PROCESS FOR SEPARATING AND RECOVERING THE SUSPENDING FLUIDS CONTAINED IN EXHAUSTED SLURRIES FROM THE MACHINING OF SILICON

A process for the complete separation of the suspending fluid from the solid components contained in an exhausted slurry, either abrasive or not, coming from the cutting operation or other mechanical working of materials of monocrystalline or polycrystalline silicon, or of quartz or other ceramic materials, or contained in the sludge obtained from a previous centrifugation of such exhausted suspension. The process involves the immediate separation of all the solid components contained in the slurry through one or more stages, in counter-current, of extraction of the suspending fluid with a suitable solvent or mixture of solvents, followed by sedimentation of the suspension diluted with the solvent, and by recovery by overflow of the surnatant, consisting of the mixture of suspending fluid and solvent. The residual phase left from the last recovery by overflow undergoes a final separation by filtration of all the solids present, while from the mixture of suspending fluid and solvent obtained from the first recovery by overflow the suspending fluid is recovered by distillation.
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— with international search report
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FLUIDS CONTAINED IN EXHAUSTED SLURRIES FROM THE MACHINING
OF SILICON

The present invention concerns a process for separating and recovering the suspending fluids contained in exhausted slurries from the machining of silicon. More specifically, the invention concerns a process, with the necessary equipment for implementing it, for the complete separation of the suspending fluid from the solid components contained in an exhausted suspension, either abrasive or not, coming from the cutting operation or other mechanical working of materials of monocrystalline or polycrystalline silicon, or of quartz or other ceramic materials, or contained in the sludge as obtained, for instance, from a previous centrifugation of such exhausted suspension.

As is known, in the production of components for applications in the electronic field and in the field of photovoltaic energy thin silicon slices of either circular shape ("wafers") or square shape are used, which are obtained by cutting monocrystalline silicon ingots (semiconductors) or polycrystalline silicon "bricks" (solar applications) perpendicularly to their axis.

Typically, this "slicing" operation is carried out by means of wire saws or cutters in which a metal wire of considerable length and suitable mechanical resistance, wound in a system of rollers and spools, is contacted while moving with the ingot, perpendicularly to the ingot length, at the points where the cut is to be made. At the same time, a slurry containing abrasive grains or particles (abrasive slurry) is fed to the contact area between the cutter wire and the ingot or "brick".

The conventional abrasive slurries used for cutting silicon, quartz or other ceramic materials with a wire saw consist of a suspending, lubricant or cooling fluid, such as a mineral oil or water-soluble organic liquids of high molecular weight - in particular, polyethylene glycol, PEG - in which abrasive particles of suitable hardness, generally of silicon carbide (SiC), are suspended.
Other abrasive suspensions, prepared using abrasives different from silicon carbide, such as alumina (Al$_2$O$_3$), are used in other silicon machining operations different from cutting, such as lapping or the final thickness reduction of the slices, known as "back lapping". Such operations are carried out after cutting by means of lapping machines, essentially consisting of two perfectly flat and round horizontal cast-iron plates, that are able to overlap and rotate in opposite directions to one another. The silicon slices coming from the cutting operation are placed between these plates and the slurry of abrasive particles is fed therein. The slurry normally consists of a mixture of suspending fluid, proper abrasive - typically made of alumina - and a commercial suspending additive.

During the machining operations described above, namely cutting, lapping and back lapping, part of the abrasive grains lose their characteristics useful for the functioning of the process and, at the same time, the abrasive slurry becomes enriched with fine silicon particulate, coming from the silicon ingot or form the silicon slices, and also with fine iron particulate, coming from the cutter wire or from the lapping machine plates.

As the amount of fine particulate increases, the abrasive slurry loses its mechanical characteristics; the efficiency of the slicing operation and the product quality decrease, to the extent that the slurry becomes ineffective and must be discarded and replaced with fresh abrasive slurry. The exhausted slurry is sent to recovery of the reusable components, namely the abrasive grains having size above a given threshold and the suspending fluid used in the slurry itself. The latter (be it based on mineral oil or on organic liquids such as PEG), if efficiently purified from the suspended fine particles of metal residues and of silicon, as well as from the non-reusable abrasive grains, would be perfectly reusable in the process because it keeps its own characteristics unaltered in the course of the process.

The conventional approach to this recovery is to first separate the suspending liquid from the solids contained therein by filtration or by centrifugation, and then recover the abrasive grains that maintained a minimum size necessary to the cutting operation. However, the high viscosity of the ex-
hausted suspensions and the presence of fine particles of silicon, abrasive and iron makes the filtration very difficult, and sometimes impossible, to carry out in a cheap way, specially in the case of oil-based slurries. On the other hand, the alternative operation consisting of centrifugation only allows to obtain some thickened products (commonly referred to as "sludge"), that still contain, however, a significant amount of suspending liquid.

Considering in more detail the suspending fluids and the solids present in exhausted abrasive slurries, the suspending fluids used for machining silicon for electronic and photovoltaic applications are oil-based, or PEG-based (where PEG has different molecular weights). The oils used as suspending agents may be mineral oils with linear chains $\text{C}_10 - \text{C}_2 \text{Aor}$ synthetic oils with aromatic chains $\text{C}_1\text{B} - \text{C}_26$, to which small amounts of additives are added, these additives being specific for each application and having a proprietary formulation, which is unknown at the moment of treating the slurry for the recovery and the separation of the suspending agent from the fines. These additives, in combination with the abrasive fines and the fines of silicon and other metals, may render the direct filtration not applicable or, at least, very difficult.

The powders representing the solid part of the exhausted slurries mentioned above typically consist of the following components:

- silicon carbide (SiC) or other abrasives, such as for instance diamond or alumina (Al$_2$O$_3$), with grain size above 5 $\mu$m, reusable as abrasive in the machining operations on the slices or the ingots of monocrystalline or polycrystalline silicon;
- silicon carbide (SiC) or other abrasives, referred to as fines, having grain size below 5 $\mu$m, which are not reusable as abrasives in the machining operations cited above;
- silicon wastes (Si), coming from the machining of silicon ingots, typically having size below 5 $\mu$m;
- iron wastes (Fe), coming from the tool used (cutting wire or lapping plates) in silicon machining, having size typically lower than 5 $\mu$m.

The patent literature concerning the treatment of abrasive slurries
coming from machining operations on the silicon slices has already proposed several techniques, which, however, are all mainly aimed at the separation by size and by chemical nature of the solids present in the exhausted slurry, besides the recovery of the liquid component. Substantially for this reason, as it may be observed, all processes used turn out to be rather complex.

Both in the case of oil-based abrasive slurries and in the case of slurries based on a water-soluble organic liquid, the proposed techniques variously combine the following basic operations:

a) preliminarily reducing the viscosity of the exhausted slurry, in particular by dilution with a solvent or by heating, in order to be able to treat it in the further operations;

b) separating the recoverable abrasive grains by wet size-sorting, such as by centrifugation or by passing the slurry through a hydrocyclone (a static separator of solid particles entrained by a liquid, which exploits the action of centrifugal force);

c) separating the recoverable abrasive grains by treating the exhausted slurry with a solvent miscible with the basic suspending fluid of the slurry;

d) filtering the liquid phases resulting from abrasive grain separation;

e) distilling the liquid mixtures of solvent and cooling fluid making up the filtrate;

f) drying the reusable abrasive grains.

The technologies used up to date, as it will be clear in the following with reference to some examples of prior art solutions, all have the two coexisting primary objects mentioned below, and are always carried out starting from exhausted slurries, rather than from their thickened products:

1. separating that part of abrasive that is still reusable from the part of abrasive that is no more reusable and from the working wastes such as silicon and metals;

2. recovery of the suspending fluid, as well as of the solvent used to reduce the viscosity of the exhausted slurry or for separating the recoverable abrasive.
The European patent application EP-A-786317 (Shin-Etsu Handotai Co.) describes a system for reusing an exhausted abrasive slurry of the oil-based type wherein water is first added to the exhausted slurry in order to reduce its viscosity, and then the resulting mixture is fed to a hydrocyclone to separate the reusable abrasive grains. As is known, in a hydrocyclone the feed to be treated is fed from the top at high speed and tangentially into the apparatus, so that the centrifugal force pushes the heavier particles towards the outer walls the container. Moving in a spiral manner, the heavier particles are then collected in the container's conical bottom (underflow), while the clarified liquid comes out at the top from a central duct (overflow). In the solution proposed in the aforesaid document, the hydrocyclone overflow, that contains the oily suspending fluid, water and all those solid particles that have not been sorted out by passing through the hydrocyclone, is then fractioned into three phases by centrifugation. This operation yields an oily phase that is reused in the cutting process, the water that is reused in the preliminary exhausted slurry dilution phase, and a residue suspension containing the solids to be discarded, that is sent to the waste treatment plant.

The unwanted fine powders tend to build up in the abrasive slurry as it is recovered and reused according to the teachings of the aforesaid document. The same applies for the oily slurry recovered from the centrifugation operation, which inevitably contains traces of fine solid particles that return to the cutting process and accumulate in the system.

A process that uses solvents in great amounts, but with procedures and objects that are different from the process of the present invention is described in the international patent application No. WO 01/43933 (Fraunhofer-Gesellschaft zur Forderung der angewandten Forschung e.V.), concerning a method meant to be an improvement of the previously described one. The operational stages are virtually the same as the ones described in document EP-A-786317, but the auxiliary process fluid that is added in the preliminary phase in order to reduce the viscosity of the exhausted slurry (which was water in the previous case of oil-based abrasive slurry) is selected in this case so that it is miscible with the suspending liquid of the abrasive slurry. There-
fore, in the case of oil-based abrasive slurries, the diluting fluid is selected from among the lipophilic solvents (such as n-hexane or n-heptane), while in the case of water soluble-based slurries amphiphilic solvents are used (such as acetone).

Since in this case the liquid added is miscible with the suspending fluid, the suspension obtained after separating the reusable abrasive grains must be treated by distillation, after the necessary filtering of the suspended fine solids, in order to recover the suspending fluid and the solvent. In this way, however, as the distillation separates the lower-boiling component, i.e. the solvent. The fines left in the suspension after the separation of the recoverable abrasive remain in the recovered suspending fluid and when the latter is reused they gradually build up.

The European patent EP 0791385 (Shin-Etsu Handotai Co. et al.) describes a method for the separation and reuse of exhausted abrasive slurries similar to the two methods described above, but mainly intended for use in the case of water soluble-based slurries. Here, too, the first operation consists of diluting with water the suspension to be treated, in order to reduce its viscosity. Then, the mixture is treated by wet size-sorting to separate the reusable abrasive grains; here, too, the preferred apparatus is a hydrocyclone.

The part of the process that differs most from the aforesaid two systems concerns the recovery and separation treatment of the liquid suspension obtained from the overflow of the hydrocyclone. A coagulating agent is added to this liquid suspension in order to favor the separation of suspended solids, and then the whole lot undergoes distillation, from which water is recovered, as the lightest fraction, which is reused for the initial dilution of the exhausted slurry.

The mixture of water-soluble slurry, suspended solids and coagulant undergoes solid-liquid separation treatment, preferably by centrifugation, to obtain, on the one hand, a solid residue to be discarded and, on the other, the water-soluble slurry. This can be reused in the cutting process after further treatments, among which the addition of a dispersion agent to adjust the viscosity of the slurry.
As regards the purity of the recovered suspending fluid, that is fed back into the cutting process, the same considerations made for the two previous processes mentioned above are applicable also in this case.

The US patent No. 6,010,010 (Elektroschmelzwerk Kempten) proposes a treatment of exhausted abrasive slurries with a recovery scheme completely different from the processes considered so far. In this case, in the first phase the whole solid component is dried, such as via evaporation under vacuum or by spray-drying, which involves heating the exhausted slurry to some extent. The evaporated liquid, largely consisting of the suspending fluid of the abrasive slurry, is condensed and can be reused in the cutting process.

The technological proposal of totally drying the solids suspended in the exhausted slurry, cyclically evaporating and recondensing the suspending fluid, exposes the suspending liquid to heat stresses that can favor its degradation. If the suspending liquid is oil, the structure of the condensate may be different from the one of new oil, while if the liquid is polyethylene glycol (PEG), the process would not work since PEG, having a high molecular weight, cannot be evaporated without damaging its structure because of the high temperature necessary for evaporation.

The European patent EP 0968801 (MEMC Electronic Materials and Garbo Servizi) describes a method aimed at regenerating an exhausted abrasive slurry of the water soluble-based type, wherein the exhausted abrasive is firstly heated to reduce its viscosity and then subjected to an initial separation by filtering. This yields a clarified liquid largely composed of cutting fluid with traces of fine powders, and an agglomerate of wet powders containing, along with a small quantity of cutting liquid, almost all the solids suspended in the exhausted slurry. The wet powders are then diluted with water and separated using a hydrocyclone, which produces a fraction of grains of larger size (underflow) and an "overflow" fraction composed of the fine particles suspended in water, mixed with a smaller amount of suspending fluid. The "overflow" fraction from the top of the hydrocyclone is filtered, recovering the aqueous flow that serves to dilute the wet powders before the hydrocyclone separation process.
The European patent EP 0968801 (MEMC Electronic Materials and Garbo Servizi) describes a method aimed at regenerating an exhausted abrasive slurry of the water soluble-based type, wherein the exhausted abrasive is firstly heated to reduce its viscosity and then subjected to an initial separation by filtering. This yields a clarified liquid largely composed of cutting fluid with traces of fine powders, and an agglomerate of wet powders containing, along with a small quantity of cutting liquid, almost all the solids suspended in the exhausted slurry. The wet powders are then diluted with water and separated using a hydrocyclone, which produces a fraction of grains of larger size (underflow) essentially containing the reusable abrasive grains, and an "overflow" fraction composed of the fine particles (non-reusable abrasive, silicon powder and metal powders) suspended in water, mixed with a smaller amount of suspending fluid. The fraction containing the abrasive grains is oven dried, while the overflow fraction from the top of the hydrocyclone is filtered, recovering the aqueous flow that serves to dilute the wet powders before the hydrocyclone separation process and obtaining a solid residue essentially composed of silicon powder and metals.

The suspending liquid, which is recovered from the first filtering of the hot exhausted slurry, is freed from further traces of powders by means of a further filtering operation, after which it is sent to the cutting process.

A non-negligible drawback in the process under examination, besides the need to heat the exhausted slurry beforehand in order to reduce its viscosity, is the need to add considerable amounts of water to the wet powders obtained from the first filtering in order to carry out the separation process in the hydrocyclone. Further, it must also be noted that a smaller amount of cutting fluid is lost because it is left in the solid after the first filtering, thus reducing the yield of recovery of the suspending fluid.

Another proposed process for treating exhausted abrasive slurries that have a water soluble liquid base (specifically, polyethylene glycol, PEG) is described in international patent application No. WO 02/096611 (MEMC Electronic Materials and Garbo Servizi), wherein the exhausted slurry is first divided into a solid fraction and a liquid fraction (the suspending fluid) not com-
pletely devoid of solids, by means of filtering. The filtration cake, which contains a residual amount of suspending liquid, is washed in water and then treated with a sodium hydroxide solution in order to effect the dissolution of the silicon fine particulates and eliminate them. The filtrate obtained from the aforesaid operation is then treated with an acid leaching agent in order to effect the dissolution of the metal powders and eliminate them, thus obtaining from the subsequent washing of the solid fraction a mixture of only grains of reusable and non-reusable abrasive material. The yield of recovery of the suspending agent is negatively affected by the loss of a part of suspending agent in the first filtration.

Finally, also the international patent application publ. No. WO2006/137098 (SiC Holding GmbH) concerns a process intended to recover all the reusable components of an exhausted abrasive slurry; in particular, not only the PEG-based suspending fluid is recovered, but also the abrasive silicon carbide grains of suitable size, while the silicon and iron fines are disposed of. The process described involves a first solid-liquid separation by centrifugation, from which the thickened fraction is sent to a section for recovery of the abrasive grains comprising a battery of hydrocyclones connected in series and a subsequent apparatus for filtering and chemically treating the grains, while the liquid fraction, containing most of the fines and the suspending fluid, is treated in a section for the recovery of the latter. Such recovery is carried out, according to one of the solutions proposed, through subsequent operations of filtration, addition of alkaline solutions to the clarified solution, microfiltration, neutralization of the clarified liquid obtained, distillation of the minor amount of water that is added to the process, filtration and recovery of anhydrous PEG for reuse. The alternative solution proposed in the same document for the recovery of the suspending agent involves, instead of the treatment with alkaline solutions and of the subsequent neutralization, a treatment on cationic resins, followed by a treatment on anionic resins.

The process described is aimed at integrally recovering all of the reusable components of the exhausted slurry, and for this very reason it appears to be quite complex from the point of view of the equipment necessary.
In general, with respect to the object consisting in recovering the suspending fluid, all the prior art processes examined above suffer, in a more or less marked manner, from several drawbacks, including the following:

- low recovery yields of the slurry components, in particular the suspending fluid;
- complexity of the process or an exceedingly high number of operations required, or else long times necessary for the treatment;
- high consumption of solvent to be added for the separation.

In the light of the foregoing, an object of the present invention is to provide a process for the treatment of exhausted slurries from the machining of silicon, or from other similar working procedures on quartz or ceramic materials, which allows to recover in a cheap and flexible way the suspending liquid contained in the slurry in order to reuse it in the preparation of a fresh slurry. Such a process may represent a simple and convenient alternative to the complex processes for separating the suspending fluid already described. The process should be advantageously applicable to the exhausted slurries, either abrasive or not, and also to the centrifugates or thickened products (i.e., sludge) obtained from the said slurries, namely to those products derived from a pre-treatment phase, in which there are still present, typically, significant amounts of suspending fluid, for instance up to as much as 40%.

In the frame of the preliminary studies connected with the present invention, it has been observed that a scanning election microscope (SEM) examination of the solids contained in the exhausted slurries coming from the machining of silicon confirms the presence of small silicon particles, having a diameter typically below 1-2 µm, that surround the bigger particles of abrasive, such as silicon carbide, when the latter is present, having diameters comprised between 3 and 40 µm.

The particles with greater diameter, thus, essentially consist of silicon carbide, with prismatic shape and diameter above 5 µm; further, the presence of particles agglomerates is sometimes noted. By comparison, the silicon particles have a much more spherical shape and give rise to agglomerates
having size comprised between 2 and 5 µm.

It has also been observed that when a suspension, e.g. an oil-based suspension, containing a mixture of the solids cited above, is treated with a solvent miscible with the oil itself, a new suspension is obtained, more diluted in terms of solids content and having a viscosity detectably lower than the starting value. This viscosity varies as a function of the solvent used and of the dilution ratio of suspending fluid to solvent. When this diluted suspension is left to freely settle (free settling) the equilibrium speed of the particles settling (terminal velocity) is given by the Stokes law. The latter is valid for Reynolds numbers < 0.1 (which is the present case, since the liquid during the settling has a speed equal to zero):

\[ u_t = \frac{K D^2 (P_s - P) g}{18 \mu} \]

wherein \( u_t \) is the terminal velocity, \( D \) is the diameter of the solid particle precipitating during settling, \( P_s \) and \( P \) are respectively the density of the solid and that of the liquid (in this case the density of the mixture oil/PEG/solvent, \( g \) is the gravity acceleration and \( \mu \) is the viscosity of the oil/PEG/solvent mixture. \( K \) is, finally, a factor the takes into account the sphericity of the particle of diameter \( D \); typically, such factor is 1 for the silica particles and 0.81 for the silicon carbide particles.

Considering the Stokes law, the following may be observed:

a) the equilibrium or terminal velocity for equal solids contents and equal contents of oil/PEG/solvent mixture, ids proportional to the square of the particle diameter; therefore, the bigger particles will tend to settle faster;

b) at equal dilution of the mixture oil/PEG-solvent the term \( (P_s - P) \), and therefore the terminal velocity, will be bigger for the silicon carbide particles \((3.2 \text{ g/cm}^3)\) than for the silicon particles \((2.3 \text{ g/cm}^3)\);

c) lastly, the solvent choice will have to be made among those products the molecules of which, while having the necessary affinity with oil and with PEG, also have, at the same time, the lowest density and viscosity
as possible.

On the grounds of such observations, an object of the present invention is to carry out a complete separation of the suspending fluid from all of the solids present in suspension by means of a procedure simple and economically convenient wherein the suspending fluid of the exhausted slurry, consisting of oil or PEG, is immediately separated from all of the solid components contained in the suspension, in the cases where filtration is not possible, by extraction with a suitable solvent. The solid components may then be separated by chemical species and size-sorted by means of a further dedicated process, if necessary. The separation of the suspending fluid is carried out, according to the invention, by means of one or more consecutive steps of extraction of the suspending liquid with a suitable solvent, carried out in counter-current, each followed by settling of the suspension for a suitable period of time and recovery by overflow of the suurnatant, consisting of a mixture of suspending fluid and solvent. The suspending fluid withdrawn with the first recovery by overflow, which is has the highest content of suspending fluid, is fed to the recovery of the suspending fluid by distillation, while the slurry left in the last settler, consisting of the solid powders dispersed in the solvent, with a very little residual amount of suspending fluid, is diluted with a further amount of solvent and undergoes a final filtration after the extraction, for the separation of all the solids present. The cake resulting from the filtration is washed, thus recovering the solvent and the last traces of suspending fluid and then the filtration cake is dried.

Thus, the products obtained by treating an exhausted slurry or a thickened sludge thereof with the proposed process are the following:

a) the basic suspending fluid of the slurry, which is sent to the reuse, with a recovery yield > 99%;

b) a dry powder containing all the solid components of the slurry; the possible chemical separation or the size-sorting of this powder into its components may be carried out with techniques which do not fall within the scope of the present invention.

Therefore, the present invention specifically provides a process for
separating and recovering the suspending liquid contained in an exhausted slurry, either abrasive or not, coming from the cutting operation or from other machining of silicon materials, or quartz or other ceramic materials, or contained in a thickened fraction of the said exhausted slurry, comprising the following operations:

a) extraction of the suspending liquid from the said exhausted slurry/thickened fraction by dilution with a solvent or a mixture of solvents miscible with the suspending liquid;
b) treatment of the diluted suspension resulting from the previous operation by means of a liquid-solid separation;
c) recovery of the surnatant obtained from the previous operation, consisting of a mixture of the suspending liquid with the solvent or mixture of solvents;

the said sequence of operations a)-c) of the first stage being optionally repeated in one or two further stages, in counter-current,
d) separation of the solvent or mixture of solvents from the surnatant obtained from the operation c) of the first stage by distillation, with recovery of the suspending liquid; the surnatant obtained from the operation c) of each of the said possible further stages being fed to the extraction operation a) of the previous stage;
e) dilution of the residual phase from the operation c) of recovery of the last stage with the said solvent or mixture of solvents and filtration of the diluted suspension obtained, to yield a filtration cake containing substantially all the solids originally present in the exhausted slurry/thickened fraction.

Preferably, after the filtration of the operation e) the following operations are carried out:

f) washing of the filtration cake, with recovery of the solvent or mixture of solvents with traces of suspending liquid;
g) drying of the filtration cake resulting from the previous operation.

As it will be clearer with reference to a specific exemplary embodiment of the process claimed, reported further on, according to a scheme of the
process in stages fed in counter-current, the stream of liquid obtained from the filtration of operation e) is fed to the extraction operation a) of the last stage.

The operation b) of liquid-solid separation may be carried out by means of a separation by density difference, in particular a centrifugation process, which affords a thickened product containing the whole amount of solid particles on one hand, and on the other hand the liquid phase, consisting of the suspending liquid diluted in the solvent (or in the mixture of solvents). Such separation by density difference, however, is preferably realized through an operation of sedimentation or settling, carried out for a period of time necessary and sufficient to afford the sedimentation of all the particles. This operation is followed by the said operation c) of recovery of the Supernatant obtained from the previous operation, which consists of an operation of recovery by overflow of the mixture of suspending liquid and solvent.

The operations (a), (b), (c) may be repeated in the proposed process up to a maximum of two times, thus bringing, according to the preferred solution that employs sedimentation, to a total of three the operations of extraction-settling and recovery by overflow. The number of times the operation of extraction-sedimentation-recovery by overflow is repeated is chosen in dependence of the characteristics of the suspending fluid to be separated from the powders contained therein and also in dependence of the solvent used for the extraction of the suspending fluid, as a last issue, however, the parameter that indicates how may times such operations are to be repeated is the filterability of the suspension that is obtained after the last recovery by overflow, which consists of solvent, powders and of the suspending agent is minimal amount.

In the process according to the present invention the sedimentation time is set so as to give to all the silicon carbide particles, and the fine particles of silicon and "attrition materials" (substantially iron) fines, independently of their size, the necessary time for a complete sedimentation. The times experimentally established for a complete sedimentation to occur are from 1 to 24 hours, using a solvent to suspension dilution ratio from 1:3 to 1:20.

In particularly favourable conditions of filterability of the exhausted
slurry - after dilution with the solvent (depending on the characteristics of the suspending fluid, e.g. PEG or oil, and on the size of the particles in suspension) the liquid-solid separation by density difference may be replaced by a liquid-solid separation by filtration. The filtration may be performed in one only step, for instance in a filter-press, where it also possible to wash the filtration cake to fully recover the suspending fluid and finally dry the cake.

In the operation a) of extraction with solvent of the proposed process, the dilution ratio of solvent or mixture of solvents to exhausted slurry/thickened fraction is normally comprised between 2:1 and 10:1 v/v, and is preferably equal to 1:7. The sedimentation operation b), which follows the mixing with the solvent, has a duration comprised between 1 and 7 hours, and preferably has a duration of about 4 hours.

As it will be more clear further on, the solvent for the extraction of the suspending fluid is preferably methylene chloride (also known as dichloromethane, DCM), which is suitable both for the treatment of PEG-based suspending fluids and for the treatment of oil-based suspending fluids. When the suspending fluid is oil, the solvent may also be selected from perchloroethylene and n-hexane, while when the suspending fluid is polyethylene glycol two additional preferred choices for the solvent are ethyl acetate and 2-buthanol.

As an alternative to one only solvent, a mixture of solvents may be advantageously used, in particular a mixture of methylene chloride and toluene, the features of which are reported in the following, or a mixture of cyclohexane and methylene chloride.

In the process according to the invention realized by means of one, two or three stages of extraction, sedimentation and recovery by overflow, the last recovery by overflow leaves in the reactor a solvent-solids slurry very rich in solids and having a low content of residual suspending fluid; this slurry is mixed with some fresh solvent and is then fed to the final separation, by filtration, of all the solids present.

According to some preferred embodiments of the invention, the cited dilution e) of the residual phase coming from the operation c) of recovery of the last stage with fresh solvent is carried out with a dilution ratio of the sol-
vent (or the solvents mixture) to the exhausted slurry/thickened fraction comprised between 2:1 and 10:1 v/v, the preferred ratio being about 7:1 v/v.

After the filtration the cake washing is performed, the solvent and the last traces of suspending fluid are recovered and finally the filtration cake is dried. Preferably, the said operation f) of washing the filtration cake is carried out with an amount of solvent (or mixture of solvents) equal to about 0.5 times the volume of exhausted slurry fed to the process.

As it appears from the foregoing description, the object of the proposed process is the complete separation of all the suspended solids, in order to obtain on one hand the purified suspending liquid and, on the other hand, all of the solids present in the starting exhausted slurry/thickened sludge in the form of a dry powder free from any residues of suspending liquid. These objects are obtained by using the process in stages according to the invention, where the number of stages of extraction-sedimentation-recovery by overflow and the amount of solvent added for each settling are varied depending on the characteristics of the suspending fluid present in the exhausted slurry/thickened sludge and on the filterability of the suspension coming from the last recovery by overflow.

Therefore, a very flexible process results, where the number of stages of liquid-solid extraction may be varied as a function of the physical-chemical characteristics and the viscosity of the suspending fluid, and of the filterability of the slurry.

The proposed process may equally be applied, besides the exhausted slurries, to the respective thickened fractions (sludges) obtained, for instance, by centrifugation, coming from the machining operations of the semiconductors industry as well as from analogous operations of the photovoltaic energy industry, which as is known, contain considerable amounts of suspending fluid.

In addition, the process also may be applied in those cases where machining operations on silicon are performed without involving the use of an abrasive added to the cutting wire, but still in the presence of an oil- or PEG-based cooling fluid that is to be recovered. In this case the solids of the slurry
from which the suspending liquid s to be recovered will consist of silicon fines and metal fines (coming from the cutting tool).

In practice, a summary of the slurries/thickened fractions that may be proficiently treated with the proposed technology, with the aim of separating the suspending fluid from the solids contained therein and therefore to recover it for the preparation of fresh slurries, is shown in the following table.

<table>
<thead>
<tr>
<th>Exhausted slurries /Thickened fractions</th>
<th>Abrasives</th>
<th>Silicon</th>
<th>Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Based on oil / PEG</td>
<td>Silicon carbide</td>
<td>fines</td>
<td>fines</td>
</tr>
<tr>
<td>Based on oil / PEG</td>
<td>-----------------</td>
<td>fines</td>
<td>fines</td>
</tr>
<tr>
<td>Based on oil / PEG</td>
<td>alumina</td>
<td>fines</td>
<td>fines</td>
</tr>
<tr>
<td>Based on oil / PEG</td>
<td>Other abrasives</td>
<td>fines</td>
<td>fines</td>
</tr>
</tbody>
</table>

For the choice of the solvent to be used for the separation of the suspending liquid from the solids contained in the slurry the characteristics of each solvent have been considered, as reported in the following Table

**TABLE 1**

Characteristics of the solvents to be used for extraction of the suspending fluid

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling point (°C)</th>
<th>Flammability index</th>
<th>Toxicity index</th>
<th>Comments</th>
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<td>69</td>
<td>4</td>
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<td>80.1</td>
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<td>40</td>
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<td>2</td>
<td>For apolar and polar suspending fluids</td>
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<td>ethyl ether</td>
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<td>4</td>
<td>2</td>
<td>General solvent</td>
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<td>99.5</td>
<td>3</td>
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<td>For very polar suspending fluids</td>
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<td>perchloroethylene</td>
<td>121</td>
<td>0</td>
<td>3</td>
<td>For apolar suspending fluids</td>
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Based on the data presented above, the criteria of choice are given by the following objects:

a) in order to use the same solvent for the suspending fluids extraction both from oil-based and from PEG-based slurries the solvent must have affinity with both apolar liquids, such as oil, and polar liquids, such as PEG;
b) a solvent with low flammability index and low toxicity is preferred;
c) a solvent with low boiling point and latent heat of evaporation lower than, or equal to that of other solvents is preferred.

The analysis of the characteristics of the different available solvents, with the aim of treating both oil-based and PEG-based slurries with the same solvent and the same process/apparatus evidenced the convenience of using methylene chloride (DCM) as a solvent, while for the only treatment of slurries based on PEG the solvent usable (as only solvents) are, besides DCM, ethyl acetate and 2-buthanol. For the only treatment of slurries based on oil and in case of use of one only solvent, the usable solvents are, besides methylene chloride, perchloroethylene and n-hexane.

As an alternative to one only solvent, the choice of using a mixture of two or more suitably dosed solvents (technique of the co-solvents) allows to better adjust the characteristics of the solvents to be used for the extraction of the suspending fluid on the basis of the characteristics of the suspending fluid itself, thus improving the suspending fluid extraction, with respect to the use of one only pure solvent. An alternative to the use of the pure methylene chloride is, for instance, a mixture of toluene and DCM, or a mixture of cyclohexane and DCM.

The use of co-solvents has the disadvantage of requiring some more storage tanks, but affords better performances of the extraction-sedimentation process also in terms of volumes of solvent required.

Starting from the analysis of the physical characteristics of the pure solvents, reported in the following table, it is possible to evidence the advantages that may be obtained by using methylene chloride and toluene in a mixture.
For example, by mixing the two above solvents in the ratio 1:3.7 in volume, a mixture is obtained having different physical characteristics with respect to pure DCM, according to the following table:

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<th>Property</th>
<th>DCM</th>
<th>Toluene</th>
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<tr>
<td>Density</td>
<td>1.326 kg/l</td>
<td>0.867 kg/l</td>
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<tr>
<td>Evaporation heat</td>
<td>79 kcal/kg</td>
<td>86.7 kcal/kg</td>
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<tr>
<td>Hildebrand N° (solvent power)</td>
<td>10.4</td>
<td>8.7</td>
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<tr>
<td>Surface tension</td>
<td>28.1 dyne/cm</td>
<td>28.5 dyne/cm</td>
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<tr>
<td>Dipole moment</td>
<td>1.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>9.1</td>
<td>2.38</td>
</tr>
<tr>
<td>Viscosity at 20°C</td>
<td>0.8 cps</td>
<td>0.6 cps</td>
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</table>

- evaporation heat: increased to 84.45 kcal/kg
- surface tension: similar to that of toluene
- dipole moment: reduces towards 0.6-0.5 (improved); the mixture is less polar than pure DCM but more polar, e.g. than hexane
- dielectric constant: reduced with respect to that of DCM
- expected viscosity of the mixture: 0.7 cps

The two solvents are miscible, and therefore their use in a mixture will require a distillation column with 5-6 trays in enrichment and 3-4 trays in exhaustion instead of the simple evaporation.

As far as the mixture flammability is concerned, the flammability of pure toluene is reduced as a result of the enrichment of the emitted vapours in methylene chloride.

In general, the choice of using a mixture of solvents instead of a pure solvent allows to optimize the extraction-sedimentation process and the filtration as a function of the features of the exhausted slurry to be treated.

The specific features of the present invention, as well as its advantages and relative operational modalities, will be more evident with reference
to the detailed description below, presented merely for exemplification purposes. The same are illustrated in the attached drawings, wherein:

**Figure 1** shows an overall block diagram of a process for separating and recovering the suspending liquid contained in an exhausted slurry, according to a preferred embodiment of the invention.

**A. Counter-current extraction of the suspending liquid**

As it is shown in the block diagram of **Figure 1**, the process according to the invention is carried out with n stages (n ranging from 1 to 3) of extraction-sedimentation-recovery by overflow in counter-current. In this case the example is referred to a total of 3 stages.

**1st STAGE**

**Extraction I, reactor R01**:

The exhausted slurry is mixed in the reactor R01 with the mixture coming from the recovery by overflow of the reactor R02, with a dilution ratio, in volume, ranging from 1:2 to 1:10 - volumes of exhausted slurry : volumes of solvent - depending on the type of suspending liquid that characterises the exhausted slurry and on the type of solvent employed.

In the description of the Example the preferred solution using a dilution ratio of 1:7 is considered.

**Sedimentation I, reactor R01**:

The suspension so diluted 1:7 is left to settle, for a period of time such that all solid particles in suspension are able to reach the terminal equilibrium velocity and to reach the zone below the level at which the recovery by overflow of the mixture of solvent and suspending liquid will be effected. The sedimentation time varies as a function of the suspending liquid (whether oil or PEG) and of the solvent used (e.g. DCM, or hexane o mixtures of co-solvents) and may be comprised between 1 hour and 7 hours; typically, it is about 4 hours.

**Recovery by overflow I, reactor R01**:

This operation consists of withdrawing the surnatant of the diluted suspension settled in the reactor R01; the surnatant is fed to a collection tank (suspending liquid + solvent) D1 and then to a separation system for separat-
ing the solvent from the suspending liquid by distillation, that operates with a yield not lower than 99%.

The amount of suspending agent present in the liquid form the 1st recovery by overflow is about 6-7%.

The volume of the clear phase withdrawn is equal to 7 times the volume of the exhausted slurry fed to the reactor R01.

2nd STAGE

Extraction II, reactor R02:

The rest of the slurry left from the recovery by overflow I (the volume of which is equal to the volume of the exhausted slurry loaded in the reactor for the extraction I), is sent to the reactor R02 and then mixed with the solvent-suspending liquid mixture coming from the recovery by overflow III (reactor R03), again with a dilution ratio equal, in volume, to about 1:7.

Sedimentation II, reactor R02:

The suspension so diluted 1:7 is left to settle, for a period of time comprised between 1 hour and 7 hours; typically, it is about 4 hours.

Recovery by overflow II, reactor R02:

This operation consists of withdrawing the surmatant of the diluted suspension settled in the reactor R02; the surmatant is fed to a collection tank D2 and then to the sedimentation in the reactor R01.

The amount of suspending agent present in the liquid form the 1st recovery by overflow is about 2-3%.

The volume of the clear phase withdrawn is equal to 7 times the volume of the exhausted slurry fed to the reactor R01.

3rd STAGE

Extraction III, reactor R03:

The rest of the slurry left from the recovery by overflow II (the volume of which is equal to the volume of the exhausted slurry loaded in the reactor for the extraction I), is sent to the reactor R03 and then mixed with the solvent-suspending liquid mixture coming from the filtration operation, again with a fixed dilution ratio equal, in volume, to about 1:7.

Sedimentation III, reactor R03:
The so resuspended solids are left to settle, for a period of time such that the solid particles in suspension are able to reach the terminal equilibrium velocity and to reach the zone below the level at which the recovery by overflow III will be effected. The sedimentation time comprised between 1 hour and 7 hours and is, typically, about 4 hours.

Recovery by overflow III, reactor R03:

This operation consists of withdrawing the surnatant of the diluted suspension settled in the reactor R03; the surnatant is fed to a collection tank D3 and then to the sedimentation in the reactor R02.

The amount of suspending agent present in the liquid form the 1st recovery by overflow is about 0.5%.

The volume of the clear phase withdrawn is equal to 7 times the volume of the exhausted slurry fed to the reactor R01.

B) Filtration

The suspension left in the reactor R03, consisting of the solid powders dispersed in the solvent, with a residual percent of suspending liquid lower than 0.5-1%, is sent to the tank D04 and mixed with an amount of pure solvent equal to about 7 times its volume, and then sent to the filtration operation. The latter, as a result of the low viscosity of the suspension consequent to the extreme dilution of the starting suspending liquid, is quite rapid.

The filtration cake is then washed with a small amount of pure solvent (about 0.5 V); this operation brings the residual content of suspending agent, with respect to the solid to about a few tens of ppm.

Finally, the solvent used for washing the cake is added to the liquid coming from the extraction itself and then sent to the extraction in the reactor R03.

The final yield of recovery of the suspending liquid present in the exhausted suspension appears to be above 99%.

Solid Fraction:

The filtration cake consists of all of the solid components present in the starting exhausted slurry/thickened sludge and wet as a result of the residual presence of the washing solvent.
For this reason, therefore, the filtration cake is sent to a drying operation, from which the dry powder making up the solid constituents are obtained, while the solvent vapours are sent to condensation and recovery.

**Liquid fraction:**

The liquid fraction consists essentially of the solvent, with a residual content of suspending agent lower than 0.5%; from the filtration this fraction is sent to the tank D5, and from this it is sent for settling to the reactor R03.

The present invention has been disclosed with particular reference to some specific embodiments thereof, but it should be understood that modifications and changes may be made by the persons skilled in the art without departing from the scope of the invention as defined in the appended claims.
CLAIMS

1. A process for separating and recovering the suspending liquid contained in an exhausted slurry, either abrasive or not, coming from the cutting operation or from other machining of silicon materials, or quartz or other ceramic materials, or contained in a thickened fraction of the said exhausted slurry, comprising the following operations:

a) extraction of the suspending liquid from the said exhausted slurry/thickened fraction by dilution with a solvent or a mixture of solvents miscible with the suspending liquid;

b) treatment of the diluted suspension resulting from the previous operation by means of a liquid-solid separation;

c) recovery of the supernatant obtained from the previous operation, consisting of a mixture of the suspending liquid with the solvent or mixture of solvents;

d) separation of the solvent or mixture of solvents from the supernatant obtained from the operation c) of the first stage by distillation, with recovery of the suspending liquid; the supernatant obtained from the operation c) of each of the said possible further stages being fed to the extraction operation a) of the previous stage;

e) dilution of the residual phase from the operation c) of recovery of the last stage with the said solvent or mixture of solvents and filtration of the diluted suspension obtained, to yield a filtration cake containing substantially all the solids originally present in the exhausted slurry/thickened fraction.

2. A process according to claim 1, wherein after the filtration of the operation e) the following operations are carried out:

f) washing of the filtration cake, with recovery of the solvent or mixture of solvents with traces of suspending liquid;

g) drying of the filtration cake resulting from the previous operation.

3. A process according to claims 1 or 2, wherein the liquid phase
obtained from the filtration of operation e) is fed to the extraction operation a) of the last stage.

4. A process according to any of the claims 1-3, wherein the said operation b) of liquid-solid separation is a separation by density difference.

5. A process according to claim 4, wherein the said separation by density difference of operation b) is a centrifugation.

6. A process according to claim 4, wherein the said separation by density difference of operation b) is a sedimentation and the said operation c) of recovery of the surnatant obtained from the previous operation is a recovery by overflow.

7. A process according to any one of claims 1-3, wherein the said operation b) of liquid-solid separation is a filtration.

8. A process according to any one of claims 1-7, wherein in the said operation a) the dilution ratio of solvent or mixture of solvents to exhausted slurry/thickened fraction is comprised between 2:1 and 10:1 v/v.

9. A process according to claim 8, wherein the said dilution ratio is about 7:1 v/v.

10. A process according to any one of claims 1-9, wherein the said solvent is methylene chloride.

11. A process according to any one of claims 1-9, wherein the said suspending liquid is oil and the said solvent is selected from methylene chloride, perchloroethylene and n-hexane.

12. A process according to any one of claims 1-9, wherein the said suspending liquid is polyethylene glycol and the said solvent is selected from methylene chloride, ethyl acetate and 2-buthanol.

13. A process according to any one of claims 1-9, wherein the said solvent or mixture of solvents is a mixture of methylene chloride and toluene, or a mixture of cyclohexane and methylene chloride.

14. A process according to claim 6, wherein the said sedimentation of operation b) has a duration comprised between 1 and 7 hours.

15. A process according to claim 14, wherein the said sedimentation of operation b) has a duration of about 4 hours.
16. A process according to any one of claims 1-15, wherein the said dilution e) of the residual phase from the operation c) of recovery of the last stage with the said solvent or mixture of solvents is carried out with a dilution ratio of solvent or mixture of solvents to exhausted slurry/thickened fraction comprised between 2:1 and 10:1 v/v.

17. A process according to claim 16, wherein the said dilution ratio is about 7:1 v/v.

18. A process according to any one of claims 2-17, wherein the said operation f) of washing the filtration cake is carried out with an amount of solvent or mixture of solvents equal to about 0.5 times the volume of exhausted slurry fed to the process.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D21/00 B24B55/12 B24B57/00 B28D5/00 B01D21/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D B24B B28D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>WO 2006/137098 A (SIC HOLDING GESCHAEFTSFUEHRUNG [DE]; FRAGIACOMO GUIDO [IT]) 28 December 2006 (2006-12-28) cited in the application page 1, line 6 - line 16; figures 2,3</td>
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<td>A</td>
<td>WO 01/43933 A (FRAUNHOFER GES FORSCHUNG [DE]; EISNER PETER [DE]; MALBERG ANDREAS [DE]) 21 June 2001 (2001-06-21) cited in the application</td>
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D. Further documents are listed in the continuation of Box C

- Special categories of cited documents
  "X" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier document but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  "O" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed

Filing date of the international application 12/05/2009

Date of the actual completion of the international search 4 May 2009

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Authorized officer
Roider, Josef
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<td>WO 2006137098</td>
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