Material emission for controlled environments used in space, semiconductor and medical device industries

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Abstract
Materials implemented in controlled environments used in space, semiconductor and medical device industries need to be assessed for VOC emissions and classified in order to permit direct comparisons to be made and to select material without any emission of process critical contaminations, such as phthalates, siloxanes and organophosphates. The newly described method uses a holistic approach. First, emission testing is done using a micro chamber and analysis via thermodesorption coupled with gas chromatography and mass spectrometry. The resulting material classification enables a material selection already in the planning phase of a cleanroom. Then a simulation model for cleanroom settings enables the user to estimate the expected VOC-level of the environment to be constructed depending on the selected materials. Two different cleanroom settings (Space technology and research cleanrooms) were planned and built for low VOC concentration using classified materials depending on their outdoor environment. The final VOC concentration is verified to the prior defined specifications.

1. Introduction

Chemical surface contamination is becoming an increasingly important issue in controlled production environments for space, semiconductor and medical device industries [1]. The contamination concerned may be caused by the adsorption of chemical compounds in gaseous form. Many materials emit gaseous chemical substances into the atmosphere [2] that lead to chemical surface contamination with major consequences for industrial processes [3].
The structures on semiconductor wafers range in the dimensions of single molecules [4]. In order to keep pace with decreasing structure widths in semiconductor manufacturing, the reproduction accuracy of lithographic units has to be constantly optimized. The tool life of lithographic masks can be drastically reduced due to the deposition of VOC [5] leading to tiny reproduction errors. Organic compounds and phthalates have been identified as causes of fogging on lenses [6]. Airborne chemicals can lead to nanoscale particle formation on surfaces known as time dependent haze [7]. Re-agglomeration can lead to larger particles [8]. Organophosphates can cause wrong doping of wafers [9]. Photoresist coatings may become so badly damaged by condensed amines that it is impossible to subsequently expose it correctly [10]. Outgassing phthalates from polymer materials used for wafer transport boxes can lead to severe damage [11]. Siloxanes can alter the wetting characteristics of wafer surfaces [12].
Airborne contamination by chemicals (ACC) has to be reduced to a minimum. In consequence, the requirements for cleanrooms with a defined high degree of chemical indoor air quality (IAQ) are constantly rising. The IAQ in a cleanroom is mainly influenced by the contamination potential of used materials. ACC are given off into the surrounding atmosphere by building products [13]. Materials with large surface areas (floor, wall, ceilings) or with a known high emission potential (sealants, adhesives and plastics) have to be especially considered for their outgassing potential [14]. Material outgassing contaminates the manufacturing environment with ACC. One of the most discussed critical ACC-groups are volatile organic compounds (VOC), especially reactive VOC species as amines [15, 16]. Other substance classes critical to semiconductor processes as amines, organophosphates,

phthalates and siloxanes [17] need to be controlled and minimized. Increased IAQ without critical contaminants can be attained by implementing materials with low outgassing characteristics that do not emit any of the above-named critical compounds [18]. Alternatively, the recirculated air can be ACC-filtered [19]. However, the average ACC reduction rate of 90 % for VOC air filters is low.
Consequently, planners of cleanrooms have to know about the outgassing behavior of each material. Well-known certification schemes for the assessment of VOC-emissions from building products lead to a yes/no decision for accreditation purposes and not to a detailed final outcome [20]. Standard methods for building products refer to an air exchange rate of 0.5 h^{-1} (ISO 16000-9) and can't be transferred to cleanroom applications with a circulation air exchange rate of up to 800 h^{-1} [21]. Different air exchange rates result in different emission behavior of materials [22]. Different emission chambers sizes result in a variation of the final result up to 60 % [2]. This has led to the development of a new method presented here for classifying gaseous emissions from cleanroom suitable materials [23]. The method is based on a micro emission chamber test first described by Schripp et al. [24] and standardized in ASTM D5116 [25]. Currently available dynamic IAQ simulation models refer to living houses and offices and can't be used for cleanroom applications [26]. Therefore, a calculation model for cleanroom applications with high air exchange rates and ACC-filtration techniques needs to be set up.
The presented method begins with the preparation and storage of the sample materials. Sampling and analysis procedures are then explained. A standardized key figure is then determined to classify the materials. An extended simulation model previously verified by experiment demonstrates the influence of ACC emissions from materials on the quality of air in cleanrooms. From the test results obtained through application of the method, two new manufacturing environments with reduced ACC levels have been planned and built. Tests carried out on the newly-built cleanrooms demonstrate the success of the targeted selection of materials in attaining optimized air quality as far as organic chemicals are concerned.

2. Methodologies

2.1. Material Classification

Material samples were prepared according ISO 16000-11 [27] and stored for 28+-2 days in a mini-environment at 23 °C and 45 % rel. humidity. To avoid VOC cross-contamination, the minienvironment is equipped with a filter-fan-unit and activated charcoal filtration with unidirectional air flow from the top to the perforated bottom (M+W Products GmbH, Stuttgart). A thermostatted micro emission chamber µCTE120 is used for the material emission assessment (Markes, Llantrissant) with automation kit [28]. Quantitative VOC classification measurements were done using humidified ultrapure nitrogen 5.0 at 23 °C and 45 % rel. humidity with a preconditioning time of 5 min and a sampling duration of 60 min. Qualitative emission screening regarding the critical contamination groups of siloxanes, some amines, phthalates and organophosphates was done at 90 °C directly after the classification measurement using the same sample. All emissions were trapped using stainless steel Safe-Lok adsorber filled with und mit Tenax TA (Markes, Llantrissant) and subsequent analyzed using TD-GC/MS by using the method described in standard VDA 278 [29]. Used TD-GC/MS instrumentation, all from PerkinElmer: Clarus 600T with Turbomatrix ATD 650; column: Elite 5-MS, l = 60 m, ID = 0.25 mm, film = 0.25 µm.Obtained surface emission rates SER_a at 23 °C are converted into a material classification ISO-ACC_m-class N (VOC) using the logarithmic value of the SER_a (in g/m^2s) with one decimal place (Gommel et al. 2012).

2.2. Dynamic model

Due to their high air exchange rate, cleanrooms can be modeled as continuous stirred tank reactor [30]. The following formula 1 based on the equation for non-ACC-filtered cleanrooms [28] considers possible ACC-filtration of the inlet and recirculated air flow. Following variables are used: exposed material surface area A, ACC-concentration c, filter efficacy η, flow rate of fresh air F, relation factor

between F to the recirculated air flow $\alpha = F_{recirculated\ air}/F$, time t after changed emission characteristics and the surface specific emission rate SER_a.

$$c_{indoor}(t) = \left[c(t=0) - \frac{1}{1+\alpha\cdot\eta}\cdot\left(c_{outdoor}\cdot(1-\eta) - \frac{\sum_{i=1}^{z}(SER_a\cdot A)}{F}\right)\right] e^{-\frac{F}{V}(1+\alpha\cdot\eta)\ t} + \frac{1}{1+\alpha\cdot\eta} \cdot\left(c_{outdoor}\cdot(1-\eta) + \frac{\sum_{i=1}^{z}(SER_a\cdot A)}{F}\right)$$

Formula 1. Dynamic model to estimate the indoor ACC concentration in a controlled environment (IAQ of a cleanroom)

2.3. TVOC-Assessment of newly built cleanrooms

The TVOC-values of a laminar and a turbulent cleanroom especially designed for very low VOC contamination were determined according ISO 16017-1 [31] by air sampling for four hours with a sample air flow of 100 ml/h directly after end of construction. The following picture illustrates the different air flow pattern present in laminar and turbulent air flow cleanrooms:

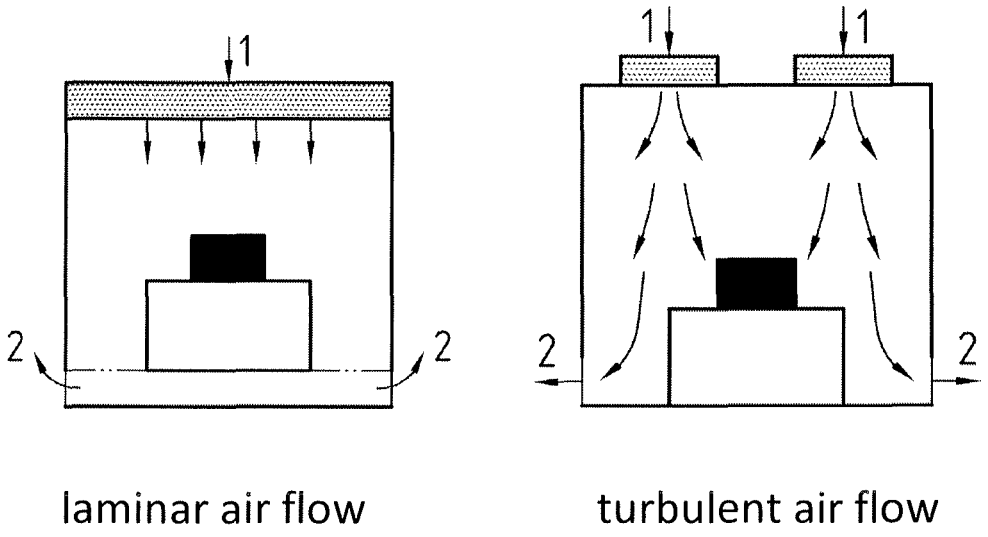


Figure 1: Air flow profile in different cleanroom settings 1: air inlet, 2: air outlet.

The newly built ISO class 7 (ISO 14644-1) cleanroom at Fraunhofer IPA, Stuttgart with 48 m^2 floor and ceiling surface, 91 m^2 wall surface und 144 m^2 Volume is operated with a turbulent air flow pattern with an air exchange rate of 30 h^{-1} and 2 % fresh air inlet, all not VOC-filtered. The used materials for the walls and ceiling are powder-coated panels with an anodized aluminum frame and glass windows. The floor is an extremely low outgassing PVC sheet material. As sealant, low-outgassing materials without any emissions of silicones are used. The selection of the material was done using the formula and defining limit values for material emissions. The location of the cleanroom represents a typical rural inland setting. TVOC-values were measured during 106 days after completion of construction in spring 2011. During the measurement campaign, personnel were only entering the cleanroom for installing the adsorber tubes for VOC measurement for maximum 5 min. At the end of the measurements, outdoor TVOC-values were measured onto the roof of the cleanroom building.

The new ESA-ESTEC cleanroom built for the Exo-Mars project is situated at the European Space Research & Technology Center directly at the coast of the north sea. The particulate cleanliness level

equals class ISO class 1. The dimensions are 58 m^3 floor and ceiling surface, 59 m^2 wall surface und 173 m^3 Volume. The cleanroom is operated with a laminar air flow pattern with an air exchange rate of 280 h^{-1} and < 2 % fresh air inlet, all not VOC-filtered. The used materials for the walls are mainly glass supported by an anodized aluminum frame. The lower concrete floor is coated with Sikafloor-269 CR ECF. The hollowed raised floor panels made of aluminum are covered with sheet flooring system showing extremely low VOC-emisssion during the material tests. As filtration media for the recirculated air, U16-filters made out of polytetrafluorethylene (PTFE) with very low VOC-emissions are used (MEGAcel, AAF International, Luisville)

3. Results and Discussion

3.1. Material classification

Following materials are classified according the described method [32]. The presence of amines, siloxanes and phthalates in traces or significant amounts is expressed using the SER_a values obtained from the emission measurements at 90 °C. The values at 90 °C can´t be taken for calculation purposes, but only for comparison between the materials.

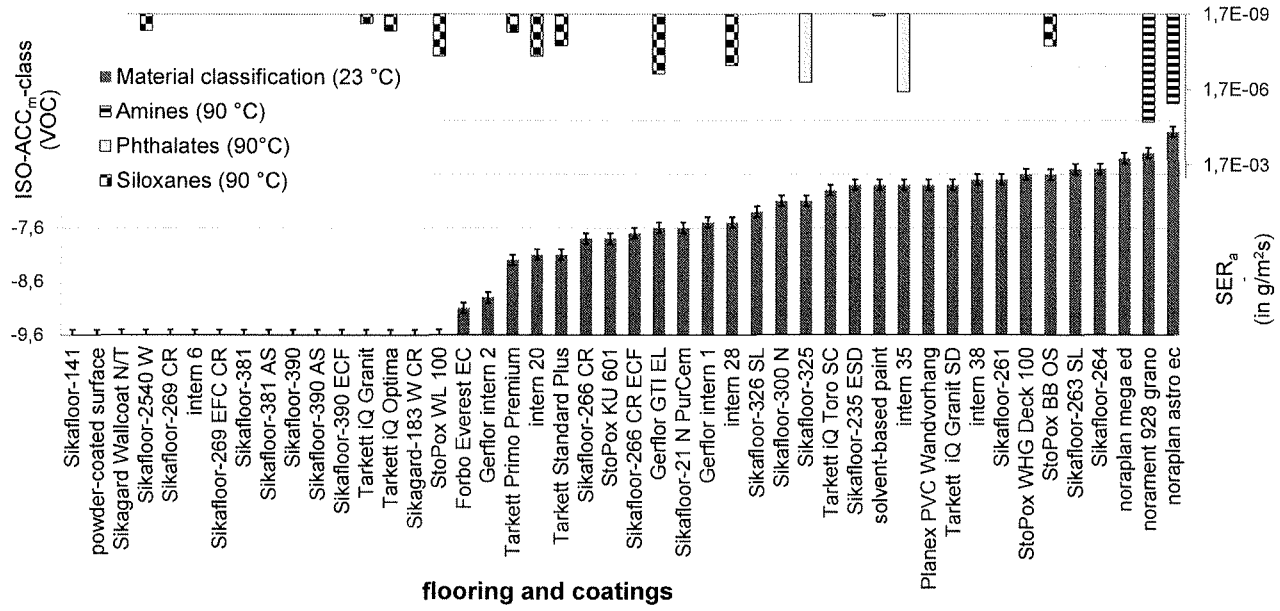


Figure 2: ISO-ACC_m-Classification for VOC (23 °C measurements) and SER_a-values for amines, phthalates and siloxanes (90 °C measurements) regarding flooring and coatings

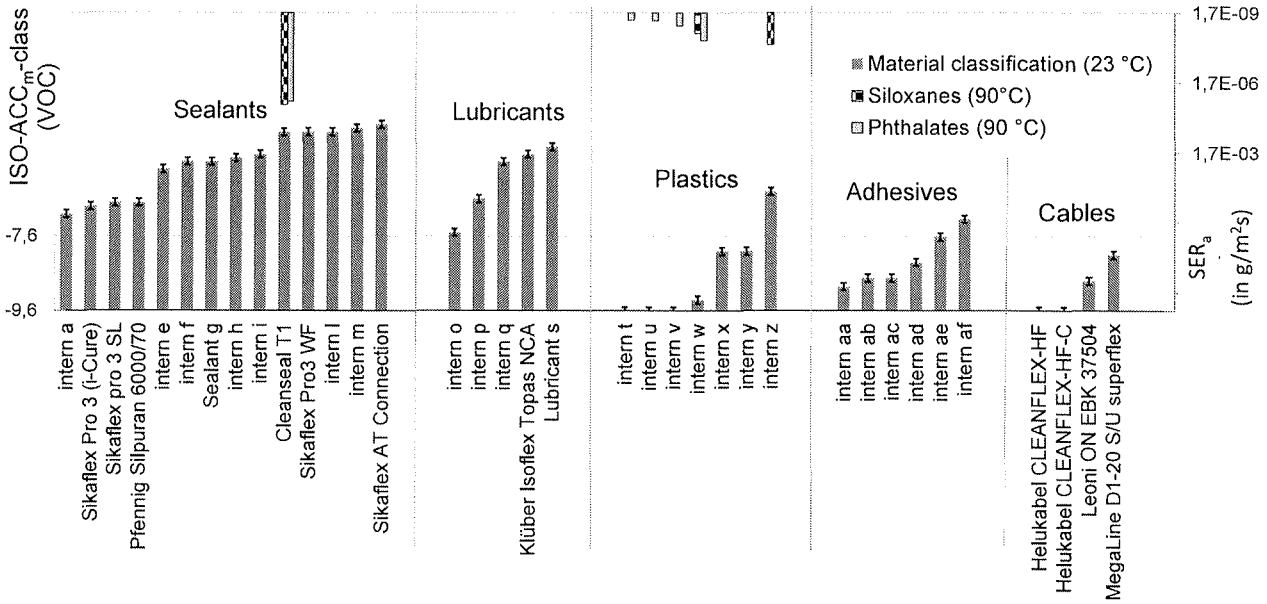


Figure 3: ISO-ACC$_m$-Classification for VOC (23 °C measurements) and SER$_a$-values for amines, phthalates and siloxanes (90 °C measurements) for sealants, lubricants, plastics, adhesives and cables. The presence of amines could not be detected at any tested samples.

None of the materials showed trace emissions of organophosphates. The limit of quantification is ISO-ACC$_m$-class -9.6 (VOC) for the measurement at 23 °C and SER$_a$ = 1.7 · 10^{-9} g/m^{2}s at 90 °C. Error bars refer to a standard deviation of 0.1 ISO-ACC$_m$-classes (VOC), defined by previous repetitive measurements [18]. Not all materials tested at 23 °C were subsequently tested at 90 °C (either no need as the chemical composition is well known or degradation of the material at 90 °C).The classified materials show a huge difference in VOC emissions at 23 °C. For many materials especially designed for cleanroom applications, no VOC emission could be detected at all. Regarding the critical substance groups, organophosphates could not be detected at all. Several of the tested materials contain traces of amines, siloxanes or phthalates. These materials can´t be used if a detected presence of a critical substance group is in conflict with possibly defined material requirements for a cleanroom to be built.

3.2. TVOC-Assessment of newly built cleanrooms

The following diagrams show the detailed results of TVOC-measurements for the turbulent cleanroom:

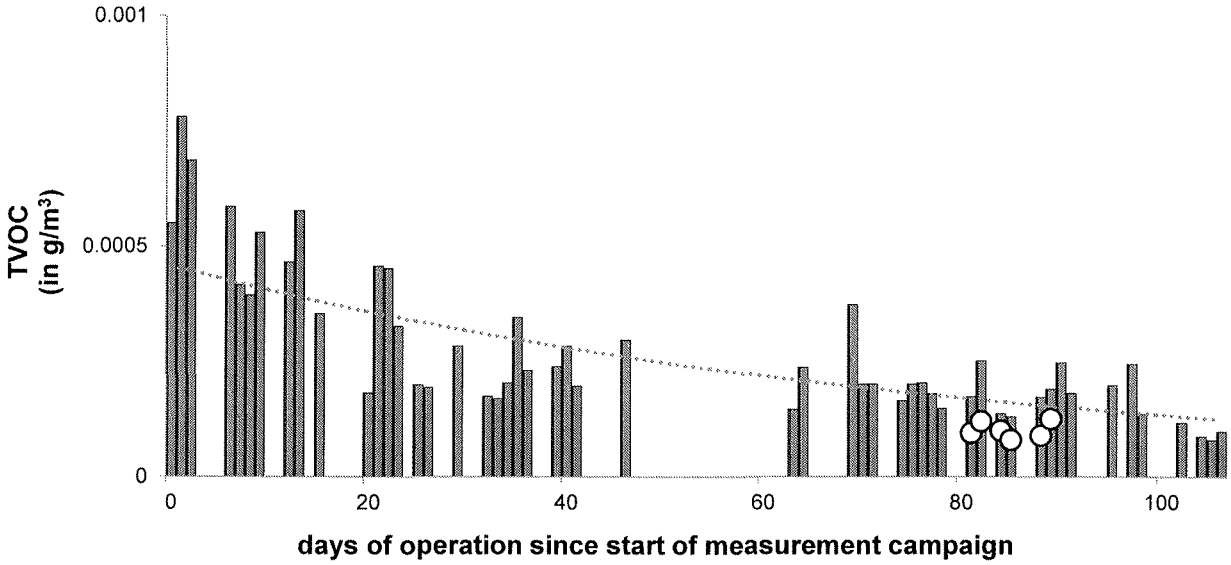


Figure 4: Results of the TVOC assessment of the turbulent cleanroom at Fraunhofer IPA and the corresponding outdoor air quality (O) during 6 days. The regression curve (••••) based on the individual TVOC values showed an exponential decrease with a R2-value of 0.63.

Although the TVOC-values vary significant from day to day, the initial TVOC-concentration of the turbulent cleanroom at Fraunhofer IPA can be expected as three times higher as value after 60 days of operation, which equals the measured outdoor air quality. The outdoor air quality varies during sping → summer → autumn less than 20 % (Cheng et al. 1997), so this variation can´t be the reason for the initially increased TVOC-value. Chemicals with major amount are xylene, butylated hydroxytoluene (BHT) and alkanes not present in equal quantities in the outdoor air. The presence of these airborne chemicals are based on material emissions (solvents) and decline over time until, after 80 days, their value reaches background values. After 80 days, the indoor air quality regarding VOC equals the outdoor air quality. Without additional VOC filtration techniques, a further reduction of the TVOC-value is not possible.

During another measurement campaign as part of qualification measurements directly after completion of the laminar cleanroom at the European Space Research & Technology Center in Noordwijk, the measured TVOC-concentration in the cleanroom (N = 6) equals the measured outdoor TOVC-values. The building material selection for the cleanroom regarding low VOC emission resulted in – if present – not detectable influence of possible material emissions to the overall indoor air quality. Compared to the outdoor TVOC-values at the inland rural setting of average 100 µg/m^3, the measured outdoor TVOC-values directly on the coast were 10 times less with average 10 µg/m^3. Therefore, the maximum possible indoor air quality regarding VOC for controlled environments on the coast is without any VOC-filtration ISO-ACC class -5 (VOC) and thus one ISO-ACC-class better as in rural inland settings with ISO-ACC class -4 referring to the measurements at the premises of Fraunhofer IPA.

4. Conclusions

SER_a-values for VOC-emissions vary over five decades regarding different building products defined for cleanroom applications. Some of the tested materials even showed no VOC-emission at all 30 days after preparation. Regarding the indoor air quality for VOC of cleanrooms, materials with large surface areas (floor, wall, ceiling) and materials with by nature higher emission rates (sealants, adhesives) have to be focused on during material selection. Some materials contain substances regarded as critical for sensitive manufacturing processes, such as amines, phthalates and siloxanes. Therefore, these materials can't be used if an exclusion criterion for the usage of materials containing one of the mentioned compounds is defined by the operator. None of the tested material contains volatile organo-phosphorous compounds. Appropriate material selection with regards to low VOC emissions results in cleanrooms with low airborne organic contamination. If only materials with extremely low outgassing behavior are selected, the influence based on material emissions to the overall indoor air quality can be neglected. The maximum reachable indoor air quality without VOC-filtration equals the TVOC-value of the surrounding outdoor air. Further improvement of the TVOC-values in controlled environments such as cleanrooms can only be made by using appropriate VOC-filtration techniques.

However, if material outgassing results in elevated TVOC-values, the indoor air quality can be improved by increasing the rate of fresh air introduced into the cleanroom. But this results in higher energy consumption, as fresh air has to be conditioned to 23 °C and 45 % relative humidity. This fact illustrates that appropriate material selection is one of the major key factors for energy efficient cleanrooms with low TVOC-values.

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