industrial process.

More specifically, the present invention relates to the removal of solid particles, particularly silica and/or alumina particles, contained in such effluents.

10 The use of silica or alumina suspensions for the polishing of silicon wafers in the microelectronics industry is becoming widespread.

It is necessary to treat the resulting effluents so as to be able to discharge them without polluting the environment or else to reuse them in other industrial processes.

To do this, the microelectronics industry is presently equipped with neutralization stations and, in some cases, with settling tanks.

20 Nevertheless, the suspensions that have to be treated pose problems associated with their physicochemical characteristics which contribute to make them easily solidifiable.

Thus, the formation of deposits is observed in 25 the neutralization tanks and the settling tanks, which deposits have to be removed periodically, which means that this equipment has to be taken out of service.

More specifically, the treatment systems used hitherto comprise ultrafiltration and the use of a 30 filter press.

Ultrafiltration is effective essentially for suspensions containing a small amount of solid particles. This is because when the concentration of solid particles becomes high, the filters very quickly 35 clog up. The maintenance cost of the plants is thus very high, something which constitutes a major drawback with this technique.

Furthermore, because of the need to clean the filters periodically, this treatment can only be carried out intermittently.

Moreover, some of the effluents recovered after the ultrafiltration are enriched with solid particles and require yet another treatment before discharge. The treatment of this concentrate from the ultrafiltration is usually carried out in a filter press or possibly by centrifuging.

Filter presses have the drawback that their operating process is intermittent and requires a systematic cleaning operation.

One objective of the present invention is to provide a process for purifying aqueous suspensions containing solid particles, particularly silica and/or alumina particles, to an acceptable degree in order to allow them to be discharged without polluting the environment or to allow them to be recycled and which process does not have the aforementioned drawbacks.

Another objective of the invention is to provide a simple process which can be carried out at a lower cost.

Yet another objective of the invention is to provide such a process which can be carried out continuously.

These objectives, as well as others, are achieved with the aid of a process for the separation of solid particles, especially silica and/or alumina particles, in suspension in an aqueous effluent, characterized in that it comprises the steps consisting in:

- adding powdered lime to the aqueous suspension of solid particles;
- adding a polymer-type flocculant to the aqueous suspension treated with the lime;
- separating the agglomerated solid particles from the aqueous phase by centrifuging;

- recovering the separated liquid resulting from the centrifuging in order to produce a purified effluent;

- discharging the solid particles separated by the centrifuging.

According to other characteristics of the invention:

- the purified effluent coming from the centrifuging may be neutralized;

- the purified effluent, possibly neutralized, may be subjected to additional purification by ultrafiltration.

The present invention also relates to a plant for carrying out the aforementioned process, characterized in that it comprises:

- a tank for receiving the aqueous suspension of solids to be treated, fitted with stirring means;

- a tank of lime;

- means for feeding the lime into the aqueous suspension;

- a tank containing a polymer flocculant;

- means for feeding the flocculant into the aqueous suspension treated with the lime;

- a centrifuge;

- means for feeding the aqueous suspension treated with the lime and with the flocculant into the centrifuge;

- a tank for recovering the separated liquid;

- means for recovering the solids separated by the centrifuge.

According to other characteristics of the invention, the plan furthermore comprises:

- a station for the dilution and maturation of the polymer flocculant, which station is connected to the tank containing this flocculant;

- a neutralization tank and means for feeding the neutralization solution into the separated liquid coming from the centrifuging;

- an ultrafiltration system and means for feeding the separated liquid into the said ultrafiltration system.

5 The inventors have shown, unexpectedly, that it is possible to purify, to a satisfactory degree, effluents in the form of an aqueous suspension of solid particles, of the type coming from the microelectronics industry, by centrifuging when the said effluents are pretreated with lime and then with a polymer
10 flocculant.

Thus, they have demonstrated that it is possible to dispense with the use of a filter press and to carry out a continuous operation to purify effluents containing a relatively large amount of solid
15 particles.

The present invention will now be described in greater detail with reference to the appended single figure which illustrates, schematically, the process according to the invention and the main elements of a
20 plant for carrying out this process.

The aqueous suspension treated according to the invention is of the type coming from the microelectronics industry and contains solid particles, such as silica and alumina particles.

25 Such a suspension generally contains from 0.1% to 10% by weight of solid particles.

Referring to Figure 1, the aqueous suspension
12 to be purified according to the process of the invention is contained in a tank 2 fitted with stirring
30 means 11.

In a first step, lime 13 contained in a tank 3 is added to the stirred aqueous suspension 12 via the pipe 23.

35 Preferably, powdered lime is added in an amount from 0.1 to 50 g/l, more preferably 2 g/l, of suspension.

The solid particles in the resulting suspension 22 are observed to coagulate.

The volume of lime is adjusted with respect to the volume of treated effluent in order to promote coagulation without adding an excessively large amount of solid matter into the said effluent or reaching too high a pH, which would be deleterious to the subsequent treatment or recycling.

In a second step, this suspension 22, which is transferred with the aid of a positive-displacement pump 5, is mixed with a flocculant 14 contained in a tank 4 and transferred via the pipe 24 with the aid of the positive-displacement pump 6. The mixing occurs in the pipe 25 which extends from the outlet of the pump 5 to the inlet of the centrifuge.

The flocculant used according to the invention comprises a polymer or blend of polymers of cationic, nonionic or anionic, more preferably cationic, polyacrylamide type.

As representative examples of these polymers, mention may be made of those sold under the reference EM640TRM (a strongly cationic polyacrylamide polymer, as an emulsion containing 40% active substance) or AN905SH (a weakly cationic polyacrylamide polymer as a powder consisting 100% of active substance) by the company Floerger, preferably the EM640TRM emulsion polymer.

The plant according to the invention furthermore comprises means 15 for the dilution and preparation ("maturation") of the flocculant. The polymer, in powder or emulsion form, is diluted in the water therein, until the desired flocculant concentration is obtained, in order thereafter to be transferred into the tank 4 and then added to the suspension pretreated with the lime.

The concentration of active flocculant after preparation is generally between 0.1 and 50 g/l, preferably 2 g/l.

The amount of flocculant added with respect to the treated suspension is between 10 g and 50 kg/tonne of dry matter (TDM), preferably between 1 and 5 kg/TDM.

The suspension resulting from this flocculation step is then introduced into a centrifuge 7 via the pipe 25. An in-line centrifuge of conventional type may be used.

5 A centrifuging operation to separate the solid matter is carried out at a speed generally of between 2000 and 7000 rpm, preferably at a nominal speed of the order of 4000 rpm.

10 After the centrifuging step, the sediments 26 are recovered in the form of a quite sticky white paste which generally has a solids content of the order of 25% to 30%. This solid matter is discharged.

15 The separated, thus clarified, liquid 18 is taken from the outlet of the centrifuge 7 via the pipe 27 into a tank 8.

The total suspended matter (TSM) in this liquid is of the order 10 to 20 mg/l.

20 The separated liquid 18 has a pH of about 11 and can then either be discharged into the effluent treatment station, like any basic effluent, or recycled in other industrial processes, especially, after neutralization, as cooling water, or as ultra-pure water in the feed loop for the CMP (Chemical Mechanical Planarization) process after treatment in a suitable
25 plant.

The figure illustrates the case in which the purified effluent recovered at the outlet of the centrifuge is neutralized in order to be recycled in another industrial process.

30 To do this, a neutralizing solution 19 contained in a tank 9 is used, this neutralizing solution being introduced into the separated liquid 18 via the pipe 29 with the aid of the positive-displacement pump 10.

35 The neutralizing solution may consist of a hydrochloric acid solution defined according to the effluent to be treated and the required final pH.

Depending on the situation, if it is desired to purify the resulting effluent 28 further, it may be

treated in an ultrafiltration system 20 into which it is fed with the aid of a pump 21.

This ultrafiltration system is of a conventional type. Its essential characteristics are recalled below.

The fluid to be filtered flows parallel to the filter element, consisting of an inorganic porous membrane or of an organic polymer of known type. It is subjected to pressure which results in part of the liquid passing through the membrane. The particles are retained in the solution in which their concentration gradually increases. Recovered from the ultrafiltration module is thus a clarified liquid, constituting the permeate, and a liquid enriched with particles, constituting the concentrate.

The concentrate 31 is reinjected upstream, either into the tank 8 or into the tank 2, and the permeate 30 (the aqueous phase of the purified suspension) is discharged or recycled, as indicated above.

The process according to the invention allows effluents having a relatively high content of suspended solid particles to be effectively treated, continuously, and it avoids high plant maintenance costs.

The invention is illustrated below with the aid of the following examples:

EXAMPLES

An effluent consisting of an aqueous suspension of solid silica particles with a concentration of 1.2% is treated by adding 1.8 g of lime per litre of suspension. This coagulation allows small flocs to form.

Added to the resulting solution is a flocculant obtained by diluting, down to 1 g/l of the polymer sold under the reference EM640TRM by the company Floerger, an emulsion containing 40% active substance.

This suspension is centrifuged in a Guinard D1LC20 centrifuge at a speed of 4500 rpm.

Five different trials were carried out, varying the volume of the suspension pretreated with the lime, the volume of flocculant and the bowl/screw relative speed of the centrifuge.

- 5 The speed of rotation of the bowl and the liquid annulus height on the bowl were fixed at 4500 rpm and 110 mm, respectively.

The results are given in the table below:

Trial	1	2	3	4	5
Volume of the treated effluent (l/h)	600	600	720	720	720
Bowl/screw relative speed (rpm)	13	5.7	7.2	4.6	5.2
Flocculant volume (l/h)	62	62	62	100	40
Dry content of the sediment (%)	24	29	23	26	27
Solids content of the separated liquid (mg/l)	21	22	12	22	

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A low relative speed favours a high dry content of the sediments.



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CLAIMS

1. Process for the separation of solid particles, especially silica and/or alumina particles, in suspension in an aqueous effluent (12), characterized in that it comprises the steps consisting in:
 - adding powdered lime (13) to the aqueous suspension of solid particles;
 - adding a polymer-type flocculant (14) to the aqueous suspension treated with the lime;
 - separating the agglomerated solid particles from the aqueous phase by centrifuging;
 - recovering the separated liquid (18) resulting from the centrifuging in order to produce a purified effluent;
 - discharging the solid particles separated by the centrifuging.
2. Process according to Claim 1 characterized in that the separated liquid (18) coming from the centrifuging is neutralized in order to produce a neutralized purified effluent (28).
3. Process according to Claim 1 or 2, characterized in that the purified effluent (28) is subjected to an additional treatment by ultrafiltration (20).
4. Process according to any one of the preceding claims, characterized in that the aqueous suspension (12) contains from 0.1 to 10% by weight of solid particles.
5. Process according to any one of the preceding claims, characterized in that the powdered lime (13) is added in an amount from 0.1 to 50 g/l, preferably 2 g/l, of suspension.
6. Process according to any one of the preceding claims, characterized in that the flocculant (14) comprises a polymer or blend of polymers of cationic, nonionic or anionic, preferably cationic, polyacrylamide type.



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7. Process according to Claim 6, characterized in that the flocculant is obtained by dilution, starting from an emulsion in water containing 40% active substance, or from a powder consisting 100% of active powder, preferably from an emulsion.
8. Process according to either of Claims 6 and 7, characterized in that the concentration of active flocculant is between 0.1 and 50 g/l and is preferably 2 g/l.
9. Process according to any one of Claims 6 to 8, characterized in that the amount of flocculant added to the treated suspension is between 10 g/TDM and 50 kg/TDM, preferably between 1 kg/TDM and 5 kg/TDM.
10. Process according to any one of the preceding claims, characterized in that the centrifuging to separate the solid matter (26) in the centrifuge (7) is carried out at a speed of between 2000 and 7000 rpm, preferably 4500 rpm.
11. Plant for carrying out the process according to any one of Claims 1 to 10, characterized in that it comprises:
- a tank (2) for receiving the aqueous suspension of solids (12) to be treated, fitted with stirring means (11);
 - a tank (3) of lime (13);
 - means (23) for feeding the lime (13) into the aqueous suspension (12);
 - a tank (4) containing a polymer flocculant (14);
 - means (24; 6) for feeding the flocculant (14) into the aqueous suspension (12) treated with the lime;
 - a centrifuge (7);
 - means (5; 25) for feeding the aqueous suspension treated with the lime and with the flocculant into the centrifuge (7);
 - a tank (8) for recovering the separated liquid (18); and
 - means for recovering the solids (26) separated by the centrifuge.



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12. Plant according to Claim 11, characterized in that it comprises a station for the dilution and maturation of the polymer flocculant, which station is connected to the tank (1) containing this flocculant.
- 5 13. Plant according to Claim 11 or 12, characterized in that it furthermore comprises:
- a tank (9) of neutralization solution (19);
 - means (29; 10) for feeding the neutralization solution (19) into the separated liquid (18) coming
- 10 from the centrifuging.
14. Plant according to any one of Claims 11 to 13, characterized in that it furthermore comprises an ultrafiltration system (20) and means (28, 21) for feeding the separated liquid (18) into the said.
- 15 ultrafiltration system (20).