Industrial implementation of processes to render RCS safer in manufacturing processes

Final Report Summary - SILICOAT (Industrial implementation of processes to render RCS safer in manufacturing processes)

Executive Summary:
It is long established that prolonged inhalation of respirable crystalline silica (RCS) particles cause lung inflammation and development of the granulomatous and fibrogenic lung disease known as silicosis. In 1997, the International Agency for Research on Cancer (IARC) classified RCS in the form of quartz and cristobalite as carcinogenic to humans (Group 1).
As quartz-containing raw materials are indispensable for the manufacturing processes of traditional ceramics industry (wall tiles, tableware, sanitary ware, etc.), many workers are potentially at risk to develop respiratory diseases, e.g. lung inflammation, silicosis, or even lung tumours.

In return, studies suggest that silica toxicity can be nullified by certain substances. These substances are capable of forming a coating onto the RCS particles surface, blocking its reactivity in biological media.

It may be noted that, though this research line was started in the 1960s, none of these substances had been used for these purposes on an industrial scale. In all likelihood, the low added value of quartz as raw material had been of influence in this regard. However, given the wide range of available compounds and the potential benefit in terms of worker health protection, it was deemed appropriate to explore this possibility for the traditional ceramic sectors.

In the SILICOAT project, the most economical compounds that exhibit the above property have been identified. A wide number of compounds were systematically tested. It was verified whether the quartz was appropriately coated by the compound involved. The incorporation of these compounds was conceived such that no substantial alteration of the ceramic process would be required. In addition, compounds were selected that would not adversely affect product behaviour during the process.

Technically and economically feasible coating treatments were defined. These were based on treating quartz with propyltrimethoxysilane (PTMO), a commercial aminosilane (SIVO160), and nano-alumina. Samples of quartzes treated with these compounds were tested for toxicity.

Toxicological results obtained in vitro demonstrated that, by coating industrial quartzes with all of the above treatments, quartz cytotoxicity could be fully suppressed, while genotoxicity was reduced by more than 80%. Furthermore, organosilane coatings were found to be stable under physiological conditions. In particular, the protective effect of the aminosilane coating was confirmed in vivo in animals sacrificed 90 days after the administration of treated quartz.

The treatment designed at pilot scale was demonstrated at industrial scale at the facilities of the four participating SMEs. The process routes where the coating stage was incorporated were selected to represent most of the different traditional ceramic processes. A quartz coating treatment could be incorporated in the processes of all of the participating SMEs, thus demonstrating its technical feasibility. Toxicological analysis of powder samples collected during the industrial trials showed that the impressive toxicity reduction obtained at pilot scale was reproduced at full scale.

The costs of the coating treatments were realistically assessed. For most ceramic compositions, the treatment would involve a cost increment of the raw materials of less than 2%. Therefore, treatment costs were very reasonable and comparable, or even better, to those associated to dust abatement measures.

Overall, the SILICOAT project has contributed a technically and economically feasible treatment to render the quartz used in the traditional ceramic industries intrinsically safe. In contrast with traditional measures of corrective nature, the SILICOAT treatment enables the RCS exposure risk to be addressed from its origin: the substance itself.
Project Context and Objectives:
Total European usage of crystalline silica (i.e. quartz and crystobalite) is measured in thousands of millions of tonnes per annum. It is used in many manufacturing industries such as cement, ceramics, steel foundries, glass, mineral wool, aggregates, mortar or concrete sectors. Hence, a vast number of European workers —4 millions— are potentially exposed to Respirable Crystalline Silica (RCS) at their workplace.

It is generally recognized that prolonged inhalation of RCS cause the lung disease known as silicosis. Even though the incidence is highest in under-development countries, nowadays a highly concerning number of silicosis diagnoses still occur in European countries. The European Industrial Minerals Association has reported that, in three of the most advanced countries of the EU (Germany, France and the UK), silicosis diagnosis rates of non-coal workers are nowadays higher than 100 cases/year.

Furthermore, the International Agency for Research on Cancer (IARC) classified RCS in the form of quartz and crystobalite from occupational sources as carcinogenic for humans (category 1). This classification was, when published, very controversial because the IARC itself recognised that a causal relationship between RCS exposure and lung cancer hazard was either negative or equivocal in some cohorts. Nevertheless, it is generally accepted that silicosis increases the risk of lung cancer. In fact, silicosis may be necessary to cause silica-related lung cancer. However, even accepting this premise, the burden of lung cancer in UK due to past exposures to silica has recently been estimated to be nearly 800 deaths per year.

The ceramics industry is particularly concerned as this wide variety of industrial products (heavy clay products, floor and wall tiles, sanitary ware, tableware, glass, refractories, etc.) are based on silicates (clays, feldspars, sands, etc.). The relevant bodies (i.e. mixtures of raw materials) used in the manufacture of these products include considerable amounts of quartz, which plays indispensable functions during the different phases of the manufacturing process.

Despite having found “sufficient” evidence for the above classification, the IARC recognises that silicosis appears to be a necessary precursor for the increase in the risk of lung cancer. In addition, this increased risk is not detected in every industrial scenario, and it would appear to depend on characteristics inherent to the silica itself and/or on external factors.

The fact that the toxicity of RCS is conditioned by “external factors” suggests two possibilities: that RCS is not toxic of itself, but that it needs to be activated by another substance or, which is more plausible, that other substances that accompany RCS could inhibit its toxicity. In any event, in practice, this means that one might find two chemical agents with the same nominal composition (SiO2), but with a radically opposed toxicity.

Schlipköter and Brockhaus postulated that the silanol groups (Si-OH) at the surface of the quartz are precisely the mediators in the pathological effect of RCS and, even more remarkably, that it should be possible to neutralise these active centres by means of molecules that were strongly adsorbed on them. Polyvinylpyridine-N-oxide (PVPNO) has this characteristic. The O– group of this compound forms hydrogen bridges with the silanols, thus coating the RCS particles. The treatment of RCS with PVPNO
Another substance that is able to inhibit the toxicity of quartz is aluminium lactate. Aluminium lactate has a comparable efficiency to that of PVPNO. Its effect is so evident that it has been used to distinguish the specific toxicity of quartz in dust mixtures.

The use of organosilanes has also yielded excellent results in this regard. Unlike PVPNO, which forms hydrogen bridges with quartz, organosilanes react chemically with the silanol groups at the quartz surface (figure 1).

Finally, certain authors have shown that strong Lewis acids, such as AlCl3 or FeCl3, are also able to modulate the harmful action of RCS. Moreover, these authors verified that the quantity required to produce the maximum inhibition coincided exactly with the quantity required to make quartz iso-electric, thus endorsing the hypothesis of the silanol-based mechanism.

Therefore, it had been repeatedly demonstrated that, by coating the quartz surface so that its silanol groups are no longer accessible for interaction with biological media, it is possible to suppress RCS toxicity. However, though this research line was started in 1960, none of these substances had been used for preventing RCS exposure risk on an industrial scale. In all likelihood, the low added value of quartz as raw material has been of influence in this regard. However, given the wide range of available compounds and the potential benefit in terms of worker health protection, it was considered convenient to explore this possibility for the traditional ceramic sectors.

The main objective of the SILICOAT project consisted of developing and implementing RCS coating technologies into the ceramic processes in order to render the use of materials containing crystalline silica intrinsically safe from the toxicological viewpoint.

This general objective could only be attained by achieving a number of milestones:
- Identify the most cost-effective coating agents that were available in industrial amounts.
- Design a technically and economically feasible pilot-scale treatment for coating the quartz contained in the ceramic compositions without adversely affecting the manufacturing processes.
- Verify that the toxicity of the treated quartzes becomes almost fully suppressed.
- Demonstrate the coating treatment on an industrial scale.
- Validate the toxicity reduction on samples obtained in the industrial trials.

The attainment of the above goals resulted in a cost-effective, highly relevant measure for the prevention of the RCS exposure risk from its origin, whereby a coating renders any remaining airborne quartz safe.

Even though the SILICOAT concept might appear to be extremely innovative, it actually fits very well to the current European legislation. For example, Directive 98/24/EC on the risks related to chemical agents at work accounts for this possibility in its Article 6: “the employer shall avoid the use of a hazardous chemical agent by replacing it with a chemical agent or process which, under its condition of use, is not hazardous or less hazardous to workers’ safety and health”. In fact, this is the prevention measure to be preferred over any other prevention means. Therefore, SILICOAT made a very important contribution for the SMEs
to comply with the legislation and to improve the working conditions of the European workers.

Project Results:
The technical work comprised collecting all the necessary baseline information, development of pilot-scale coating processes, demonstration of the pilot coating processes at full, industrial scale and toxicological characterisation of powders.

Options for integrating coating into processing

The first task of the project consisted of examining the current manufacturing processes of the whole European traditional ceramic industries and, in particular, those of the participating SMEs, in order to identify the process stages where the quartz coating should take place.

The preferred process stages were those where aqueous suspensions are processed. This conception had two important advantages: (i) aqueous suspensions are ideal media for the dispersion of additives and subsequent interaction with the quartz particles via chemical reactions or colloidal processes, (ii) current traditional ceramics manufacturing processes would not needed to be modified at all to embrace the coating technology. Furthermore, the use of aqueous suspensions is common to many ceramic subsectors and represents the early stages of the ceramic process. The objective was to have the RCS coated in the majority of the workplaces where there can be exposure. Therefore, by coating the quartz in the first stages, in terms of workers’ exposure, silica dusts would be coated in most of the production process.

On the basis of the above premise, the process stages where the coating process was to be incorporated were defined for each participating SME:
- ATOMIZADORA: wet milling of body wall tile compositions.
- PORVASAL: wet mixing of body tableware compositions.
- FLAMINIA: wet mixing of body sanitary ware compositions.
- WALKÜRE: wet milling of glazes for tableware.

Through this selection, together with an appropriate choice of process routes for each SME partner, representativeness of the whole traditional ceramics sector was adequately attained (figure 2).

Quartz types used in the SMEs

Once the process routes to be studied had been selected, it became necessary to study the raw materials involved, with particular attention to the quartz-containing ones. The selected compositions encompassed a broad collection of raw materials. The quartz content of each of them was determined, which allowed classifying them into three categories: quartz per se (siliceous sands, quartz flours), quartz containing raw materials (clays and feldspars) and quartz-free raw materials (calcite, dolomite, and alumina). Samples of every raw material were prepared for toxicity testing, in order to establish the baseline situation.

Definition of the in vitro/in vivo test battery for toxicity screening

An optimized battery of in vitro/in vivo toxicological tests was defined for all the necessary toxicological
determinations to be conducted throughout the project. Toxicological assays were selected based on the previous experience of ITEM in measuring the toxicity of quartz-containing dusts.

In vitro tests, using alveolar macrophages as cell model (first site of contact for dusts in the lung), targeted the study of cytotoxicity (lactic dehydrogenase [LDH] assay), genotoxicity (comet assay), pro-inflammatory potential and oxidative stress (TNF-α, IL-8, and HMOX-1).

Besides quartz, other constituents of the ceramic compositions may also exhibit a certain biological response that need to be quantified in order to distinguish quartz-specific effects. To distinguish between quartz-specific and non-quartz effects, the samples were decided to be incubated with and without aluminum lactate. Aluminum lactate is known to be a quencher of biological effects of crystalline silica (in fact, it is a coating agent that was considered in the project, see below). The differences between the results in the presence or absence of aluminum lactate could thus be attributed to quartz-specific toxicity.

To demonstrate the relevance of the results obtained with cell cultures, selected results obtained in vitro were validated by in vivo testing in the rat model. The selected procedure involved intratracheal instillation of dust samples, sacrifice of the rats after a preset period, and subsequent analysis of the bronchoalveolar lavage fluid (BALF).

Results of the screening of the different quartz varieties

The toxicological screening of the relevant raw materials led to important findings. As a first screening endpoint involving all the raw materials (25), LDH activity revealed that, as expected, only quartz-containing raw materials exhibited quartz-related toxic effects. However, certain clays (especially all the studied red clays) showed very little quartz-specific cytotoxic activity, despite they contained up to 30% quartz. Most crucially, one of the quartzes showed almost no toxicity. This quartz specimen was prepared by milling the raw quartz in planetary mills with alumina balls in the laboratory. It was hypothesised that the milling with alumina balls was precisely what caused the toxicity quenching, which was subsequently confirmed by measuring the toxicity of the bulk quartz. Therefore, circumstances led to a first method for reducing quartz toxicity, which was further studied all along the project.

Eight raw materials were selected for further in vitro genotoxicity screening using the comet assay and gene expression analysis. This additional testing demonstrated that separate quartzes were the only raw materials with a clear quartz-specific DNA-damaging potential. Nevertheless, the quartz milled with alumina balls exhibited very little genotoxicity. In contrast, clays and kaolins showed a relatively high genotoxic response, though it did not appear to be quartz related.

The results obtained in vitro were validated in vivo in the rat model. After intratracheal instillation (two aliquots of the total dose on two consecutive days), 5 rats per group were sacrificed after 3 and 28 days, respectively. Analysis of the BALF showed that for the groups sacrificed on day 3, kaolin and clays mediated a stronger response than that of the quartzes. However, for the rat groups sacrificed on day 28, the BALF of the clay and kaolin groups had returned to normal values, while quartz groups showed a significant toxic effect. In other words, the kaolins elicited an acute response, whereas the quartzes a retarded, progressive effect. Again, the quartz milled with alumina balls showed very little in vivo toxicity.
Materials, compositions and coating agents selected for conducting the study

The formulas of the selected compositions were defined. The representativeness of the ceramic sector as a whole was adequately addressed: the composition of ATOMIZADORA was a mixture of red clays for spray drying to produce tiles; FLAMINIA represented wet mixing for slip casting of sanitaryware; PORVASAL and WALKÜRE produce tableware, but the selected composition of the former was for the body, while the one of the latter was a glaze composition.

A first list of coating agents was also defined at this point. This list was established based primarily on the industrial availability of the products at reasonable cost. Certain coating agents that were found to be effective in the toxicological literature were discarded because of the lack of available suppliers of industrial amounts. For example, polyvinylpyridine-N-oxide is a very effective and thoroughly tested compound for quartz toxicity suppression. Unfortunately, there are only lab-grade qualities of this product in the market, which in turn are supplied in milligrams at exaggeratedly high price (at least for the project purposes).

Other compounds were thought to cause problems in the production process and thus, were also early discarded. For example, strong Lewis acids (AlCl3 and FeCl3) have the considerable drawback of raising the ionic strength when dispersed in an aqueous suspension. Therefore, they were prone to have a marked negative influence in the ceramic process, since they may cause the flocculation of the ceramic suspensions.

After applying all the above criteria, an initial list of potential coating agents was reduced to 3 relatively broad families of compounds: (organo)silanes, aluminium lactate, and nano-alumina. Organosilanes were, by far, the broadest family of compounds to test: there were literally a plenty of different substances that potentially can suppress quartz toxicity.

Protocol for coating characterisation and studying process behaviour

Once a first selection of coating agents was defined, it was necessary to establish the experimental methods to determine:
• Whether the relevant coating agent actually coats the quartz surface
• The minimum proportioned quantity for a complete coverage of the quartz surface (this information was essential for a preliminary economical assessment of the treatment)
• Whether the coating treatment affects negatively (or positively) the manufacturing processes.
These experimental methods can thus be classified according to whether they aimed at coating characterisation (the first two items of the above list) or determining the influence on process behaviour (the last item).

Regarding coating characterisation, it was necessary to devise specific methodologies. Furthermore, each of these was more or less appropriate depending on the nature of the coating agent. These methodologies involved combinations of the following instrumental techniques: thermogravimetry (TG), ζ-potential measurement, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM).
Regarding the study of process behaviour, the most critical variables were identified, and the usual control techniques were used.

Pilot coating trials

Contacts were established with the main suppliers of the coating agents preliminarily selected. As a result, the most economical compounds were identified. This enabled the relatively broad list of potential coating agents to be reduced to around 10 compounds that, when supplied in industrial amounts and in certain form, would entail a cost of less than 5 €/kg of compound. This maximum tolerable cost was defined by assuming a reasonable proportioned quantity of coating agent to attain a complete coverage of the quartz surface, and the current cost of the quartz-containing raw materials.

Most of the selected compounds were organosilanes with different functional groups and thus, widely different properties. Organosilanes (or simply silanes) are well-known industrial products that are used for the functionalisation of surfaces and fillers. The term functionalisation stands for forming a layer of organic nature with the desired properties (functional groups) onto the substrate surface. This layer is chemically bond to the base surface so that it becomes permanently modified. This behaviour totally fitted to the SILICOAT concept.

Selected silanes were primarily alkoxysilanes, though some of them were already hydrolysed. The hydrolysis of the alkoxy groups is a first reaction of the silanes with water giving rise to silanol-containing species. The silanol-containing species are highly reactive intermediates, which are responsible for bond formation with the substrate. Unfortunately, silanol-containing species are generally unstable and thus, in most cases they cannot be readily supplied in this form for surface treatments. With aging, silanols condense with other silanols or with alkoxysilanes to form siloxanes. Eventually, precipitation occurs.

Hydrolysis/condensation testing allowed already discharging certain compounds. In particular, tetraethyl orthosilicate (TEOS) was found to be hard to hydrolyze (it took almost 4 h in the best case scenario). Furthermore, TEOS is a very peculiar silane, as it condenses into amorphous silica. The resulting precipitated silica tended to got stuck to the labware, thus suggesting powder agglomeration problems. Furthermore, it was not clear whether coating the quartz particles with an amorphous precipitated silica layer actually reduces its toxicity.

The rest of the selected silanes were either stable hydrolysed solutions or became hydrolysed more easily. Therefore, the extent to which they react with the industrial quartzes was determined. Many tests were made in this regard. In this summary a few notes will be given on the two silanes that provided the best results in terms of coating quality and cost effectiveness: propyltrimethoxysilane (PTMO) and a commercial aminosilane (SIVO 160).

The degree of reaction between PTMO and the quartz surface was studied with a combination of the TG and XPS techniques. On the basis of these results, the necessary reaction time and appropriate proportioned quantities were defined. SIVO 160 (and other aminosilanes) coating could be studied with an additional, very sensitive instrumental technique: ζ potential measurements. In contrast to neutrally
charged silanes (e.g. PTMO), aminosilanes have positive charge in aqueous media. However, because of
the presence of silanol groups at the quartz surface, quartz exhibits a very low iso-electric point of about 2.
Therefore, in aqueous suspensions at pH>2, quartz particles will have negative charge. Aminosilanes,
when coating quartz, should ultimately render the quartz surface positively charged, meaning that silanol
groups became completely covered (figure 3). This phenomenon enabled the necessary proportioned
quantities of aminosilanes to be accurately determined.

Besides organosilanes, other coating agents were studied. In spite of not being previously tested in the
literature, nano-alumina was predicted to reduce quartz toxicity. The iso-electric point of alumina is about 9.
This means that, in a wide range of pH (i.e. 2
Nano-alumina was used in form of aqueous suspension to minimize the opportunities of airborne dust, in
consideration of health and safety, and to encourage proper dispersion in the quartz suspensions.
Because of the reason above, nano-alumina coating could also be studied by measuring the ζ potential of
quartz (in addition to XPS, etc.). However, in contrast to other coatings, nano-alumina coatings could be
directly observed by SEM (Figure 4).

Finally, aluminium lactate was also considered in the project. A German manufacturer was found that
provided a semi-finished aluminium lactate solution (containing 30% w/w of the salt at issue). This semi-
finished solution was available for less than 3 €/kg. A different approach was adopted for determining the
coating effectiveness of aluminium lactate. As this compound was used for resolving the quartz-specific
toxicity (see above), ITEM could identify the minimum proportioned quantity for the quartz toxicity to
vanish by in vitro testing.

On account of the above results, the most promising coating agents, treatment conditions, and
proportioned quantities could be identified. The selected coating agents were PTMO, SIVO 160, nano-
alumina, and aluminium lactate.

Once the most promising treatment conditions had been defined, the feasibility of the integration of these
treatments in the ceramic processes was examined. The process behaviour of the treated compositions
was compared in every case with that of the corresponding untreated industrial composition.

Aluminium lactate caused very important problems in the processing of the targeted compositions. It
turned out to be a flocculant that made the treated ceramic suspensions unworkable. In contrast, the other
selected coating agents did not cause significant modifications in the control parameters, with the
exception of PTMO that produced the positive effect of reducing the suspension viscosity, thus being likely
to reduce the amount of necessary deflocculant.

A preliminary economical assessment was made for the treatments that did not influence negatively
process behaviour. This information, together with the associated toxicological results (discussed below),
allowed defining a ranking of feasible treatments. A treatment based on the proportioning of 0.5% (w/w of
quartz) of hydrolysed PTMO was selected as the most promising coating process for industrial
demonstration. The second candidate treatment consisted of the use of SIVO 160 at a proportioned
quantity of 0.2% (w/w of quartz). Both treatments would involve a cost increment for the composition of
less than 4 €/t.
Effectiveness of the different coating options in reducing toxicity

Based on the work described, specimens were prepared by treating industrial quartz with the most promising coating treatments at different concentrations and reaction times. This specimens were tested for toxicity and compared against the reference uncoated quartz, so that coating effectiveness in reducing quartz toxicity could be quantified.

The study was not limited to acute in vitro effects, but the coating was verified to be stable with time in biological media in order to ensure that the protective effect persists up to the clearance time in the lungs, at least in the animal model. Coating stability in biological media was assessed by two approaches:
- incubating the coated quartzes in artificial lung fluids;
- prolonged in vivo testing with animal sacrifice after clearance half-time.

The samples of the coated quartzes were first tested in vitro in their bulk form (as received). All the selected treatments were found to virtually nullify quartz toxicity, as measured in terms of cytotoxicity (LDH activity) and genotoxicity (comet assay).

When it comes to the PTMO treatments, the treatment based on proportioning of 0.1% significantly reduced cytotoxicity (67%) and genotoxicity (72%) in relation to the uncoated quartz. By increasing the proportioned quantity to 0.5% and 1.4%, cytotoxicity was effectively fully suppressed (100% reduction), while genotoxicity was reduced by >80%.

SIVO160 was also equally effective in reducing quartz toxicity. The treatments with either 0.2% or 0.4% SIVO160 virtually eliminated cytotoxicity and reduced genotoxicity by at least 80%.

Nano-alumina was also extremely effective in reducing the quartz toxicity. Both the cytotoxicity and the genotoxicity of the quartz was diminished by >98% by treating it with 1.5% nano-alumina.

Therefore, all the selected treatments provided very satisfactory results in terms of toxicity reduction. In order to demonstrate that the toxicity reduction was effective in the finer fraction of the quartz dusts, the samples were sized in a water column to obtain the respirable fraction (i.e. those particles that can enter the alveoli).

The industrial uncoated quartz did not lose its cytotoxicity. Furthermore, as one might expect, citotoxicity of the fine fraction was higher than those of the bulk sample and the coarse fraction, probably because of the higher surface area of the fine fraction. Compared with the respective fractions of the uncoated quartz, the quartz treated with 0.5% PTMO exhibited a 100% reduction in cytotoxicity. Concerning genotoxicity, the treatment with PTMO mediated a 74% reduction in tail intensity of the fine fraction, while the DNA damage of the (less important) coarse fraction was reduced by 60%.

In sum, a treatment with 0.5% of hydrolysed PTMO in relation to quartz was found to be very effective in reducing quartz toxicity. This outcome, together with the positive results obtained in the pilot trials with this compound, led to the decision of deeming it as the preferred option for the industrial trials. Therefore, in
vitro stability testing was focused on a coating treatment based on PTMO.

Coating stability of PTMO-coated quartzes was tested in vitro in two different physiological media: artificial alveolar fluid (AAF) and artificial lysosomal fluid (ALF). The reference uncoated industrial quartz and the PTMO-coated quartz were incubated in AAF and ALF for 24 h, 48 h, 72 h, and 1 week.

The uncoated quartz exhibited a time-dependent increase in genotoxicity and cytotoxicity (especially in the presence of ALF), while the PTMO-coated quartz mediated a cyto- or geno-toxic potential that was not significantly different to the negative particulate control for all incubation times. Therefore, in vitro experiments with simulated lung fluids suggested that the PTMO coating was stable in physiological conditions up to a week, which was attributed to the chemical bond between PTMO and the quartz.

However, as previously noted, the above in vitro results were validated in vivo, with especial emphasis on coating stability. SIVO160, as the second best candidate treatment, was also included in the analysis.

28-day BALF analysis revealed a clear protective effect of both PTMO and SIVO160 coatings. SIVO160 was particularly effective, as the biological responses remained almost the same as those of the saline group. After 90 days, however, the protective effect of PTMO, though still present, was reduced to a significant extent. In contrast, after 90 days, the SIVO160 coating still reduced mean lung effects of the industrial quartz by 76% (total leukocytes), 68% (polymorphonuclear cells), 87% (lymphocytes), 56% (LDH), and 80% (β-glucuronidase), indicating a persisting coating effect.

Therefore, the toxicological testing of coated quartzes confirmed that all the devised treatments were very effective in reducing quartz toxicity. In particular, a treatment based on coating quartz with 0.2% SIVO160 almost nullifies quartz toxicity. Furthermore, in vivo results showed that this effect persists up to 90 days after deposition of the particles of the lung. PTMO was also effective, but to a lesser extent.

Industrial coating trials

A series of industrial trials were scheduled in the facilities of the participating SMEs. The objective of these trials was to demonstrate that the coating treatments can be performed at industrial scale, without adverse effects in the production process, and with a comparable toxicity reduction to that obtained at laboratory scale. Industrial trials were first scheduled on the basis of a PTMO coating, which was what the available information suggested at this time.

The first trial was conducted in wet milling of body wall tile compositions (figure 5). A coating treatment based on 0.5% w/w of hydrolysed PTMO in relation to quartz was used. No problems were found in milling and spray drying of the treated slips. Furthermore, the treatment had a side benefit of at least 12% savings in deflocculant. With respect to the end product (glazed ceramic tiles), no significant differences were observed between the tiles produced with either treated or untreated spray-dried powders.

PTMO treatment was unworkable in wet milling of glazes for tableware because of the formation of foam. On account of these problems, the second best treatment candidate (0.2% SIVO160) was tested, which was successful (figure 6). An additional trial was also made in this process. As mentioned above, milling
quartz with alumina balls in the laboratory was able to reduce its toxicity. Therefore, such a relatively simple coating treatment was tested by milling the quartz alone with flintstones (usually used) and alumina balls for the sake of comparison.

For wet mixing of body sanitary ware compositions, PTMO was also tested as a first candidate. As the foam problem also occurred in this process, SIVO160 was used as an alternate treatment without problems (figure 7).

For wet mixing of body tableware compositions, both PTMO and SIVO160 where tested. Therefore, two slips were prepared with the respective treatments, both of which were satisfactorily processed (figure 8).

The results of the industrial trials suggested that PTMO may be used for spray drying processes, while SIVO160 should be preferred for casting and glazing (by immersion). However, it has already been pointed out that the last in vivo results suggested that SIVO160 is indeed more effective in reducing quartz toxicity, which makes it the best candidate in almost every aspect.

Toxicity of the industrial powders before and after the coating treatment

Samples of untreated/treated quartzes/compositions were collected during the industrial trials and were tested for toxicity using the optimised in vitro test battery described above.

It is appropriate to distinguish between composition and separate quartz samples. In general, compositions were much less active than separate quartz. Certain components of the compositions appeared to reduce quartz toxicity. In fact, body wall tile and tableware glaze compositions showed no quartz-specific toxicity. Tableware body and sanitary-ware body compositions exhibited quartz-specific effects, though they were very moderate so that the modulation of these effects by treatment with either PTMO or SIVO160 was not obvious.

On the other hand, samples of separate quartz enabled the benefits of the treatments to be appropriately addressed. The cytotoxicity and genotoxicity of the quartz used for body tableware compositions was almost reduced to negative control levels with both PTMO and SIVO160. The toxicity of the body sanitary ware composition quartz was effectively counteracted by treatment with SIVO160. Therefore, the toxicity reduction potential obtained at pilot scale was confirmed at full scale.

Body tableware composition contained no separate quartz and thus, the effect of PTMO was masked by other composition components. In contrast to body sanitary ware and body tableware composition, where the treatment was made on separate quartz, for glazes for tableware the treatment was made on the composition as a whole since it was subjected to a very long milling that could degrade the additive. However, as noted above, an additional test was made for separate quartz of glazes for tableware facilities: milling with alumina balls instead of flintstones. The toxicological analysis of this quartz milled with alumina balls demonstrated that it was much less active than quartz milled with flintstones. Therefore, an alternate, very affordable prevention measure was identified.

Technological, economical and cross-media effects for the SME ceramic industries
At least three technical and economically feasible treatments for the suppression of the toxicity of the quartz contained in the ceramic compositions were designed. These coating treatments are based on the surface modification of quartz with:

- SIVO160 (a commercial aminosilane)
- PTMO (propyltrimethoxysilane)
- alumina particles (either as nano-particles or alumina balls debris)

The preferred treatment is that involving SIVO160 because technically outperformed the other treatments and, from the toxicological viewpoint, produced a very persistent, protective coating.

The treatment was designed from the very beginning to be very simple and integrable into the current manufacturing processes of the ceramic processes. Therefore, the process stages where quartz-containing aqueous suspensions are processed were selected. The treatment basically introduces an additional stage in which the quartz is dispersed together with the coating agent for a specified reaction time. Once the reaction time has ended, the remaining components of the formula can be added in the usual manner.

The cost of the treatment was deemed tolerable. A SIVO160-based treatment cost would entail a cost of around 2 €/t for typical compositions, which would mean a cost increment of less than 2%. For compositions with a lower added value, such as that of body wall tile compositions, the cost increment would amount to less than 5%, which still sounds quite reasonable.

Possible cross-media effects were also examined. For example, PTMO is able to reduce the amount of necessary deflocculant, which is a side benefit. Environmental aspects were also considered. SIVO160 is an aminosilane and thus, might increase the emissions of CO2 and NOx during the firing stage where the coating will become thermally decomposed. The associated CO2 emissions are obviously negligible compared with combustion emissions. Regarding NOx emissions, the proportioned quantity is so small that even assuming that it is a pure, undiluted aminosilane with the highest nitrogen content (which is not), it would have a negligible impact on NOx emissions.

Potential Impact:
SILICOAT project has contributed a technically and economically feasible treatment to render the quartz used in the traditional ceramic industries intrinsically safe. In contrast with traditional measures of corrective nature, the SILICOAT treatment enables the RCS exposure risk to be addressed from its origin: the substance itself.

These results will have a potential impact on the competitiveness of SMEs. The EU ceramics industry, 90% being SMEs, records total sales of around €26 billion and employs about 220 000 people. The substitution of quartz by other substance is not possible in traditional ceramics because the essential raw materials for the production of these products are clays, feldspars, sands, etc., which contain quartz that plays a key role in the process.

However, the formal classification of quartz as a category 1 carcinogen in the EU implies a big challenge for the employers, from the economic and operative point of view. Amounts of quartz containing raw materials processed in these industries are measured in hundreds or thousands of tonnes per day. Total
enclosure of the operations is very difficult and measures with equivalent efficiency are likely to entail very high costs. On the other hand, there is a potential danger that companies using RCS (especially SMEs) will be faced with extortionate abatement capital equipment costs, in-house administration / testing costs etc. to comply.

From data by Timellini and Fregni [Cer. Acta, 13(4-5), 88-92], a reduction of the occupational exposure limit to 0.025 mg/m³ would require an extraction rate of at least 500 m³/m², the necessary investment being around 600 000 € for each process stage, only in the fabric filter. Costs needed to complete the whole extraction system should be added to this figure. Moreover, operational cost will be very significant, since the resulting flow rates will surpass 200 000 m³/h. Alternatively, SME companies will achieve the new limits by employing corrective measures that entail a significant investment cost and probably would fail to consistently deliver the new very low occupational limit values. Hence, a combination of affordable corrective and preventive measures may lead to optimal solutions.

The treatment procedures developed in this project do not entail significant cost to the companies, besides slight losses of productivity associated to enhanced preparation times.

Consequently, coating treatment costs are dominated by that of the coating agent. These agents were selected such that they are currently available in large quantities and their cost is affordable. The extra costs (%) of the coating agent treatments for the different SMEs, ranges in the following figures:

- PTMO: 1.9 - 9.3 %
- SIVO160: 1.0 - 5.0 %

Side-effects of the coating treatments were also considered, for example a reduction of the amount of deflocculant needed in some cases.

This project aims at encouraging sensible European standards for RCS based on scientific evidence, ensuring that future proposed concentration limits will result from scientific data and correlations established between surface chemistry and toxicological studies. This information has been communicated to SCOEL, labour unions and health and safety executives through the SME-AGs project partners. At the present time, specific European legislation regarding RCS exposure does not exist. However, Directives 98/24/EC (chemical agents at work) and 2004/37/EC (carcinogens) state that not only it is desirable to eliminate the risk associated with the usage of a dangerous substance, but it is preferred from other protection measures, i.e. of corrective nature. Silica is an essential component of the concerned products and processes that cannot be eliminated and SILICOAT project is clearly linked with the improvement of the working conditions, dealing with the avoidance of a very serious hazard (cancer risk) by preventing it from the substance itself.

2 Dissemination activities
As a general approach, in order to disseminate project results as widely as possible, numerous dissemination routes were planned.

Training activities
SME-AGs and SMEs have benefited from dedicated training sessions in which the results obtained by the RTDs were communicated. All the RTD performers contributed extensively to this knowledge transfer, preparing the training material and/or executing the training sessions.
Dissemination to the industrial sector
SME-AGs were in charge of communicating the new safe process to their members. The actions undertaken in this sense have been the following:

• Organisation of seminars or workshops in the partners’ countries by the different SME-AGs in which the new technology has been presented to a diverse audience of technicians, industries and academics functioning as multipliers. These actions have the advantage over publications in devoted journals of enabling direct contact to be established with companies and other actors that might be interested in the exploitation of the project results.

• Publication of a final project newsletter, presenting the project clearly and concisely, explaining its objectives, scope, results and the potential exploitation of these results, which has been sent out to the companies.

• Publication of the most important results will be published in journals widely read by the technicians: cfi/Ber. DKG 92 (2015) No. 1-2, E63-E69 (in press).

• Presentation of the project at different international trade fairs: CEVISAMA (Valencia, Spain), CERSAIE (Bologna, Italy) TECNARGILLA (Rimini, Italy).

Key results of the project have been communicated to European Cerame-Unie, umbrella organisation with an overview of the whole ceramic industry capable to act as the mouthpiece of around 2000 ceramic companies.

External Dissemination
During the first stages of the project, dissemination of information about the project has been remained limited, until the project became mature enough for the results to be sufficiently comprehensive. Nevertheless, during the last stages of the project, and when intellectual protection was effectively ensured, several dissemination actions have been carried out through different channels:

• SCOEL and other regulatory bodies. Project results have been communicated to SCOEL, labour unions and national health and safety executives through the project partners, i.e. the SME-AGs.

• European Network on Silica (NEPSI). It is probably the most suitable forum for performing such dissemination. NEPSI gathers 18 European industrial sectors, for which silica is an indispensable component, representing more than 2 million employees. The new technology for making ceramic processes intrinsically safe has been communicated and, if possible, this technology will be included into its Good Practice Guide.

• Scientific Journals: Some scientific papers are being prepared for publication in national and international scientific journals, although, owing to the fact that the main results and conclusions of the project have been obtained in the last period, there was not enough time to finish them for this report.

• Participation at conferences, seminars and similar events related to ceramics, toxicology and particle technology, such as: Conference and Exhibition of the European Ceramic Society (ECERS), World Congress on Ceramic Tile Quality (QUALICER), European Congress on Advanced Materials and Processes (EUROMAT), German Society for Experimental and Clinical Pharmacology and Toxicology (DGPT).

• A website dedicated to the SILICOAT project has been created (http://www.silicoat.eu). Indeed, all the project partners have published references to SILICOAT in their websites

• Video Clip. A very didactic video clip, summarizing the project and addressed to the general public, has been made: (https://www.youtube.com/watch?v=B-kq-bOcaOk).
Exploitation
In order to carry out the work plan of the project, previous background knowledge was required from the partners. The Consortium agreed to share part of this knowledge to be used in the project with royalty free access for the partners. All the preexisting know-how is exclusive property of the owning partners. Due to the nature of this project, the consortium has agreed not to exploit economically the results obtained. Since this project is linked with health issues, the exploitation is addressed to dissemination activities and to share the knowledge obtained within the sector affected.

The collaboration of the RTD performers with the SME-AGs and other enterprises has allowed creating foreground knowledge which will be exploited by SME-AGs and SMEs participating in the project. Several solutions or results have been identified:

• Database ranking toxicity of the quartz varieties used by the SMEs.
• New silica detoxification agents.
• Process behaviour of the coating agents added to the body compositions.

List of Websites:
Public website: [http://www.silicoat.eu](http://www.silicoat.eu)

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Verwandte Dokumente

[final1-silicoat-final-leaflet-web.pdf](file)

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