

Summary of evidence – solvent-based hydrophobic coatings and risks for acute respiratory toxicity

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Water repellent coatings are increasingly used by different industries to reduce water and dirt sticking to surfaces. The coatings can be applied by processes that minimise the risk that operators inhale the product but there is evidence that some products are applied by spraying, creating an inhalable mist.

This review examined evidence about these coatings and whether lung disease occurs when applied by spraying. Scientific studies on the hazardous properties of these products, and clinical studies reporting lung disease in people using them, were considered.

A consistent finding was that some people develop an acute lung inflammation when applying these coatings by spray misting. Studies across Great Britain, Europe and the United States reported several hundred cases of serious lung disease and some fatalities, mostly in consumers applying such products using pressurised spray cans in poorly ventilated spaces. Experimental studies suggest that the different water repellent ingredients and solvents in which they are dissolved combine to damage the delicate lining of the lung.

Smart surface coatings offer many industrial and societal benefits. However, they should be applied by methods that minimise the risk of inhaling the product.

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Summary of evidence – solvent-based hydrophobic coatings and risks for acute respiratory toxicity

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KEY MESSAGES

- Evidence from published research supports concerns that some solvent-based ‘water-repellent’ coatings are hazardous to the lung and that applying these coatings in fine sprays increases the risk for inhalation.
- These coatings are applied to glass windows as well as other materials to enhance water repellency and to reduce dirt sticking to surfaces. In window manufacture these coatings are usually added during manufacture and the glazing industry guidance advises their application by methods that minimise the risk for inhalation.
- There is consistent published evidence from many countries that inhalation in fine mists of some water-repellent coatings can cause an acute inflammation of the lung. Hundreds of cases of acute illness have been reported, and some fatalities involving consumers, since these products were first introduced over thirty years ago.
- Incidents to consumers involved using water repellent coatings to treat clothing, furniture, or footwear. Occupational cases were associated with the application of coatings to floors.
- The most severe cases were associated with spraying the coatings in confined spaces with poor ventilation.
- Experimental studies showed that water repellent coatings applied with spray-misting devices, or propellant cans, created large numbers of particles sufficiently small to enter the lung.
- The acute inflammation of the lung is likely to be caused by the combined toxic effects from water repellent chemicals and their solvents.
- These chemicals are thought to disrupt the fluid ('surfactant') lining that protects the delicate gas exchange surfaces of the lung leading to an acute inflammation.
- Appropriate measures need to be implemented to minimise the risk for occupational exposure by inhalation to hydrophobic coatings.
- Smart surface coatings offer many industrial and societal benefits. However, as this technology develops the hazardous nature of these coatings may change and dutyholders will need to take this into account when they assess the risks associated with the application of these coatings.

EXECUTIVE SUMMARY

This document has been prepared to consider published information about solvent-based hydrophobic coatings that are being applied to glass during manufacture of windows. Some hydrophobic products have been reported to cause acute lung inflammation and injury in exposed individuals. These products may contain high concentrations of solvents (up to 90% of the content) and these can add to the overall toxicity of the inhaled mixture.

International scientific databases were searched from 1990 to 2015 for peer-reviewed studies of ill health attributed to exposure to hydrophobic coatings and this search included experimental toxicity studies of hydrophobic coatings. The conclusions were as follows:

- There is consistent evidence from incidents with consumers and occupational groups that inhaling hydrophobic coatings causes an acute inflammation of the respiratory tract in some individuals. This outcome is not limited to perfluoro-octyltriethoxysilane (PFOTS) coatings and other types of hydrophobic coatings have caused respiratory inflammation.
- In the last 30 years in Europe and America, several hundred cases of severe and acute respiratory illness were reported mostly in consumers using hydrophobic ‘spray on’ fabric coatings. Most cases required hospital admission and some incidents involved a fatality.
- Experimental animal studies have shown specific hydrophobic chemicals and solvents used in glass coatings cause acute lung toxicity. A smaller number of occupational cases of acute lung inflammation in workers applying these coatings were published.
- The evidence suggests that acute lung inflammation and injury is caused by the combined toxicity of hydrophobic chemicals and solvents. Ultrafine particles (smaller than 100 nanometres) composed of surface- modified synthetic or amorphous silica may also be added but their contribution to the toxicity of these mixtures is an area of uncertainty.
- Not all individuals show the same adverse reaction suggesting that some are predisposed to react more acutely when they inhale these products.
- Most cases in consumers of acute respiratory illness were caused by spraying in confined spaces with poor ventilation. Applying hydrophobic coatings using spray applicators close to the breathing zone increases the risk for acute inflammatory reactions in the lungs.
- Not all of the reported incidents of respiratory inflammation were caused by exposure to sprays; some individuals developed an adverse reaction after being exposed to freshly applied coatings.
- Hydrophobic coatings containing PFOTS in a solvent base are acutely toxic to the respiratory tract in mice according to published experimental studies.

- Experimental studies comparing ‘hand-held’ misting devices versus propellant gas-driven misting devices, found that the propellant systems produced large numbers of respirable and ultrafine particles sufficiently small to enter the conducting airways and gas exchange surfaces of the lung.
- Recent experimental studies demonstrated that hydrophobic chemicals and solvents used in products that are applied to glass surfaces can disrupt the fluid surfactant layer that protects the delicate gas exchange surfaces of the lung, causing an acute inflammation.

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1.0 Background

This review has been prepared to consider the published evidence about the toxicity of hydrophobic (water repellent) coatings applied to window glass. There have been many reported cases of an acute respiratory inflammation, including fatalities, in consumers who breathed in different hydrophobic products used for glazing as well as in other circumstances. However, recent studies have considered the toxicity of hydrophobic coatings composed of perfluoro-octyltriethoxysilane (PFOTS) in a solvent base (ethanol or isopropanol) which are used in products applied to glass.

The current revolution in smart surface- coating technology offers many industrial and societal benefits. Hydrophobic coating technology was developed several decades ago, but this technology is constantly undergoing innovation including nanoscale patterned coatings to create high surface contact angles to enhance water repellency

An ongoing issue from the reported cases of acute respiratory inflammation is that application of these products using propellant cans or hand-misting devices generates fine mists which readily penetrate to the gas exchange surfaces of the lung.

The specific issue is:

- That hydrophobic chemicals and solvents may cause acute inflammation and lung injury if they are applied to window glass surfaces using misting devices (either mechanical or propellant-driven) without using suitable control measures to minimise the risk for inhalation.

Many types of hydrophobic coatings are used in fabric manufacture (water and dirt repellent), construction work (clean surfaces, anti-graffiti), for transport vehicles (antifouling), or in engineering processes (reducing biofilm in pipes). Many cases of acute respiratory inflammation, and on occasion fatalities, have been reported mostly in consumers but also some employees using these products. Most cases occurred in Europe or the United States with only a few cases reported from Great Britain (GB).

Based on peer-reviewed research the key hazards and risks have been identified as follows:

- The chemicals in solvent-based hydrophobic coatings can disrupt the protective fluid surface of the alveolar gas exchange surfaces (alveoli) of the lung causing an acute inflammation and injury.
- Organic solvents used to disperse hydrophobic coatings may contribute to the overall toxicity of this mixture.
- Acute respiratory inflammation mostly occurred when users applied these products using mechanical or propellant sprays which produced mists containing large numbers of ultrafine particles sufficiently small to reach the gas exchange surface of the lung.
- Cases of acute respiratory inflammation typically occurred when users sprayed hydrophobic coatings in confined spaces without adequate circulation of air.

One compound, polyfluorooctyl-triethoxysilane (1H,1H,2H,2H-perfluorooctyl triethoxysilane), has been banned in Denmark and its use is restricted in Canada¹. No such restrictions apply in Great Britain (GB). Wider concerns about the toxicity of perfluorinated organic polymers to humans, to the food chain, and to the wider environment, have also prompted some countries to review the wider risks (Lassen C *et al* 2013; Borg D and Håkanson H: 2012; Posner S *et al* 2013).

This summary considers the published evidence about risks to health from exposure to hydrophobic chemicals. After extensive searches, only a small number of published studies had specifically examined exposure to PFOTS. Therefore, studies about similar hydrophobic coatings reported to cause acute respiratory inflammation were also included in the review as they shared common elements. Animal toxicology studies were included because they provided evidence on the potential mechanisms of lung toxicity and the impact of spray misting on the risk of inhaling these products.

1.1 Hydrophobic coatings and perfluorinated polymers

Polyfluorinated organic compounds are based on the replacement of hydrogen atoms in the carbon aliphatic chain by fluorine; compounds in which all of the hydrogen atoms have been replaced are termed perfluorinated. The high proportion of fluorine in the organic molecule creates a water repellent hydrophobic/oleophobic ‘tail’. Polyfluorinated organic compounds do not occur naturally and have been manufactured for 50 years.

Perfluorinated-silanes are part of larger group of polymers based on fluorination of organic and inorganic chemicals. There are many different applications for fluorinated polymers (see Table 1) including surface coatings. For some of these compounds there is sufficient evidence to support wider concerns about their toxicity to humans, to animals, and to the environment.

This summary focusses on a specific group of perfluorinated compounds used in solvent-based hydrophobic coatings applied to substrates like glass. This technology is not new and is based on developments made over two decades ago. However, smart surface-coating technology is constantly being modified using novel chemistries including addition of ultrafine surface-modified silica particles to increase the surface contact angle and reduce the ‘wettability’ of treated surfaces. Some distributors of hydrophobic coating products claim that their products are based on ‘nanotechnology’ with very small nano-particles added to increase the contact angle. It is not clear yet whether these ultrafine particles contribute to the overall toxicity of hydrophobic coatings in the lung.

¹ Guidance on alternatives to perfluoro-octane sulfonic acid, its salts, perfluoro-octane-sulfonyl fluoride and their related chemicals Second revised draft: 26 (April 2013) (www.chm.pops.int/)

Table 1 Examples of the wider groups of fluorinated organic polymers

Main group	Examples	Uses
Fluoropolymers: Carbon only polymer backbone with fluorine atoms attached to backbone of carbon atoms	Polytetrafluoroethylene (PTFE) Polyvinylidene fluoride (PVDF) Polyvinyl fluoride (PVF) Fluorinated ethylene propylene (FEP)	Plastics for a variety of uses The fluorine atoms provide these plastics with a high thermal and chemical resistance as well as other properties. Safety concerns relate to the emission of polyfluoroalkyl substances and impurities from non-reacted raw materials
Perfluoro-polyethers (PFPEs): Ether polymer backbone with fluorine atoms directly attached to backbone of carbon atoms	Polymers, in whose backbone CF_2 , CF_2CF_2 , and possibly $\text{CF}(\text{CF}_3)\text{CF}_2$ units are separated by oxygen atoms	Functional fluids, surfactants, and surface protection products
Side-chain-fluorinated polymers: Non-fluorinated polymer backbone with fluorinated side chains, ending in $-\text{CnF}_2\text{n}^{+1}$	Fluorinated acrylate and methacrylate polymers Fluorinated oxetane polymers Fluorinated urethane polymers	Surfactants and surface protection products e.g. waterproofing, stain proofing and grease-proofing finishes for textile, leather and paper surfaces Surfactants and surface protection, mainly for textile products Offered in many forms and functionalities primarily as fluoro surfactants and coatings additives

Taken from Lassen C *et al* 2013

2.0 Sources of Evidence and Search Terms

To summarise the evidence for risks to health a thorough search of the peer-reviewed literature from 1990 to 2015 was undertaken using several search engines for published research in chemical, biological and health sciences. Government and industry technical reviews were included. The search terms and search engines used are summarised below in Tables 2 and 3.

Table 2 Search terms

Major term (combined with major	Sub terms terms or sub terms)
Coating* (s)	Monolayer, bilayer, composite, organic / inorganic hybrid, sol:gel
Hydrophobic* (ity)	Water-repellent, waterproofing,
Glass	Glazing, windows,
Fouling	Anti* (-fouling)
Poly* (mer) (s)	Co-polymer Perfluor* (inated, ination etc..) Silane* (s); siloxanes* (s); silicate*(s), silicone*(s) Alkoxy
Solvent	Ethanol, Isopropanol, heptane, ethyl acetate, volatile
Propellant* (s)	Gas
Respiratory	Lung* (s), alveol* (i,ar), bronch* (l, ioles), Pulmonary, Chest
Disease* (s)	Acute, respiratory, distress, syndrome (ARDS) Reactive, airway, disease Cough, wheez* (e, ing), Dyspn(o)ea Hypoxi* (a, c) Bronch* (ial, iole) Injury Symptom*(s)
Toxic* (icity)	Cytotoxic* (ity) Inflammat* (ory, ion) Irritat* (ant, ion)
Spray (s, ed)	Mist* (s, ing), aerosol* (s) cloud* (s), particle*(s), ultrafine* (s), nanoparticle * (s)

Table 3: Search engines

Search engine	Address
Web of Science	http://pcs.webofknowledge.com/
ToxNet	http://toxnet.nlm.nih.gov/
Pubmed	http://www.ncbi.nlm.nih.gov/pubmed
Science.gov	http://www.science.gov/
Google and Google Scholar	https://www.google.co.uk/
Haz-map	http://hazmap.nlm.nih.gov/

The searches located some peer-review studies about respiratory toxicity in humans (or relevant animal test species) caused by exposure to perfluorinated-silanes. Most of the published studies concerned perfluoro-organic compounds used for other applications and outside of the scope of this summary. Studies about respiratory toxicity of different hydrophobic coatings applied by spraying were included for consideration.

2.1 Contextual information

Hydrophobic coatings

There is an ‘ever expanding’ list of hydrophobic coating technologies including those based on manganese oxide polystyrene (MnO₂/PS) composites, zinc oxide polystyrene (ZnO/PS) composites, precipitated calcium carbonate, carbon nanotube structures and silica coatings (Lathe *et al* (2012). This technology is expected to bring economic and societal benefits for example, reducing costs associated with operating or maintaining machinery; reducing risks for transmission of infective agents from surfaces in healthcare settings (see Table 4). Different technologies have also been developed to coat the surface of glass to repel water and dirt, and this is being used in window manufacture.

Hydrophobicity is demonstrated when water droplets form a contact angle greater than 90° or more from the horizontal surface of the glass (based on the ASTM C813-90 test method²). It is unlikely that any of these current glass-coating technologies provide permanent hydrophobic properties and their duration depends on their chemistry, method of application, and the environment conditions such as levels of ultra-violet light, temperature and surface abrasion.

Three different technologies are generally used for hydrophobic treatment of glass; dried, or cured forms (a cross-linked surface layer that chemically bonds to the surface forming a multi-molecular structure); direct bonding to the surface (forming a mono-molecular structure); and those which deposit as a coating. Silicone polymers (e.g. polydimethylsiloxane - PDMS) form mono-molecular layers whereas ‘sol-gel’ technologies form a bi-layered structure *in situ* composed of organic and inorganic components. Bi-functional silane coatings which assemble *in situ* form a mono-layered hydrophobic

² <http://www.astm.org/Standards/C813.htm>

surface. The range of methods for producing hydrophobic coatings has been extensively summarised by Latthe SS *et al* (2012).

Technology used in perfluorinated hydrophobic coatings:

The sol-gel coating process (Hench and West 1990) employs perfluorinated organic molecules attached to silane groups providing a hydrophilic (silane group) and hydrophobic domain (the perfluorinated organic moiety). When applied to a glass surface the solvent evaporates and the polymer self assembles to form a highly orientated layer with the hydrophobic domain facing away from the surface of the glass

Table 4 Examples of industrial and other applications of hydrophobic coatings

Application	Benefits
Bio-fouling	Marine applications to reduce operational and cleaning costs for shipping Medical and health applications such as those preventing adherence of bacteria and micro-organisms to surfaces
Pipe Corrosion and chemical fouling	Reducing corrosion effects on pipes as well as reducing fouling on the outside and inside of piping
Bridge and metalwork corrosion	Reducing corrosion and prolonging painted surfaces
Protecting power lines	Reducing water attachment and ice formation on power lines
Anti-condensation	Reducing condensation in electrical equipment and growth of mould in confined spaces
Anti-friction	Enhancing movement of components by preventing surface fouling that increases resistance
Chromium plating	Replacing the need for hexavalent chromium in surface treatments of metal
Anti-clotting	Preventing blood clotting in tubing or containers when used for transfusion
Fabrics	Producing stain resistant and water repellent materials
Sealants	Producing water- repellent sealant materials
Evaporative desalination	Reducing formation of salt layers in evaporative desalination processes

These polymers can lack surface resistance and alone do not provide sufficiently high contact angles to achieve super hydrophobicity. Key to the development of super hydrophobicity was the development of very high contact angles above 120°. This was described by a research group at the Leibniz Institute for New Materials in Saarbrücken Germany in 2006 (Taurino R *et al* 2006). In this process, the hydrophobic component was built around a core-shell based on silica particles of ~100 nm in radius. The particles were modified either by thin layers of chemically-anchored polystyrene or by chemisorbed (tridecafluoro-1,1,2,2-tetrahydrooctyl) dimethylchlorosilane (FSI). The process requires the formation at a sub-micron scale of irregular surfaces due to uncontrolled evaporation of

concentrated particle suspensions. An alternative method for this is the Langmuir–Blodgett technique in which monolayers of an organic material are deposited by immersing a solid substrate into the liquid (Xiaodong C *et al* 2007). Based on these technologies, measurements showed that contact angles for water were in the range of 160° .

2.2 Application of solvent-based hydrophobic coatings

The actual process of application can either involve manually rubbing the solution onto a small surface area of glass (0.5 m^2 or less) or spraying onto larger areas. This is followed by sintering or heating in an oven at an elevated temperature until the solvent dries to form a two-layer (organic/inorganic) composite. When water falls on this surface, a high contact angle is maintained and the droplets run off rather than spreading. Perfluoro silane-based coatings are usually suspended in $\sim 90\%$ concentration organic solvents. Evaporation of the solvent drives an alignment of the hydrophobic polymer chains (see Figure 1) and activation of the silane groups through hydrolysis and condensation reactions. This self-assembling film bonds covalently to the glass via hydroxyl residues on the silane and further loss of hydrogen ions leads to more stable oxane bonding.

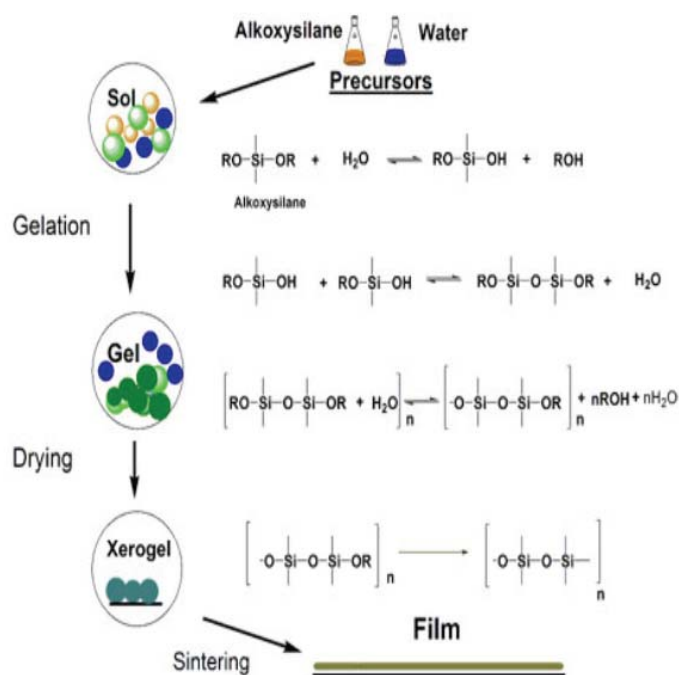


Figure 1 Sol-gel process in which the evaporation of the solvent (alcohol water mix) causes an alignment of the organic and inorganic components³.

³ from <http://www.sigmaldrich.cpm>

2.3 Particulate content of hydrophobic coatings

The suppliers of some glass surface hydrophobic coatings state that they contain “nano scale silica particles” but do not state the form of silica used (e.g., amorphous or crystalline). Kousaalya *et al* (2012) investigated a range of methods for producing super hydrophobic coating containing silica particles summarised in Table 5. This study refers to a method by Bravo J *et al* (2007) in which sequential adsorption of silica ultrafine particles and poly (allylamine hydrochloride) renders a super hydrophobic coating of trichloro (1H, 1H, 2H, 2H perfluoro-octyl) silane. Other publications refer to the use of ‘silica’ particles of differing size and surface modification (epoxy modified nanosilica of 20 nm particle size; Jeevajothi K *et al* 2013); non-modified silica particles of 50 and 100 nm sizes (Ramaratnam K *et al* 2008); or silica particles (20–40 nm) made by the Stöber sol-gel process (Stöber W *et al* 1968).

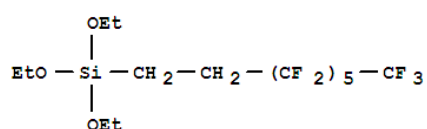


Figure 2 Structure of perfluoro octyl triethoxysilane

Table 5 Types of hydrophobic coatings using silica particles to increase water repellence

Type of process	Method of application / coating
Silica prepared from Stöber process coated and modified with FAS	Colloid assembly method
Two different sizes of modified silica, coated and modified with poly-dimethyl-siloxane layer	Drop coating
Polyelectrolyte/silica nanoparticle multilayers followed by fluoro-alkylsilane treatment	Electrostatic layer by layer assembly
Silica-polystyrene sol-gel coated and modified with FAS	Dip coating
Silane (METES and METES/DECYS) precursor with silica particles	Spin coating
Colloidal silica particles and fluoroalkylsilane in TEOS	Spin coating
TEOS/MTMS in different ratios	Dip coating
Silica nanoparticles coated and modified with tridecafluoro-1, 1, 2, 2-tetrahydro-octyl-dimethyl-chlorosilane	Dip coating
Silica obtained from tetramethylsilane or tetramethoxysilane, coated and modified with (heptadecafluoro-1, 1, 2, 2-tetrahydro-decyl)-1-trimethoxy-silane	Plasma-enhanced chemical vapour deposition
Silica deposited and modified with trichloro(1H, 1H, 2H, 2H perfluoro-octyl) silane	Layer-by-layer processing

3.0 Assessment of Risks to Health

This summary focuses specifically on evidence about the risk to health attributable to PFOTS and closely related compounds used for hydrophobic coatings. There is good evidence for concern about risk to human health and the environment for some perfluorinated products. Reviews of evidence have been commissioned by the US and European governments. These reports are detailed in the attached bibliography (Lassen C *et al* 2013; Borg D and Håkanson H, 2012; Posner S *et al* 2013).

3.1 Spray Particle Size and Risk for Acute Respiratory Inflammation and Injury

Several Nordic countries have focused on the environmental impact of perfluorinated siloxanes used in industrial processes and consumer products (e.g., sealants, fuel, car polish, cleaners, anti-foaming agents, car waxes, personal care and biomedical products) (Lassen C *et al* 2013). The widespread use of perfluoro organic and inorganic polymers has raised most concern with respect to their environmental impact. However, for specific classes of these compounds there is also a strong evidence base (not dependent only on animal toxicity studies) which demonstrates harmful effects in humans under specific circumstances.

A study in Denmark (Nørgaard AW *et al* 2009) compared a pump-action spray versus compressed propellant spray to disperse a solvent-based hydrophobic coating and investigated the size distribution of the emitted particles. They demonstrated for four different hydrophobic coatings (NFP 1-4) based on perfluoro-octyl-triethoxysilane chemistry that propellant devices released very large numbers of ‘ultrafine’ particles (Figure 3). The size distribution was skewed with particles generally smaller than 100 nm in diameter. For NFP4 which was applied using compressed gas there was a large increase in the number density of ultrafine particles and the total mass of spray (13.6 g in 5 seconds) compared to using a hand pump (8.0 g in 25 seconds).

For coatings containing a solvent (e.g., ethanol) smaller particles of diameter (~30-40 nm) were formed than those formed when the solvent only was dispersed. However, the number of solvent particles formed was estimated to be ~3% of the total with the majority derived from constituents such as the hydrophobic chemicals (Nørgaard AW *et al* 2009). Use of hand-held mechanical pumps increased the particle size to larger than 100nm and overall the number density of particles released using a hand-action pump was about 15% of that obtained using a compressed gas canister (see the red line in Figure 3).

Particles

propellant spray; 13.6 g released in 5 s

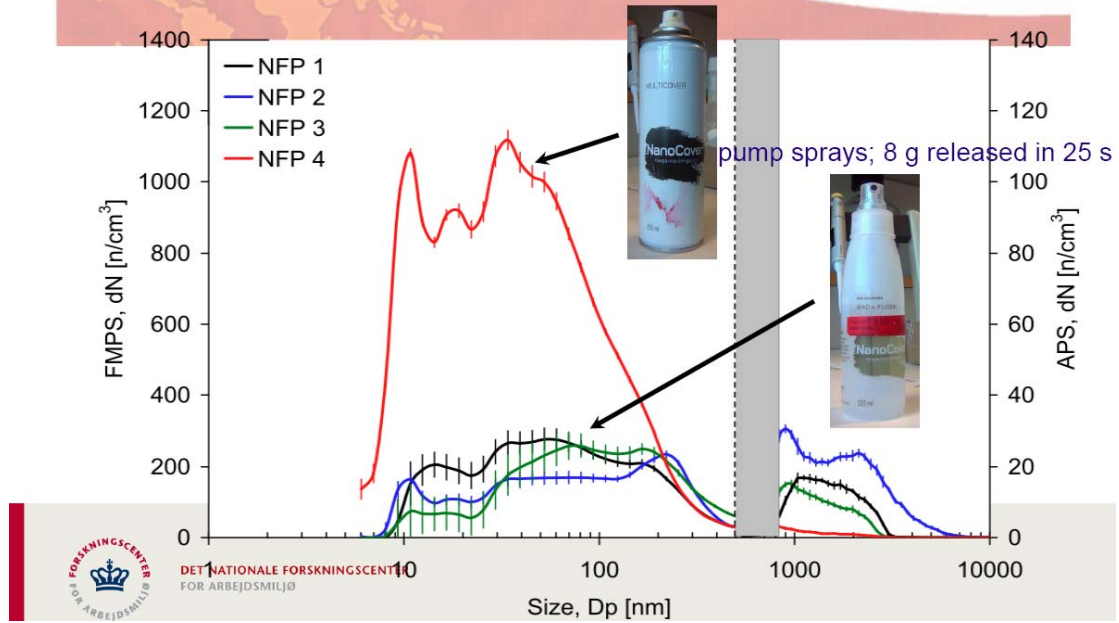


Figure 3 Data from studies conducted in Denmark on particle size distribution associated with hydrophobic coatings applied with manual and propellant-driven sprays (Nørgaard AW *et al* 2009).

4.0 Toxicological Effects of Perfluorinated Hydrophobic Coatings in Humans

Despite a number of high profile incidents of acute respiratory inflammation attributed to spraying solvent-based hydrophobic coatings there is less published evidence about the mechanism of these toxic effects. This may reflect the large number of products developed for hydrophobic coating and the complexity of assessing the toxicity of chemical mixtures.

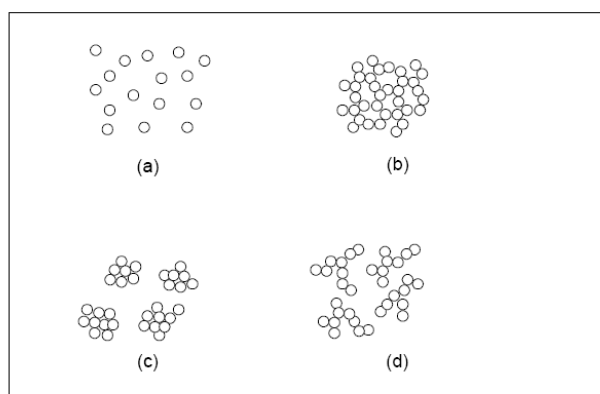
There is good evidence that application of 'solvent-based' hydrophobic coatings by spray / misting may cause acute respiratory inflammation in some individuals. This inflammation is caused by the combined effect of the hydrophobic chemicals and solvents on the gas exchange surfaces of the lung. The addition of ultrafine silica particles may also contribute to the overall toxicity of these mixtures. These conclusions are based on experimental toxicity studies and supported by case investigations of employees and consumers who suffered acute inflammatory reactions when they sprayed these products.

The published incidents have mostly but not entirely occurred in Europe and in the US and there are only a few published case reports of incidents in GB. Substantive toxicological reviews of fluorinated organic compounds have been published by several European governments and the US authorities but no equivalent reviews have been undertaken in GB.

4.1 Ultrafine particles in hydrophobic sprays

With regard to the addition of ultrafine particles of silica in some products there is little published evidence about their contribution to the toxicity of these mixtures. These ultrafine discrete silica particles are used to achieve a 'Lotus Flower' effect (Ramaratnam K *et al* 2008) providing a high contact angle across the coated surface of the glass.

These particles have been manufactured using synthetic amorphous silica (SAS) based on wet or thermal methods for their synthesis. SAS particles have a primary particle size which is very small (10's nm) but if left untreated form large amorphous aggregates up to 1000 nm diameter with uneven shapes unsuited to water repellence effects (see Figure 4). However, suitable water repellence can be achieved when these particles are surface-modified by hydrophilic silanol groups ($\equiv\text{Si-OH}$) with a high affinity for polar media or using hydrophobic Si-organic compounds such as hexa-methyl-disilazane (CAS No. 999-97-3), dimethyl-dichloro-silane (CAS No. 75-78-5) and poly-dimethyl-siloxanes (e.g. CAS No. 9016-00-6).



(a) Sol, isolated primary particles
 (b) Gel, densified aggregate
 (c) Precipitated, compact aggregates
 (d) Pyrogenic, open branched-chain aggregates

Figure 4: Aggregation of different types of primary untreated synthetic silica particles

Evidence about the toxicity of synthetic amorphous silica has been extensively summarised by Napierska D *et al* (2010). This included *in vitro* cell culture studies with animal and human cells and animal toxicity models. The evidence suggested that surface silanol groups are directly involved in damage to red blood cells as well as being directly toxic to cells that line the lung. The hydrophilicity, size, and enhanced surface physico-chemical properties of the nanoparticles of SiO₂ were linked to their toxic effects.

However, based on *in vivo* occupational health studies and experimental toxicology studies it has been concluded that unmodified forms of SAS are not harmful to humans. This conclusion has been based on animals exposed via the oral, dermal and ocular routes either acutely or chronically. Since their first manufacture over 50 years ago, no evidence of cumulative toxicity related to occupational exposure has been noted. Furthermore there is no evidence for risk of cancer, genotoxic or reproductive toxicity from exposure to unmodified SAS particles (ECETOC JACC Report: 2006) which contrasts with the well-established evidence about the toxicity of crystalline silica (Napierska D *et al* 2010).

4.2 Toxicity of hydrophobic coatings

Based on experimental studies it has been suggested that hydrophobic chemicals interfere with the surfactant fluid that lines and protects the surfaces of the lung alveoli. The disruption of the surfactant layer leaves the delicate lining of the gas exchange surfaces unprotected causing acute inflammation. Pathological studies in these animal models showed that inhalation of perfluorinated silanes damaged the lung alveoli, which led to an accumulation of inflammatory cells and fluid exudate. These inflammatory cells were mainly granulocytes whose normal role is to fight infection but they also play an important role in the pathogenesis of inflammatory lung disease (Swiss Consumer Protection Directorate 2008).

The animal tests also showed that not all hydrophobic compounds are equally toxic to the lung. Perfluorinated silane compounds were more toxic than alkylsiloxane coatings in mice (Nørgaard AW

et al 2009). The level at which these compounds are toxic in animals is likely to exceed the concentrations to which human operators are exposed as a single dose. This may indicate that human toxicity occurs under specific environmental conditions (confined spaces, inhalation of spray /mists, or persistent exposure), and is affected by variability in human susceptibility to the toxic effects of these chemicals (Duch P *et al* 2014).

4.3 Incident Case Studies:

A list of cases of acute respiratory inflammation attributed to the use of waterproofing coatings is summarised in Table 6. Most of these cases were from countries other than GB and most arose from consumers using these products not occupational cases. Some of the details of the circumstances of use of these products are also not readily available as many of the cases were referred through national poison referral schemes. Not all of these incidents were specifically caused by exposure to perfluorinated silanes others were attributable to use of different hydrophobic waterproofing coatings applied by spraying. At least half of these cases were acute cases of respiratory inflammation but others included prolonged coughing and dyspnoea (difficulty breathing).

4.4 Nature of the incidents

Cases of acute respiratory inflammation have been reported for different commercial hydrophobic products used on leather goods (Burkhart K *et al* 1996), textile waterproofing (Laliberté M *et al* 1995), ski waxes (Braco and Favre 1998), clothing (Caron and White 2001), and floor products (Lazor-Blanchet *et al* 2004). Some of the larger-sized incidents are summarised by country and in Table 6. This list is not comprehensive and does not include many reports on individuals who developed acute respiratory inflammation when applying hydrophobic coatings.

Denmark: 84 cases of acute respiratory inflammation between 1991 and 2007 were reported by the Danish Poison Centre associated with the use of waterproofing sprays. Respiratory symptoms were reported in 92% of the patients as well as fever, general malaise, gastrointestinal upset and central nervous system impairment. In a large proportion of the patients symptoms started typically one hour after their exposure. The most severe cases were from spraying of furniture. Follow-up through hospital records was successful for 33 patients (39%), of these 20 were graded with moderate/severe and 13 with mild poisoning. One set of 16 cases was related to the use of a fluoracrylate and cyclosiloxane based waterproofing product. The product had been used for several years without apparent problems, at the time of the cases its formulation was altered to include dodecyl acrylate (CAS: 2156-97-0) in high concentration; although alone this is not regarded as an acute respiratory toxicant. The majority of patients were middle-aged and young male adults exposed when spraying the product at home. One occupational case was identified. Four children below 10 years and one adult had been exposed accidentally from other peoples work (passive exposure).

Germany: In 2006, the Federal Institute for Risk Assessment in Germany registered at least 170 severe cases associated with ‘Magic NANO’ and ‘Nano HiTech’ spray products for coating glass and ceramics. At this time, the delivery system was changed from a hand pump spray to a propellant spray prior to these incidents of ill health. The persons affected were consumers using these water-repellent sprays in their households in closed rooms with insufficient ventilation. They usually developed severe acute respiratory inflammation with breathing difficulty and in several cases accumulation of fluid on the lung. This product was later classified as toxic by the German authorities and withdrawn from the market⁴. The causative agent in these products has not been identified.

This risk was associated with spray dispersal of the fluid particularly using aerosol cans. The active ingredients included fluorocarbon-based polysiloxanes with melamine resins, beeswax, or wool fat, dissolved in petrol or short-chain alcohols, and sometimes xylene. The propellants included propane, butane, dimethylether and air. The small droplet size was achieved when the liquid was applied using a propellant and small nozzle spray head to produce a fine mist. The German authorities recommended that sufficient information about the formulation of these products should be available in at least one point in the production chain and that spray devices should be tested according to internationally-accepted criteria as suitable for consumer use.

Switzerland: In 2003, about 180 cases were reported by the Swiss Toxicological Information Centre between October 2002 and March 2003, compared to fewer than 10 cases in the previous year. The symptoms commonly reported were general fever, shivers, and aches, cough, breathlessness, giddiness, headache, loss of consciousness and some reported nausea, vomiting, abdominal pain, sore eyes and throat. Three different brands of waterproofing sprays were involved which had been reformulated in the months before the outbreak. A numeric simulation of exposure was carried out for 102 of the exposed cases but no dose-response relationship between exposure and health effects was obtained. The results suggested a high inter-individual variability in these responses. No threshold could be found to define a safe level of exposure. Most of the incidents occurred after consumer application of leather and textile waterproofing sprays. Three occupational cases following the use of a stain-repellent resin on stone-tiled walls and floors were also reported (Lazor-Blanchet *et al* 2004). The exposure circumstances of these three cases were investigated in another study (Vernez *et al*: 2004) in which it was concluded that the respiratory illness was related to the fluorinated polymer itself rather than to an increase in exposure to solvents and particles.

These findings suggest that the improvement of environmental exposure conditions during spraying alone did not constitute a sufficient measure to prevent future outbreaks of waterproofing spray toxicity. More efficient preventive measures were needed prior to the marketing and distribution of new waterproofing agents.

⁴ <http://www.bfr.bund.de/cms5w/sixcms/detail.php/7750>

Great Britain: A published study (Wallace and Brown 2005) reported three definite cases and one probable case of toxic pneumonitis due to inhalation of a fluorocarbon based waterproofing agent used to treat horse rugs. Following laundering, a waterproofing fluorocarbon polymer (Rucoguard EPF 1619) containing the solvent isopropanol was applied in an 8 x 8 x 10 foot booth using a spray gun connected to an air compressor. The booth ceiling had a single extractor fan fitted and the walls and floor were found to be covered with residues of the fluorocarbon polymer and horsehair. A 23-year-old man with no previous medical history dismantled the air compressor inside the booth without wearing respiratory protection and as he did so compressed air escaped and released a cloud of fluorocarbon residues. He left the booth and within 30 minutes became breathless and found breathing difficult. At the hospital he presented with persistent cough, breathlessness and a lack of oxygen. Three other employees who undertook fluorocarbon spraying also showed similar symptoms (2 men aged 18 and 37 years and a 35-year-old female) although only two were regarded as definite cases of toxic pneumonitis. The authors of the paper concluded that these cases of pneumonitis were due to inhalation of the fluorocarbon alone or in conjunction with the horsehair.

United States of America: Outbreaks of acute respiratory symptoms recorded in the USA included 550 cases in Oregon (CDCD 1992) associated with the use of waterproofing leather protector (Wilson's Leather Protector). These cases involved householders using the product indoors with limited ventilation. The active ingredients were fluoroalkyl polymers in the solvents 1-1-1 trichloroethane or isooctane. The symptoms were typical for acute chemical pneumonitis with patients having fever, chest tightness, headaches, fever, weakness, and shortness of breath.

From 1992 to 1993 a larger outbreak involving 198 cases of acute respiratory inflammation (chemical pneumonitis) occurred when a leather conditioner (Magic Guard) was used by consumers. This contained fluoro-polymers as a water / soil repellent sprays with the solvents 1,1,1 trichloroethane to hexane and 2,2,4 trimethylpentane. Twenty three of these patients were hospitalised but none died (CDC 1993).

In 2005, in the USA, 150 patients ranging from one-year-old to 70 year-old developed acute respiratory illness. Most were householders who used the product but persons who did not use the product were affected. The product was sprayed indoors in the majority of these case investigations. Sprayed shoes and boots brought into the home from garages or outdoors continued to be a source of exposure as the product evaporated. Five occupational exposures occurred, four while spraying clothing items at work and one while demonstrating a product to a customer. Most of the patients reported respiratory illness with common symptoms being cough and breathlessness. Approximately half of the patients were admitted to hospitals and one-tenth had hospital stays of up to 5 days but no patients died. The products used included 'Jobsite Heavy Duty Bootmate', 'Rocky Boot Weather and Stain Protector' which consisted of fluoropolymer, silicone, petroleum distillates, and propellants. Neither the labels nor the material safety data sheets for the products listed fluoropolymer or silicone.

In 2005, 30 acute cases of pulmonary toxicity caused by exposures to ‘Stand’n Seal’ were reported. ‘Stand’n Seal’ is a floor waterproofing aerosol containing the propellants iso-butane and propane, C8-C9 petroleum hydrocarbon solvents, and a fluoropolymer resin. The majority of patients were adult males, with one 10 year-old child and two occupational cases. The majority of patients used the product at home in small enclosed space with inadequate ventilation and developed symptoms within 3 hours of exposure. They all used the product with little or no personal protective equipment. Approximately half of the patients required hospital admission due to the severity of their illness and nearly two-thirds complained of shortness of breath or cough within an hour of exposure. The ‘Stand’n Seal’ product was used as a “grout sealant” and was not categorised with other waterproofing products.

Table 6: Cases of acute respiratory inflammation and other symptoms associated with waterproofing coatings

Year	Country	Products/ Formulation	Cases	Symptoms	Group affected
1991-2007	Denmark	Leather / suede fluoracrylates and cyclosiloxanes waterproofing spray	84	Acute respiratory illness	83 consumers, 1 occupational case
2006	Germany	Fluorocarbon polysiloxanes, melamine resins, beeswax, wool fat, in petrol or short-chain alcohols, and or xylene for treatment of leather textiles.	170	Acute respiratory illness	Consumers
2002-2003	Switzerland	Leather / textile fluorocarbon polymer spray	180	Acute respiratory illness	Consumers
2008	GB	Fluorocarbon polymer with the solvent isopropanol for waterproofing horse riding equipment	4	Acute and chronic pneumonitis	Occupational cases
1992	USA	Fluoralkyl polymer spray application as a shoe and leather conditioner	550	Chemical pneumonitis with prolonged cough, shortness of breath, chest pain, headache, malaise, chills, and fever	Consumers
1993	USA	Fluoralkyl polymer spray application as a shoe and leather conditioner	198	Acute respiratory inflammation	Consumers
2005	USA	Fluoropolymer-based boot waterproofing spray containing petroleum distillate and silicon	150	Acute respiratory inflammation with cough and dyspnoea	Mostly consumers but 5 occupational cases
2005	USA	Fluoropolymer resin floor waterproofing containing N-butyl acetate and C8-C9 petroleum hydrocarbon solvents	30	Acute respiratory inflammation, shortness of breath, cough, chest pain, nausea, vomiting and headache. Wheezing an abnormal heart rate and increased breathing rate.	28 consumers and 2 occupational cases

General observations: In general, the acute respiratory inflammation was associated with spray application of hydrophobic coatings (particularly propellant based sprays) in confined spaces with poor air ventilation. Most of the cases were consumers but occupational cases were reported. The consequences of exposure to these hydrophobic sprays included:

- Respiratory inflammation occurring immediately (within the hour) or within hours after exposure with features consistent with chemical pneumonitis. In more severe cases pulmonary fluid accumulated in the lungs and caused a potentially life-threatening reaction.
- Other symptoms included shortness of breath, cough and wheezing, headaches, fatigue, fever, and dizziness and occasionally signs of seizure.
- Some patients were hypoxic (without sufficient oxygen in the circulation) due to reduced blood oxygen saturation and some experienced an increased resting heart and breathing rates.
- Many cases (~half) were discharged from hospital after initial treatment but others took longer to manage and occasionally fatalities have occurred. Long-term outcomes included reactive airways dysfunction syndrome (a sudden onset of an asthma-like response following exposure to corrosive gases, vapours, or fumes), persistent wheezing and shortness of breath.
- These cases of respiratory disease were not attributable to infectious agents (bacteria, mycobacteria, viruses or fungi) or to pre-existing risk factors (e.g., lung disease, allergy, or smoking).
- Patients presenting within 3 hours of exposure were more likely to require hospital admission than those presenting more than 10 hours after exposure.

4.5 Factors contributing towards lung toxicity

In most of the reported incident investigations which occurred outside GB, a specific chemical agent causing the acute respiratory inflammation was not identified. Some experts considered these effects were directly attributable to the waterproofing agents, and others considered that a mixture of chemicals (the solvent and waterproofing agents) was important. The use of pressurised propellant gases was considered to increase the risk of harm significantly by producing fine respirable-sized particles. The following conclusions were based on these incident case studies.

- There was a lack of dose-response correlation in the effects. Taken with the perceived speed and severity of the outcomes it was concluded that when hydrophobic chemicals were applied as fine sprays no safe threshold dose could be identified with confidence.
- The studies suggested a high inter-individual variability suggesting either that exposure circumstances are highly variable or that human variability dominated the respiratory response (Vernez D *et al* 2006). Personal metabolic differences might influence the toxic response to silanes and solvents.

- The harmful effects of these products may be due to single agents or to complex mixtures of chemicals including the number and size of the particles and particularly ultrafine particles.
- Fluoropolymers may act as a carrier molecule allowing hydrocarbon solvents to move across the lung alveoli (Vernez D *et al* 2006). A toxic interaction between polytetrafluoroethylene (e.g., Teflon) and its solvent base was reported (Rask-Andersen A: 1996).
- Some experts concluded that the toxicity of hydrophobic fluoropolymers was due to their disruption of the protective surfactant fluid layer of the alveolar lining, which may have damaged and provoked inflammation, fluid leakage, and impaired gas exchange (Yamashita and Tanaka: 1995). This was more likely to apply to the smallest spray particles, which by the time they reached the alveoli contained little solvent and consisted mostly of non-volatile materials.

Co-exposures that may contribute to the reported toxic effects:

- Alcohol-and kerosene solvents used with polyfluorinated silanes release aerosols and gas phase products whereas water-based polymers mainly release larger aerosols.
- Volatile organic compounds are released when polyfluorinated polymers are sprayed (Nørgaard *et al* 2009) including chloroacetones, small aliphatic ketones, limonene and kerosene but at levels unlikely to account for the reported respiratory toxicity.
- Substituted solvents (e.g., n-heptane used to replace isopropanol) that are more volatile tend to increase small droplets containing fluorinated resin. Amongst the solvents used are petroleum distillates (heptane), acetates, methylethyl ketone (but no longer 1, 1, 1-trichloroethane).

Animal toxicology:

- Studies in mice showed that the toxicity of waterproofing sprays was influenced by the particle size distribution. Four sprays with identical ingredients were generated with different particle size distributions. The least acutely toxic sprays were those in which the proportion of particles smaller than 10µm was low (e.g., 0.2 % of the particle size distribution) (Yamashita M *et al* 1997).
- A study in female mice examined inhalation of fluoropolymer and silicone resins with the solvents heptane or ethyl acetate. This study included a solvent-only control challenge. Inhalation of the fluoropolymer resins caused the lung alveoli to collapse with blood and fluid leaking across the lining of the airways (Nørgaard AW *et al* 2010). There were significant dose-dependent decreases in body weight (for exposures of 15.7mg/m³ or more) which did not occur after inhalation of the solvents heptane or ethyl acetate alone. The lungs showed an emphysema-like condition in which the lung alveoli collapsed.
- A single acute (60-min) high dose (18.4mg/m³) exposure of mice to a perfluoro-silane compound (NFP 1) markedly impaired lung function. This damage was concentration dependent within a

narrow concentration ($\sim 2.0\text{mg}/\text{m}^3$) between a 'no-observed' effect level and the lethal concentration. A newly synthesised perfluoro-silane (NFP 1) showed that hydrolysis was a critical factor in determining toxicity due to the presence of free hydroxyl groups and reduced toxicity was reported with non-hydrolysed perfluoro silanes (1H, 1H, 2H, 2H-perfluoro-octyl-triethoxy-silane and bis (1H, 1H, 2H, 2H-perfluoro-octyl) tetra-methyl-disiloxane (Nørgaard AW *et al* 2010).

- In Germany, cases of ill health attributed to use of 'Magic Nano Sprays' led to an investigation using rats to compare the effects of delivering the product using either a propellant spray or a pump spray. The rats were 'nose-only' exposed for 4 hours but significant mortality occurred and so the duration of exposure was reduced to 2 hours. Lung function was measured along with lung fluid biomarkers of inflammation and damage one day after this exposure. The propellant spray caused mortality above $2269\text{ mg}/\text{m}^3$ compared to the pump spray that approached the lethal range at concentrations above $81222\text{ mg}/\text{m}^3$. This response was consistent with upper and lower respiratory tract inflammation, haemorrhage, oedema, and airway thickening. Markers of inflammation in lung fluid were significantly increased including raised numbers of inflammatory granulocytes. The authors of the study concluded that particle size was less important and that the volatile constituents in these sprays caused most of the toxicity (Pauluhn J *et al* 2008).
- In a recent seminal study, the mechanism of lung toxicity caused by a 'nanofilm' hydrophobic product was investigated (Larsen *et al*: 2014). This product contained hydrolysates and condensates (siloxanes) of 1H,1H,2H,2H-perfluorooctyl-triisopropoxysilane (PFOTS) dissolved in 2-propanol (99.9%). Mice were subjected to an inhalation challenge to aerosolised NFP at a concentration of $18.4\text{ mg} / \text{m}^3$. The control mice were exposed to an equivalent concentration of 2-propanol solvent. The inhalation of the NFP rapidly significantly reduced the expiratory flow rate and increased airway resistance over the 60-min exposure period compared with the control group. This flow rate did not normalize within the 30-min post-exposure recovery period to clean air. Using an *ex vivo* model, the effect of NFP on the lung surfactant layer was further investigated. Lung surfactant is composed of a surface-active mixture of lipids and proteins and its organisation is an essential prerequisite for normal lung function. Damage to the lung surfactant can lead to life-threatening acute respiratory distress. The perfluorosilanes were found to interfere with the surfactant layer, interacting with one of the major surfactant proteins (surfactant-B) which is essential to form stable surfactant. Disruption of the surfactant layer leads to a collapse in the alveoli which fill with fluid increasing airway resistance and causing poor gas exchange. This acute change resulted in significant impairment and provoked damage and inflammation. It was suggested that the hydrophilic silanol groups mimic the natural phospholipids in surfactant that help organise the stability of this protective film.
- Good evidence has also been recently obtained that solvents may play a critical part in this toxicity. Nørgaard AW, *et al* (2014) published a study in which mice were exposed via inhalation to POTS

either as aerosolized water-soluble form or after being dissolved in methanol, ethanol, or 2-propanol. Acute respiratory reactions were only observed when PFOTS was dissolved in the alcohol solvents. The effects were more pronounced for 2-propanol, followed by ethanol and finally methanol. The effects were enhanced when these solvents were co-administered as a vapour reflecting the likely exposure when hydrophobic products are dispensed in solvents using pressurised propellant devices. They showed using an *ex vivo* assay that the concentration and type of alcohol solvent was critical to lung toxicity of the PFOTS. The effects were consistent with the lipophilicity of the solvent facilitating contact between perfluorosilane and lung surfactant components.

5.0 The Supply of Safety Information for Solvent Based Hydrophobic Products

Investigators of incidents that have occurred in other countries concluded that the safety information provided with some hydrophobic products did not contain adequate information about their hazardous properties. In the USA an investigation of a ‘Stand n Seal’ product demonstrated that companies manufacturing and distributing the product did not list ingredients if they comprised <1% of the composition (in this case the active fluorocarbon). Stand’n Seal was sold as a ‘grout sealant’ and not readily identified along with other aerosolised waterproofing products (Daubert GP *et al* 2009).

Other investigators have reported that tracing a product back to the original primary manufacturer was challenging because of the complex organisation of the distribution, packaging and marketing networks used to place the final product onto the market (Daubert GP *et al* 2009).

The chemical stability of perfluorosilane compounds was identified as another concern and studies showed they were only stable for ~2 weeks and then underwent hydrolysis and condensation reactions. In animal toxicity tests, the generation of these reactive hydrolysis species was shown to contribute towards the toxicity (Nørgaard AW *et al* 2010).

Within the EU, hydrophobic products meeting the criteria for classification must be placed on the market in accordance with the requirements of the Classification, Labelling and Packaging Regulation⁵.

Any safety data sheets for such products (where required) must be prepared in accordance with the Requirements of the REACH Regulation, particularly Article 31 and Annex II⁶.

The need to include the presence of a chemical substance on a product label or SDS will depend on various factors, including the hazard classification of that substance, and the quantity at which it is present.

Further information on the requirements associated with the REACH and CLP Regulations can be found on the European Chemical Agency website www.echa.europa.eu

⁵ Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures (as amended)

⁶ Regulation (EC) No 1907/2006 on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) (as amended).

6.0 Risk Factors and Industry Guidance

6.1 Risk factors

Several factors have been identified from the peer-reviewed studies included in this review:

- The risk for inhalation of hydrophobic coatings is increased by the use of spray applicators, including propellant-based spray device, as well as the duration of the spraying and whether overspray occurs increasing the risk for operator exposure.
- The mean aerodynamic particle diameter of spray emissions and their size distribution is dependent on the product ingredients, their volatility, surface tension, and viscosity. Particles smaller than 0.5 μm in diameter often remain in suspension in the lung, and may be exhaled and not efficiently deposited. However, an experimental study, in which a hydrophobic coating was modified to produce mists with particle diameters less than 62.0nm caused significantly more pathological changes in the airways compared to larger particles (Yamashita M *et al* 1997). Particles in the size range ~0.5 to 10.0 μm diameter deposited in the conducting airways (e.g., bronchioles) and the lung alveoli. Particles above 16.0 μm diameter tended not to reach the lungs.
- The design of the spray device and use of a volatile solvent that evaporates quickly can affect the formation of respirable particles. In a product containing the solvent heptane, its replacement with another solvent isopropanol produced a finer mist containing a fluorinated resin which induced alveolitis (inflammation of the alveoli) (Swiss Consumer Protection Directorate: 2008). High-pressure propellant sprays tend to release a large fraction of particles smaller than 10.0 μm diameter; in contrast airless pumps generate fewer respirable particles.
- Other factors that influenced personal exposure included the volume of spray, the rate of air exchange within the workspace, the proximity of the operator to the spray, and the duration of spraying.
- The Fraunhofer Institute for Toxicology and Experimental Medicine (ITEM) in Hannover developed a simple prediction model to determine the risk of particles in a spray falling into the <5.0 μm (respirable) and <10.0 μm (thoracic) fractions based on spraying against a surface ~30cm away. This model incorporated room volume and tasks undertaken but assumed no ventilation of the room. The fraction of the product formulation transferred to respirable and thoracic particles was calculated and potential exposures calculated for different scenarios. (Schwarz K and Koch W: 2014).

6.2 The Glass and Glazing Federation Guidance about Safe Use of Hydrophobic Coatings

The Glass and Glazing Federation (GGF) provide their members with advice about safely applying hydrophobic coatings to glass, which emphasises the following⁷:

- *“Design and operate processes and activities to minimise emissions, and the release and spread of substances hazardous to health”.*
- *“Take into account all relevant routes of exposure – inhalation, skin absorption and ingestion – when developing control measures”.*
- *“Control exposure by measures that are proportionate to the health risk”.*
- *“Choose the most effective and reliable control options which minimise the escape and spread of substances hazardous to health”.*
- *“Where adequate control of exposure cannot be achieved by other means, provide, in combination with other control measures, suitable personal protective equipment”.*
- *“Check and review regularly all elements of control measures for their continuing effectiveness”.*
- *“Inform and train all employees on the hazards and risks from the substances they work with and the use of control measures developed to minimise the risks”.*
- *“Ensure that the introduction of control measures does not increase the overall risk to health and safety”.*

⁷ *Surface Modification of Glass for Ease of Maintenance - Liquid Applied Glass Surface Treatments: (Data sheet 5.19.2) Glass and Glazing Federation) Glass and Glazing Federation 2015. <http://www.ggf.org.uk/publication/>*

7.0 Conclusions

- There is sufficient evidence that in some individuals, inhalation of hydrophobic coatings causes an acute inflammation and injury in the lung. This effect is not limited to perfluoro-octyltriethoxysilane (PFOTS) coatings, similar effects have been observed with different hydrophobic coatings.
- Experimental animal studies have shown specific hydrophobic chemicals and solvents used in glass coatings cause acute lung toxicity. However, human cases of acute lung inflammation in workers applying these coating to glass products were not found.
- Experimental studies have shown that ‘hand-held’ misting devices, and propellant gas-driven misting devices, used to disperse hydrophobic coatings produce mists containing large numbers of respirable and ultrafine particles sufficiently small to enter the conducting airways and gas exchange surfaces of the lung.
- In the last 30 years in Europe and the USA, several hundred cases of severe and acute respiratory inflammation were reported mostly in consumers using hydrophobic coating ‘spray on’ products. Many cases required hospital admission and included fatalities, although these were outside GB.
- The evidence suggests that acute lung inflammation is caused by the combined toxicity of hydrophobic chemicals, solvents, and may include the effects of ultrafine surface-modified silica particles.
- Not all individuals showed the same adverse reaction suggesting that some were more predisposed to react acutely.
- Most cases of acute respiratory illness were caused by spraying these coatings in confined space with poor ventilation. The risk for acute inflammation of the lungs is increased when hydrophobic coatings are applied by spraying without adequate preventive control measures.
- Not all of the reported incidents of respiratory inflammation were caused by exposure to sprays; some individuals developed an adverse reaction when they came close to materials recently coated with these products.
- Experimental toxicology studies demonstrated that solvent-based hydrophobic coatings containing PFOTS may be acutely toxic to the respiratory tract.
- Following previous incidents of ill-health some hydrophobic coating products were reformulated by the manufacturer but cases of ill health still occurred because users continued to applying them by spraying.

- Risks for respiratory inflammation and injury caused by exposure to hydrophobic products can be minimised using methods that do not generate fine mists (such as wipe application), and by using suitable preventive control measures.
- In GB suitable preventative control measures should be based on the requirements of the Control of Substances Hazardous to Health Regulations 2002.

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Summary of evidence – solvent-based hydrophobic coatings and risks for acute respiratory toxicity

Water repellent coatings are increasingly used by different industries to reduce water and dirt sticking to surfaces. The coatings can be applied by processes that minimise the risk that operators inhale the product but there is evidence that some products are applied by spraying, creating an inhalable mist.

This review examined evidence about these coatings and whether lung disease occurs when applied by spraying. Scientific studies on the hazardous properties of these products, and clinical studies reporting lung disease in people using them, were considered.

A consistent finding was that some people develop an acute lung inflammation when applying these coatings by spray misting. Studies across Great Britain, Europe and the United States reported several hundred cases of serious lung disease and some fatalities, mostly in consumers applying such products using pressurised spray cans in poorly ventilated spaces. Experimental studies suggest that the different water repellent ingredients and solvents in which they are dissolved combine to damage the delicate lining of the lung.

Smart surface coatings offer many industrial and societal benefits. However, they should be applied by methods that minimise the risk of inhaling the product.

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