Reactive Chlorosilane Byproducts, Popping Gels

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Research is continuing on the shock sensitive "Popping" gels that can be generated from hydrolysis of chlorosilanes. Silicon Semiconductor device integrated circuit manufacturers have increased their use of the more complex silane molecules such as. pentachlorodisilane (Si_2HCl_5), hexachlorodisilane (Si_2Cl_6) and octachlorotrisilane (Si_3Cl_8) because of their ability to uniformly deposit a dielectric layer on nanometer devices at low reactor temperatures via an Atomic Layer Deposition (ALD) process. These Si-Si or Si-Si-Si bonded molecules however have a greater tendency to form reactive byproducts at lower temperatures than the traditional dichlorosilane process. They can more easily form gels that are shock sensitive (aka Popping Gels). Under high reactor temperature conditions these can easily form a soup of polychlorosilanes upon cooling. These are flammable and will readily hydrolyze to form “Popping Gels”.

There have been reports of minor and major incidents at suppler, user and equipment supplier facilities. With increasing use these incidents are becoming more frequent. In one incident, the gel was so shock sensitive that the decomposition reaction was triggered by the act of simply peeling off a label on the piece of equipment the gel formed on top of.

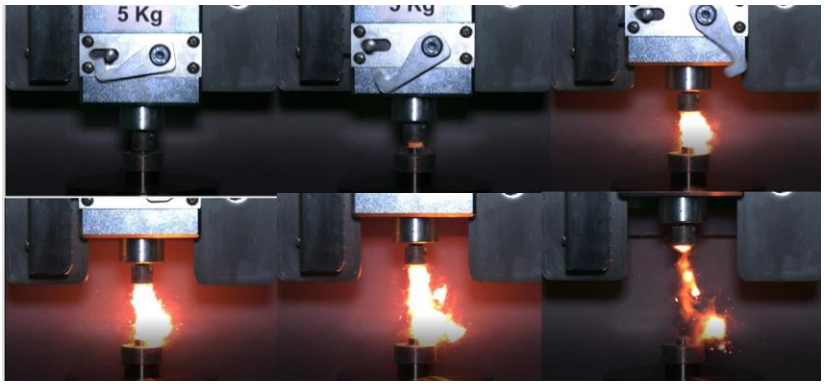
The Jan 2014 Mitsubishi Materials Corporation incident in Japan is believed to have been caused primarily by a gel formed by hydrolysis of hexachlorodisilane and other chlorosilanes.

As maintenance workers were scraping the gel out of the heat exchanger when it was opened, it exploded violently, killing 5 of them and injuring 13 others. Subsequent testing of the liquid found in the heat exchanger revealed a composition of chlorosilane polymers containing primarily hexachlorodisilane.

These incidents have created significant concern as to the safe handling of these chlorosilanes and their byproducts. Eugene Ngai of Chemically Speaking LLC championed industry funding of research studies in 2017 and 2018 to better understand how these gels could be formed, the chemistry and the energy released.

On April 20, 2018 due to wide industry interest, Eugene chaired a one day seminar during the 2018 SESHA Conference in Scottsdale, AZ, titled “Reactive Silane Byproducts”, where 2 presentations were made on research projects involving “Popping Gels”. The first was a project between Chemically Speaking LLC and Prof Chen, National Kaohsiung First University of Science and Technology (NKFUST) jointly funded by Air Liquide Advanced Materials. Prof Chen and Eugene have collaborated on numerous research projects from 2005-2017 involving silane

and trichlorosilane. For Phase 1 of the study over 1,000 hydrolyzed samples were generated and tested using the BAM Fall-Hammer test to determine shock sensitivity.



This was summarized in a presentation titled “Experimental Studies of Shock Sensitive Deposits from Hexachlorodisilane Exhaust”.
Mark Wanous of Dow Chemical, presented on a 18 month research effort on the gel formation chemistry involved in producing shock sensitive silicon suboxides from hexachlorodisilane. He discussed silicon suboxide morphology, shock sensitivity mechanisms, factors influencing sensitivity and intensity, hazard characterization and mitigation methods.
Extensive literature searches have revealed that very little research has been conducted on this issue. For both studies, the ability to grow Popping Gels reproducibly and test for reactivity was a challenge.
Edwards vacuum presented on the problems associated with gels in the rebuilding of vacuum pumps. They displayed a dramatic video of a “Popping Gel” reaction during this process.
We published a peer reviewed article “Characterization of Shock Sensitive Deposits from the Hydrolysis of Hexachlorodisilane” which Prof Chen will present on the week of Aug 12 in Kansas City at the12th International Symposium on Hazards, Prevention, and Mitigation of Industrial Explosions (ISHPMIE).
Some key findings of the research thus far are:

1. Neutralization of the hydrolyzed gel with dilute NaOH solutions made them more shock sensitive
2. The hydrolyzed gel will decompose even under inert conditions. The energy release is lower since there is not a secondary H_2 explosion.
3. Reaction of the gel in air has almost the same energy as TNT
4. Hydrolysis reaction is rapid

Phase 2 testing is continuing to uncover key characteristics of this gel and its reactivity. We hope to present these findings in a peer reviewed article in 2019 as well as at another seminar.

Eugene Ngai