Characterization of Shock-Sensitive Deposits from the Hydrolysis of Hexachlorodisilane

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ABSTRACT: In this work, the shock sensitivity of hexachlorodisilane (HCDS) hydrolysis products was studied. The hydrolysis conditions included vapor and liquid HCDS hydrolysis in moist air. Shock sensitivity was determined by using a Fall hammer apparatus. Extensive infrared studies were done for the hydrolysis products. It was found that the Si–Si bond in HCDS during hydrolysis is preserved and can be cleaved by shock, leading to intramolecular oxidation of the neighboring silanol (Si=OH) groups to form a networked Si–O–Si structure and hydrogen gas. The limiting impact energy for shock sensitivity was also found proportional to the oxygen/silicon ratio in the deposit. Finally, recommendations are given for controlling the shock sensitivity of the hydrolyzed deposit.

1. INTRODUCTION

Hexachlorodisilane (HCDS, Si₂Cl₆) is an important specialty chemical used in semiconductor manufacturing and related industries. It is one of the chlorosilanes and bears similar hazardous properties such as flammability and water reactivity in which the hydrolysis reactions produce silicon oxides and hydrogen chloride. The major difference between HCDS and other smaller chlorosilanes such as monochlorosilane, dichlorosilane, and trichlorosilane (TCS) is that HCDS has a much lower volatility with a boiling point of 144 °C or lower, which increased the sensitivity and power of ignition and explosion when the hydrolyzed deposit was dried. It also concluded that the explosion occurred as a result of physical impact when the heat exchanger cover was opened.

Although details on the mechanism of how shock impact of the hydrolysis products lead to ignition and explosion were not given, thermodynamic calculations were performed and oxygen insertion into the Si–Si bond was considered to be effective for stabilization.

Hydrolysis of typical chlorosilanes such as dichlorosilane, TCS, and silicon tetrachloride have been well-studied. The Si–Cl bonds are known to react readily with water-forming silanol (Si=OH) and hydrogen chloride. The silanols are in general unstable, rapidly condensing to form siloxanes, that is, compounds with a structure of –Si=O–Si–. The hydrolysis and condensation may occur simultaneously giving complex cyclic or linear polysiloxanes. There are, however, very few studies concerning the stability or hazard of the higher molecular weight chlorodisilane-hydrolyzed products.

High-resolution FT-ICR has been used to determine the exact mass of various polysiloxane species present in the exhaust flow from a high-temperature oxide deposition process utilizing dichlorosilane. It was found that the preferred reaction pathway of ion-molecule of the dichlorosilyl cation with water and DCS was the disiloxane formation through HCl loss. Disiloxane was a precursor to the highly flammable polysiloxanes that were identified in the exhaust gas and deposits. There are, however, no studies on the hazardous properties of these polysiloxane deposits.
The hazards of high-boiling residue from the TCS-direct process have been studied. This residue contained a mixture of chlorodisilanes and chlorosiloxanes. In particular, it was confirmed that the residue might produce shock-sensitive hydrolysis products or "popping gels". However, the detailed conditions and variables that influenced shock sensitivity of the hydrolysis products were not disclosed. One notable feature from this work is that the analysis of the residue revealed that it contained 72% HCDS along with 9% Cl₅Si₂O and 19% Cl₆Si₄O siloxanes. Therefore, it is likely that HCDS was a major contributing factor in generating shock-sensitivity products.

In the investigation report of the 2014 explosion in the Yokkaichi Plant of MMC, pure chlorosilane samples of silicon tetrachloride, TCS, HCDS, Si₃Cl₁₅, and Si₅Cl₂₀ were used to simulate the chlorosilane polymer and were hydrolyzed at temperatures between 5 and 15 °C and dried. The report concluded that the explosion power and impact sensitivity increased as a function of dryness after hydrolysis. The impact sensitivity disappeared regardless of the hydrolysis temperature if it was wet with liquid water. Thus, the report confirmed that HCDS might form hydrolysis products that were rendered shock-sensitive upon drying. Nevertheless, details of the tests were not given in the report. It is worthwhile to note that these studies described the hydrolyzed deposits of HCDS to be shock-sensitive only after an extended period of 24 h to 1 month.

Recently, a model structure of Si₈H₁₀O₁₄ for intramolecular oxidation involving HO–Si–Si–H bonds has been proposed theoretically in an attempt to find the cause of the MMC explosion. Nevertheless, there was no experimental verification of the model compound. However, the importance of Si–Si bonds was pointed out in the formation of intramolecular oxidation.

More recently, Zhou et al. performed a detailed study on the shock and heat sensitivity of the hydrolysis products of HCDS. Synthetic methods were developed to consistently prepare the hydrolysis products with high shock sensitivity. The shock sensitivity was determined by placing a sample between the jaws of a plier that was quickly squeezed to crush it. The sample was classified as shock sensitive if smoke, spark, or flame was observed. Such a classification of shock sensitivity is biased to the extreme end of high shock sensitivity. Thus, the hydrolysis products prepared by directly adding HCDS to water were found to be heat-sensitive but not shock-sensitive. Instead, molecular sieves were used as substrates, and shock-sensitive hydrolysis products from HCDS were formed as solid coatings on the substrates. The hydrogen atoms in the silanol groups or absorbed water are said to be the oxidant, and the silicon atoms in the Si–Si bonds were the reductant. When the materials are disturbed by a thermal or mechanical impact, fast redox reactions happen to form molecular hydrogen. A sequence of free radical reactions was proposed to explain the shock sensitivity and shock-induced chemical transformation. Clearly, this work aimed at the extreme end of high shock-sensitivity hydrolysis products which is possible but might not be as common as typical HCDS direct hydrolysis without any special substrate.

Earlier literature concerning the Si–Si linkages has been presented in an extensive summary by Hengge. The Si–Si bonds are said to be very sensitive to oxidation as the Si–O–Si bonding is thermodynamically strongly favored. Acid hydrolysis occurs to give polymeric compounds retaining Si–Si bonds; alkaline hydrolysis yields silicic acid with the disruption of the Si–Si bonding. The polymeric compounds with small Si–Si units are white amorphous powders, insoluble in all solvents except by decomposition. With aqueous ammonia or caustic alkalis, hydrogen is evolved. With abrupt mechanical or thermal shock, explosive reactions may occur, in which the enthalpy of oxidation of the Si–Si bonds to Si–O bonds is released. All of these reactions occur rapidly and quantitatively. There is no hindrance because of diffusion in the solid state. This is perhaps the earliest description of shock-sensitive nature of the hydrolyzed deposit from chlorosilanes with Si–Si bonds. Nevertheless, the exact mechanism and conditions that may affect the shock sensitivity remain unknown.

It is clear from the above literature that there remains no systematic study on the shock sensitivity of direct hydrolysis products of HCDS. In particular, the mechanism and parameters affecting shock sensitivity of the hydrolyzed deposit and more importantly the conditions or methods that may prevent or suppress the shock sensitivity of the deposit are crucial for safe handling/utilizing HCDS or other higher molecular weight chlorosilanes. These are the primary objectives of this work.

## 2. RESULTS AND DISCUSSION

### 2.1. General Observation of Shock-Sensitive Deposit

Contrary to the previous studies, shock-sensitive deposits with a limiting impact energy (LIE) of 5 J or more were found to be extremely easy to form, whether the HCDS is hydrolyzed as a liquid or vapor with ambient air or a controlled environment. The formation was found to be rapid, for example, less than 1 h of hydrolysis. Figure 1 shows the typical shock ignition of the hydrolyzed deposit in the Fall hammer impact. Each frame is differed by 1 ms.

![Figure 1](https://example.com/image1)

**Figure 1.** Typical shock ignition of a deposit by a Fall hammer impact. Each frame is differed by 1 ms.
25 ± 1 °C) for 10 min. The hydrolysis reaction produced a fume, and the clear transparent liquid turned into a white deposit in less than 10 min. The deposit was collected and tested by Fall hammer. The LIE was found to be 20 J.

2.2.2. Effects of Air Humidity. Under a controlled environment with precise moisture concentration, the hydrolysis rate is strongly dependent on the moisture content. Figure 2 shows the weight loss history for HCDS liquid filled in a new Fall hammer lower roller/collar combination and placed inside a balance that was purged with controlled air. The amount placed in the roller was 70 ± 10 mg. Five samples were placed in five different balances, all purged with the same source of controlled air. The dew point, however, was measured in each balance and was controlled within ±1 °C. The sample weight loss reached a maximum of approximately 50% at dew points of 15 and 10 °C. The hydrolysis was clearly incomplete in tests using air with a dew point of −5 °C as the sample was still partially transparent. The LIE for dew points of 15, 10, 5, 0, and −5 °C was found to be 30, 12.5, 10, 15, and 50 J, respectively.

2.2.3. Effects of Hydrolysis Time. The effects from the degree of hydrolysis were further studied using five sets of samples hydrolyzed using air with a dew point of 0 °C but for different hydrolysis times of 5, 10, 15, 20, and 30 min. Fall-hammer testing was carried out with a fixed energy of 50 J immediately after the target time was reached. Shock sensitivity only appeared after the sample was hydrolyzed for 30 min with a weight loss of only 28%, well before the peak weight loss (i.e., complete hydrolysis) was reached and well before a white powder was formed. For all other samples with shorter hydrolysis time, fumes were generated in the Fall hammer test. The shorter hydrolysis time generated the largest amount of fumes, as shown in Figure 3. Clearly, it is not necessary for HCDS to be completely hydrolyzed to be shock-sensitive.

In another series of tests, the hydrolysis time was extended to 80–100 min using air with a dew point of 0 °C. LIE has been known to be 15 J for 60 min hydrolysis under the same condition. The longer hydrolysis resulted in an LIE decreasing to 8 J at 81 min and then 6 J at 91 min. Note that 6 J was the lowest recorded LIE in liquid HCDS hydrolysis. This is comparable to RDX explosives which highlight the potential hazards of HCDS-hydrolyzed deposits.

Clearly, the shock sensitivity of HCDS liquid-hydrolyzed deposits not only depends on the degree of hydrolysis but is also influenced by the moisture and internal reactions once the hydrolysis is initiated. Excess moisture from humid air may not necessarily help to increase the shock sensitivity.

2.3. Vapor HCDS Hydrolysis in Moist Air. Liquid HCDS hydrolyzed by moist air suffers the disadvantage in that the moisture primarily reacts only with the surface of the HCDS liquid. Once it is hydrolyzed, it forms a crust which the water molecule must diffuse through to react with the remaining HCDS liquid. Vapor-phase hydrolysis offers no such mass-transfer limitation. An additional advantage of vapor-phase hydrolysis is that the molar ratio of HCDS and water can be controlled accurately. In the present work, tests were carried out for water/HCDS molar ratios of 1, 2, 3, 4, 6, and 12. The molar ratio of 6 is the stoichiometric ratio of HCDS that theoretically will react all Si–Cl bonds with water into silanol (Si–OH)

\[
\text{Si}_2\text{Cl}_6 + 6\text{H}_2\text{O} \rightarrow \text{Si}_2(\text{OH})_6 + 6\text{HCl}
\]

(1)

In reality, the silanol is unstable, and in most cases, condensation may occur leading to linear or cyclic siloxanes

\[
\text{Si}--\text{Si}--\text{OH} + \text{HO}--\text{Si}-- \rightarrow \text{Si}--\text{Si}--\text{O}--\text{Si}-- \rightarrow \text{Si}--\text{Si}--\text{H}_2\text{O}
\]

(2)

In each test, the reaction was continued for a period of 1–2 h. It was apparent that the deposit forms rapidly on the tube wall with the higher water/HCDS ratios providing the faster deposit formation. The corresponding LIE for water/HCDS molar ratios of 1, 2, 3, 4, 6, and 12 was determined to be 5, 10, 12.5, 12.5, 11, and 15 J, respectively. Clearly, shock sensitivity increases with decreasing water/HCDS molar ratio.

2.4. Characterization of Hydrolyzed Deposit. 2.4.1. Structure Characterization of the Deposit. Extensive infrared (IR) spectra analyses were performed for both liquid and vapor HCDS-hydrolyzed deposits. In addition, the spectra of Fall-hammer-ignited deposits were also collected. Figure 4 is an overlap of the typical spectra of liquid and vapor-hydrolyzed deposits and their shock-ignited deposits. The vapor-phase hydrolysis was done for a water/HCDS molar ratio of 6, whereas the liquid-phase hydrolysis was done at 0 °C dew point for 1 h. It should be noted that the attenuated total reflection (ATR)–Fourier transform infrared (FTIR) scans only the sample surface with a penetration depth of 0.5–2 μm. Repeat analysis of the same sample showed a slight variation in peak locations and intensity, which is attributed to the nonhomogeneity of the sample. However, the shift in peak wavenumber variation was usually limited to ±10 cm⁻¹.
The ignited deposit can be readily identified as a mixture of silicon dioxide (SiO$_2$) and silicon sesquioxide (Si$_2$O$_3$) in which the 1045 and 800 cm$^{-1}$ bands are the stretching and bending modes of Si–O–Si structure in SiO$_2$, respectively, whereas 875 cm$^{-1}$ is known for Si$_2$O$_3$. The identification of a shock-sensitive deposit is, however, not trivial. Comparison of the spectra for unignited and ignited deposit showed two new bands at 3230 and 720 cm$^{-1}$. The former is attributed to the hydrogen-bonded silanol (Si–OH), and not the absorbed water, because the absorbed water also showed at 1630 cm$^{-1}$.11 For the remaining two peaks, the 1000 cm$^{-1}$ band is still attributed to the asymmetric stretching mode of the Si–O–Si structure in the deposit, originated from the condensation of two silanol groups, and the 850 cm$^{-1}$ peak is still attributed to Si$_2$O$_3$ or Si–Si bond. The missing of the bending counterpart of Si–O–Si structure at 800 cm$^{-1}$ suggested that SiO$_2$ is not present. A notable feature of the two peaks is that their peak locations shifted simultaneously, as shown in Figure 5 in which all measured spectra were collected and compiled. The stretching mode of Si–O–Si has been known to shift nearly linearly with the oxygen content from 978 cm$^{-1}$ ([O] = 15 at. %) to 1048 cm$^{-1}$ ([O] = 52 at. %).12 The observed upper and lower bands for peak 1 in Figure 5 are 1047.6 and 960 cm$^{-1}$, respectively, which is in agreement with the above shifting range. In addition, the relative intensities of 1000–850 cm$^{-1}$ bands also increase with the increasing wavenumber of 1000 cm$^{-1}$ band. Thus, it was concluded that the variation of 1000 cm$^{-1}$ band location and intensity is an indication of the oxygen/silicon ratio in the deposit. Furthermore, the 1000 cm$^{-1}$ band location is also directly related to shock sensitivity, as shown in Figure 6, in which LIE is found to be roughly proportional to the increasing wavenumber of Si–O–Si stretching mode, regardless of whether the deposits were vapor or liquid HCDS-hydrolyzed.

The relative small band of 875 cm$^{-1}$ in the ignited deposit, as shown in Figure 4, suggests that nearly all of the Si–Si bonds in the deposit were oxidized upon shock ignition. A comparison between the spectra for a shock-sensitive HCDS-hydrolyzed deposit and a nonshock-sensitive deposit from silicon tetrachloride hydrolysis of Chen et al.13 confirms the importance of the 850 cm$^{-1}$ band and the Si–Si bonds in the appearance of shock sensitivity.

2.4.2. Morphology Studies. Figure 7 shows scanning electron microscopy (SEM) of a liquid HCDS-hydrolyzed deposit. The sample has an uneven surface with interlaced
large and small spherical particles. The smallest particle has a diameter slightly less than 1 μm. Figure 8 shows the SEM image of a vapor HCDS-hydrolyzed deposit. The transparent flake sample has a smooth surface which is composed of layers of spherical particles with roughly the same size stacked together. The particles have an average diameter of 1 μm. The morphology suggests that liquid HCDS hydrolysis is nonuniform, possibly caused by simultaneous reactions from the liquid surface and the vapor phase, where HCDS vapor reacts with moisture and deposits the byproducts on the liquid surface. Vapor HCDS hydrolysis, however, is homogeneous, depositing uniformly on the tube surface. Chemical elements detected by energy-dispersive spectrometry (EDS) indicated only silicon and oxygen with an oxygen atomic ratio of 53.85% for liquid and vapor hydrolysis, respectively. According to Section 2.4.1, hydrolysis using different moisture contents leads to different shifting of the Si=O–Si stretching model in the IR spectra, which in turn implies different oxygen/silicon ratio of the hydrolyzed deposit. The low oxygen/silicon atomic ratio measured by EDS in the vapor-phase hydrolysis is consistent with the low molar ratio of water/HCDS in the feed. It is also consistent with shifting of the Si=O–Si stretching model in the IR spectra of vapor HCDS-hydrolyzed deposit.

2.4.3. Heat of Combustion. The heat of combustion was measured for deposits from liquid HCDS hydrolysis (ambient air-hydrolyzed) and vapor HCDS hydrolysis (water to HCDS molar ratio of 6). Despite the difference in morphology and O–Si ratio, the measured heat of combustion was 4439 and 4550 kJ/kg for liquid and vapor HCDS-hydrolyzed deposits, respectively. It is likely that the combustion takes place mainly with the oxidation of Si–Si bonds that are preserved during hydrolysis. It should be noted that the measured heat of combustion is comparable to the explosion energy of TNT, which confirms the potential hazards of the deposits.

2.4.4. Shock Ignition under Inert Gases. To uncover the mechanism of shock ignition, it is necessary to know if the ignition is initiated with free oxygen from the air or from the deposit itself. The Fall hammer impact area was enclosed with a clear plexiglass box that was continuously purged with nitrogen or argon to reduce the oxygen concentration to less than 6%. Deposits from liquid HCDS-hydrolyzed with air at a dew point of 0 °C for 200 min were tested. Upon impact, the deposit ignited producing sparks but the overall fire ball was smaller than those in air, as shown in Figure 9. The measured IR spectra were nearly identical to other ignited deposits under air, which suggests that all Si–Si bonds are oxidized by oxygen from within the molecule. The oxygen will most likely come from the silanols.

The results suggest that shock ignition is a self-oxidation rather than a decomposition reaction or combustion with free oxygen as evident by the flaming particles. The fire ball that was not present in the inert environment suggests that there is a flammable gas/vapor release upon ignition. The most likely source of the gas is hydrogen, as indicated by Hengge, which is evolved from the hydrolyzed deposit with caustic alkalis. In fact, the alkaline attack has been used as a mean for determining Si–Si contents based on the volume of the hydrogen gas evolved. The corresponding mechanism is proposed as follows:

\[
\begin{align*}
-\text{Si-Si} & + \text{H}_2\text{O} \rightarrow -\text{Si-H} + -\text{Si-OH} \\
-\text{Si-H} + \text{H}_2\text{O} & \rightarrow -\text{Si-OH} + \text{H}_2 
\end{align*}
\]
FIGURE 10. FTIR spectra for heated hydrolyzed deposit.

$$\text{HO-Si-Si-OH} \rightarrow \text{HO-Si-O-Si-H}$$

(5)

It is said that this rearrangement may proceed explosively under excessive temperature rise. However, this mechanism did not include the evolution of hydrogen, which is also crucial in shock ignition.

Kudo et al. proposed a model molecule and a mechanism for intramolecular oxidation which includes oxidation of a Si–Si bond and formation of a H$_2$ molecule. The model molecule consists of four Si–Si bonds, seven Si–O–Si bonds, and one open ring in a partial hexahedral cage. Four Si–Si bonds are schematically in a parallel configuration. Three H atoms and seven OH groups are attached to eight Si atoms on each corner of the hexahedron. The first step starting from a model molecule includes 1,2-transfer of OH group and dissociation of Si–Si bond. Elimination of a H$_2$ molecule occurs in the second step. The third and the last step consists of 1,2-transfer of H atom and closure of the open ring. The mechanism can be summarized as

$$\text{Si}_8\text{H}_8\text{O}_{14} \rightarrow \text{Si}_8\text{H}_8\text{O}_{14} + \text{H}_2$$

(6)

Again, this mechanism suffers from the fact that the silicon–hydrogen bonds has a known Si–H band at 2260 cm$^{-1}$ which is missing from the recorded IR spectra in all of our HCDS-hydrolyzed deposits. A similar mechanism for hydrolyzed deposit from a mixture of HCDS and pentachlorodisilane (HSi$_2$Cl$_5$) has also been proposed. However, the model molecule also contains silicon hydride bonds. Clearly, the Si–OH silanol bonds play a crucial role alone in the shock ignition and evolution of hydrogen gas from of HCDS-hydrolyzed deposits.

2.4.5. Effect of Heating on Shock Sensitivity. To further resolve the role of silanol functional groups in shock sensitivity, direct heating was performed for known shock-sensitive deposits. The gases evolved from heating silicon sesquioxide gel prepared from HCDS hydrosylation have been studied by Belot et al. The gases evolved were mainly water until about 350 °C and hydrogen when heated above 200 °C. Between 200 and 350 °C, both water and hydrogen evolved simultaneously. The loss of water is attributed to condensation of silanols. In the present work, vapor HCDS-hydrolyzed deposits from a water/HCDS ratio of 12 were heated at temperatures from 100 to 400 °C for the same duration of 10 min. The results are shown in Figure 10.

An interesting finding was that heating at 100 °C for 10 min actually reduces the LIE to 5 J from the original 15 J, as noted in Section 2.3. Its IR spectrum is nearly identical to the spectrum of unheated deposit. It is likely that absorbed water is removed because of heating and hence reduces its LIE. Heating at 200 °C for 10 min, the deposit was nonshock-sensitive. The IR spectrum showed a diminished and shifted Si–OH band near 3300 cm$^{-1}$. Clearly, the condensation from two neighboring silanols takes place forming a cyclic Si–O–Si structure with Si–Si bond retained according to Innocenzi.

$$\text{HO-Si-Si-OH} \rightarrow \text{HO-Si-O-Si-H} + \text{H}_2$$

(7)

Heating at 300 °C and above showed similar spectra except that the silanol band disappeared completely. Innocenzi also suggested that an isolated silanol will condense with more difficulty with other silanols in comparison with hydrogen bonded neighboring silanols. Also, an isolated silanol bond has a sharp, narrow peak at 3740 cm$^{-1}$ which is not observed in all of the IR spectra in the present work. This result implies that all of the silanols that contribute to shock ignition are paired hydrogen-bonded neighboring silanols.

It should be noted that silanol (Si–OH) stretching vibrations also appear at 950 cm$^{-1}$ in addition to the 3230 cm$^{-1}$ band. Although such a distinct peak was not observed in the present work, the Si–O–Si band in the vapor HCDS-hydrolyzed deposit in Figure 4 did show an asymmetric shape with a peak at 969 cm$^{-1}$ and may include the contribution from the silanol band. Heating to 200 °C for 10 min also gave shifted, asymmetric Si–O–Si band, as shown in Figure 10, which is similar to the vapor HCDS-hydrolyzed deposit, although the 3300 cm$^{-1}$ band was already diminished. Thus, it is recommended that the 3300 cm$^{-1}$ band be used as the primary indicator for the presence of silanol groups in a hydrolyzed deposit.

2.4.6. Proposed Mechanism of Shock Sensitivity. On the basis of the above results, the following mechanism of shock sensitivity is proposed. The intramolecular oxidation of paired silanols attached on Si–Si bonds is initiated by shock, followed by the rearrangement and elimination of hydrogen gas and forming a networked silicon oxide.
The above mechanism is a direct extension of Schmeisser and Schwarzmann\textsuperscript{14} to generate $\text{Si}−\text{H}$ from silanols except that paired silanols are needed and a networked silicon oxide is formed. The above simplified mechanism explains all of the above studies on structure/shock interaction. Further work is still necessary to better characterize the exact structure of HCDS-hydrolyzed deposit.

Another implication from the above studies is that shock sensitivity of the deposit can be simply controlled by heating at elevated temperature to condense the silanol groups, according to Innocenzi\textsuperscript{11}. The remaining deposit is still flammable but not shock-sensitive and can be handled safely.

2.4.7. Effects of Excess Water. Although heating to condense the silanol groups of the hydrolyzed deposit can provide a simple means for eliminating shock sensitivity, it may not be practical to apply in real cases where the deposit is formed in an exhaust duct or liquid spills on the open ground. Results from Section 2.4.5 demonstrated that heating to remove absorbed water may reduce the LIE, whereas Section 2.2.2 demonstrated that hydrolysis with excess moisture in the air may increase the LIE. Thus, it is likely that excess water alone may provide a simple method to suppress the shock sensitivity of the hydrolyzed deposit. A series of tests were carried out to find the effects of excess water on shock sensitivity.

For simplicity, 50 J of impact energy is used as the criterion for shock sensitivity. A deposit from liquid HCDS hydrolyzed at ambient air was collected and dried in an oven at 100 °C for 1 h to remove all water absorbed on the deposit. Excess liquid water was then added to the dried deposit, placed in dry glovebox (dew point $-15$ °C) for drying until the desired deposit/excess water ratio is achieved. The wet deposit was then placed in collar/roller and shock impact tested.

The deposits with excess water weight ratios of 5:1, 3:1, 2:1, and 1:1 were tested. Only the ratio of 1:1 resulted in no ignition even with a repeated test, whereas the remaining ratios resulted in ignition. Thus, the shock sensitivity of the deposit can be suppressed by simply adding liquid water to 50 wt % and higher. Such a simple result is consistent with a wet RDX explosive (RDX/water $= 74/26$) that has a higher LIE of 30 J and higher. Such a simple result is consistent with a wet RDX explosive (RDX/water $= 74/26$) that has a higher LIE of 30 J and higher.

In the present work, 50 J was used as the impact energy when at 100 °C oven drying for 18 min, there is no ignition with a 50 J impact. With a 100 °C oven drying for 60 min, ignition was observed with a 50 J impact. The results confirm again that all HCDS hydrolyzed can be shock-sensitive as long as all of the excess water is removed.

3. CONCLUSIONS

In this work, the mechanism of shock sensitivity from HCDS-hydrolyzed deposits has been determined through extensive hydrolysis tests and IR studies. The hydrolysis processes include vapor HCDS hydrolysis in moist air and liquid HCDS hydrolysis in moist air. A BAM Fall hammer test apparatus was used to characterize the shock sensitivity of the hydrolyzed deposits. A simplified mechanism of shock sensitivity is proposed. Finally, recommendations are given for controlling the shock sensitivity of the hydrolyzed deposits by heating or adding excess water.

4. EXPERIMENTAL SETUPS

4.1. Determination of Shock Sensitivity. Shock sensitivity leading to an explosion is the major hazard of a hydrolyzed HCDS deposit. As the deposit may be formed in a process pump, process foreline, or exhaust line, any routine maintenance activities involving mechanical cleaning may trigger a shock reaction, causing an energetic event such as fire or explosion. It is important to properly characterize the mechanical energy from shock impact. A BAM Fall hammer impact test apparatus from Reichel & Partner GmbH, Germany, which meets the UN Recommendations on the Transport of Dangerous Goods test requirements, was used for determining the shock sensitivity of the deposits formed.\textsuperscript{18} The sample of the substance under test is enclosed in an impact device consisting of two coaxial steel rollers, one above the other in a hollow cylindrical steel guide collar. Rollers and collars are made of hardened, polished steel and are not recycled after the impact. Maximum sample volume is 40 μL. It was found that a sample mass less than 10 mg may produce false results as the sample is insufficient to cover the roller surface completely. Thus, a sample mass of 17 ± 1 mg was used in most of the tests whenever sufficient sample was available.

The results of the test are based on an explosion sound, flame, or color change of the sample. Distinction is made between “no reaction”, “decomposition” (without flame or explosion) recognizable by change of color or odor, and “explosion” (with weak to strong flame). The impact energy is determined from the mass of the drop weight and the height, for example, 1 kg $\times 0.5 \text{ m} \times 10 \text{ m/s}^2 = 5 \text{ J}$. The UN Recommendations define LIE as the impact energy when at least 1 in the 6 test samples results in an explosion.\textsuperscript{18} A substance with an LIE of 2 J or less is said to be too dangerous to transport. RDX, a typical explosive, has an LIE of 5 J. Japanese Standard JIS K 4810 classifies the sensitivity of explosives into eight classes with class 1 being $<2.5 \text{ J}$ and class 8 being $>25 \text{ J}$. In the present work, 50 J was used as the maximum impact energy above which the sample was classified as nonshock-sensitive. High-speed video camera with a rate of...
5000 frames/s was used to record the reaction from the impact.

4.2. Setup of HCDS Hydrolysis. HCDS has six Si–Cl bonds and thus offers the largest possibility of polysiloxanes network among other disilanes and monosilanes. It is expected that the process of hydrolysis strongly affects the rate of hydrolysis as well as the structure of the hydrolyzed products. Thus, careful control of the hydrolysis process is crucial for a reproducible result. HCDS is a liquid under ambient conditions. The HCDS hydrolysis can take place in four different processes:

- HCDS vapor hydrolyzing with water vapor (moisture)
- HCDS liquid hydrolyzing with liquid water
- HCDS liquid hydrolyzing with water vapor (moisture)
- HCDS vapor hydrolyzing with liquid water.

It is desired to study liquid HCDS hydrolyzed by moisture in air to simulate a liquid-spill scenario. The HCDS is, however, utilized in vapor form in the semiconductor manufacturing process. Thus, vapor HCDS hydrolysis in moist air is also important in simulating HCDS hydrolysis in a vapor exhaust line. These two hydrolysis processes will be the focus of this study.

4.2.1. Setup of Liquid HCDS Hydrolysis in Moist Air. HCDS is strongly moisture-sensitive; therefore, it is critical to control the environment to have a reproducible result. An analytical balance AXX220 from Shimadzu was used to record the weight loss during hydrolysis while controlling the environment. To avoid sample transfer of a shock-sensitive material, the roller/collar combination was used directly as the sample container. The HCDS liquid was filled into a lower roller/collar combination in a dry glovebox and was immediately placed onto the weighing pan. A small plexiglass chamber was placed inside a balance over the weighing pan to create better air flow and moisture control over the sample. Moisture-controlled air was prepared by mixing humid air and dry air (zero grade with a dew point less than −55 °C). This air mixture was directed upward in the balance through a tube ring with holes surrounding the pan. The balance enclosure acted as a secondary containment chamber, minimizing the interference from ambient air. When a desired hydrolysis time was reached, the top roller was placed on top of the sample and brought immediately to the Fall hammer apparatus. Tests were carried out for air with a dew point between −5 and 15 °C, and hydrolysis times between 5 min and 2 h.

4.2.2. Setup of Vapor HCDS Hydrolysis in Moist Air. The vapor pressure of HCDS is low; therefore, it is necessary to use a carrier gas to entrain the vapor. A mass-flow-controlled nitrogen stream is bubbled though the HCDS liquid to saturate it with HCDS vapor. This stream is flowed downward cocurrently with a controlled stream of moist air in a vertical tube with an internal diameter of 4.3 mm and 1.5 m long. A clear, transparent deposit (vs the white opaque powder in liquid phase hydrolysis) formed on tube wall was collected by tapping the tube wall at the bottom in a glass flask. Precise control of HCDS to water molar ratio was achieved by controlling the nitrogen flow rate, air flow rate, and moisture concentration in air. Tests were carried out for water/HCDS molar ratio = 1–12.

4.3. Characterization. To further characterize the hydrolyzed deposit, chemical functional groups, morphology, and heat of combustion were analyzed for selected samples. Chemical functional groups were determined by a Smiths IdentifyIR which is a compact ATR–FTIR spectrometer with a scan range of 650–4000 cm⁻¹. The spectrometer was placed directly inside a glovebox for sample preparation and analysis under controlled environment. An FEI Quanta 200 scanning electron microscope with EDS was used for morphology and chemical composition analyses. The heat of combustion was measured by an oxygen bomb calorimeter from Parr Inc., model 6100.

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Notes
The authors declare no competing financial interest.

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