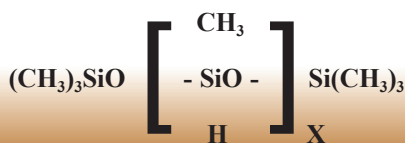


Safe Handling of Silicon Hydride Containing Polysiloxanes

Description

Silicon hydride containing polysiloxanes are a general class of siloxane polymers, the most common of which is poly(methyl hydrogen)siloxane. This linear polymer, which contains reactive hydrogen-to-silicon bonds (silicon hydride) along a polysiloxane chain, is represented by:



It is identified by the Chemical Abstracts Registry Number 63148-57-2. Siloxane polymers of this class are typified by Dow Corning® 1107 Fluid, a clear liquid with a viscosity of 30 centistokes and a closed cup flash point of 150°F.

Poly(methylhydrogen)siloxanes are used for formulating various coatings and treatments such as textile water repellents and softeners. They may be blended with other materials and/or emulsified to produce products with a wide variety of uses. They may also be used as a chemically reactive starting material to produce other silicone and organo-silicone copolymers. Other silicon hydride siloxanes may incorporate a mixture of dimethyl and methyl hydrogen, and/or SiH terminal siloxanes.

Health Hazards

Poly(methylhydrogen)siloxanes, such as 1107 Fluid, have no known adverse chronic health effects. Direct eye contact may cause slight discomfort with mild redness and dryness. Flushing the eyes with water for 15 minutes can relieve the symptoms. Users should consult the Material Safety Data Sheet for handling recommendations. Materials derived from poly(methylhydrogen)siloxanes such as blends, emulsions, or reaction products must be evaluated for health effects based on all of the constituents or reaction products present.

Chemical Reactivity

Poly(methylhydrogen)siloxanes, such as 1107 Fluid, are stable materials at ambient temperature and will not vigorously polymerize, decompose or condense AS ORIGINALLY PACKAGED. The value of these polymers as a source of industrial products is the extreme chemical reactivity of the silicon hydride bond with a multitude of other chemicals. These include alcohols, aldehydes, ketones, olefins, acids, acid catalysts, bases and silanol. Many metals such as zinc, tin, nickel, chromium, cobalt, platinum, and their metal halides catalyze the reaction with water, alcohols or silanol. These reactions can be very rapid and are extremely exothermic. All reactions, except those with olefins, aldehydes and ketones evolve gaseous flammable hydrogen as a by-product. This fact must be taken into account when processing and storing such materials.

About this brochure

This brochure contains hazard and chemical reactivity information along with fire and spill control information for silicon hydride-containing polysiloxane materials, plus recommendations for equipment design and sound operation. It is Dow Corning's intention that sharing this information with you will ensure that our materials are used in a safe and efficacious manner.

Two of the most commonly used reactions are:



A common, unwanted side reaction caused by the presence of water or alcohols is:



Where ROH is water or an alcohol

Even in the absence of an active hydrogen source, SiH products can pose hazards. Polymerization, de-polymerization, and equilibration processes can lead to side reactions producing flammable gasses or vapors other than hydrogen.

In the presence of acid or basic catalysts (e.g., Lewis acids or bases, clays, etc.) -even in the absence of humidity- redistribution of the siloxane chain has been observed associated with the formation of highly flammable by-products such as Me₃SiH, Me₂SiH₂, and MeSiH₃, depending on the nature of the siloxane backbone.

In extreme conditions where tri-functional HSiO_{1.5} units are present, the formation of silane gas (SiH₄) is possible. SiH₄ is a highly volatile (b.p. -112 °C) and pyrophoric (self-ignitable gas) in air.

Poly(methylhydrogen) siloxanes such as 1107 Fluid can decompose at elevated temperatures and rapidly release significant quantities of hydrogen gas which can over-pressure equipment. Engineering measures should therefore be taken to prevent situations where SiH siloxanes can be heated above 270°C.

Equipment Design

A Process Hazard Analysis should be completed for all processes using SiH siloxane particularly where exothermic reactions such as those shown are being performed. The aim of this analysis is to identify situations where runaway reactions or cross contamination could occur and identify procedural and engineering measures that should be put in place. Customers unsure of how to proceed with this type of risk analysis should contact Dow Corning for advice via their sales representative. If exothermic chemical reactions are being performed, an automated cooling system possessing a large safety factor is a desirable design feature. Adequate instrumentation should be provided to monitor and control critical process conditions such as temperature and pressure.

Poly(methylhydrogen)siloxane as supplied is essentially non-corrosive, therefore steel is a satisfactory material of construction. Stainless steel can be used for an extra measure of protection of product quality if desired. The suitability of these or other materials of construction is dependent on both the components present during processing and on process conditions such as temperature. Each situation must be evaluated to determine the optimum construction materials.

Processes should be designed so that SiH siloxanes are provided with dedicated charging systems (lances, hoses, piping and

pumps) to prevent contamination with other materials that could promote side reactions and the generation of hydrogen gas.

Reactors and storage vessels should be provided with vent systems to release any hydrogen generated and other gases during normal process operations. Great care should be exercised to prevent unintended contamination of storage tanks or process vessels with alkalis/acids, for example by back flow from caustic vent scrubbing systems. This could result in excessive rapid pressure generation through hydrogen evolution which is considered to be impractical to vent through standard relief systems.

Vessels should be provided with an inert gas (e.g., nitrogen) purging system that will insure the oxygen concentration is maintained below 2 percent before loading material to the vessel and throughout the processing operations. (The minimum concentration of oxygen needed to support combustion of hydrogen is 5 percent, and it is recommended that an adequate safety factor be applied to this value.)

Oxygen levels can be verified and controlled through use of a continuous oxygen monitoring system that samples the vapor space of the vessel. Over time, volatile silicon-containing materials can affect the accuracy of some oxygen analyzers; consult the analyzer manufacturer for specific application and maintenance recommendations.

All processing and storage (vessels) equipment should be designed with adequate electrical bonding and grounding to reduce the potential for static electricity as hydrogen has a relatively low ignition energy. Loading and unloading of materials by the use of dip pipes or by bottom filling is also recommended to reduce the generation of static electricity. It is recommended that all equipment, packaging and containers be inerted with nitrogen or other inert gas to prevent a static charge from igniting a potentially flammable atmosphere. Local ventilation should be considered for applications where material may be exposed to air.

The manufacturing process should be designed to prevent situations where SiH siloxane can be heated above 270°C. Particular care should be taken with pump systems where running a pump against a closed valve can result in heating of the liquid in the pump to this sort of temperature.

Operating Procedures

Operating procedures should be designed with emphasis placed on minimizing the possibility of uncontrolled reactions. In the case of exothermic reactions, it is advisable to control the reaction by controlled addition of the poly(methylhydrogen)siloxane to the other reactants in the reaction vessel. This minimizes the amount of silicon hydride available in the vessel at any time, allowing the reactants to act as a heat sink for the reaction.

In the case of exothermic reactions, it is important to monitor the temperature early in the reaction to ensure that the reaction has initiated hence avoiding a potentially dangerous over addition of poly(methylhydrogen)siloxane to the reactor. If the reaction does not initiate or stops after starting, addition of poly(methylhydrogen)siloxane should be stopped immediately to prevent the build-up of reactants in the vessel and a possible subsequent uncontrolled exothermic reaction. Addition should not be resumed until the situation is understood and corrected.

It is extremely important to keep a well mixed environment while performing reactions with SiH containing materials. The lack of agitation can build up un-reacted materials in process zones which may react in an uncontrolled manner upon later mixing or pumping of the fluid. The uncontrolled reactions may exhibit extremely exothermic heat generation, high gas production, or a combination of both.

If “reverse order addition” is attempted, in which the full quantity of poly(methylhydrogen)siloxane is initially loaded to the vessel and other reactants are subsequently added to the vessel, a thorough understanding of situations that could lead to undesirable side reactions should be known and measures taken in design and operating procedures to prevent such situations from occurring. It is extremely important to control the pH of aqueous emulsions of poly(methylhydrogen)siloxanes to minimize the evolution of hydrogen gas. Laboratory work has shown that for optimum stability, the pH of the aqueous phase should be in the range of 4 to 6.0. Deviation outside of this range particularly in the alkaline range, can result in extremely rapid evolution of hydrogen gas.

Operating practices need to ensure that only designated equipment is used on SiH siloxanes service. Consideration needs to be given to control the use of equipment that could potentially be shared such as hoses or portable pumps. Equipment dedicated for SiH handling should be clearly labeled to help identification.

Particular attention should be placed on equipment clean-out procedures to ensure that all vessels and associated piping systems are clean and dry before use. Trace acids and bases must be removed prior to conducting reactions or filling storage tanks and packaging. Primary alcohols should not be used to clean out equipment on SiH siloxane service.

Packaging

Dow Corning has chosen to package most materials containing poly(methylhydrogen)siloxanes in small plastic containers or containers that are provided with a venting device because of the potential for the generation of small amounts of hydrogen during transit and storage. The vent is part of the container closure and allows excessive internal pressure, which may be caused by the formation of hydrogen, to be relieved thus preventing package deformation or failure. Hazardous materials that are packaged in vented containers are not allowed to be shipped by air. (Reference IATA Dangerous Goods Regulations 5.0.2.13.2)

Storage of SiH containing fluids in closed glass containers is not recommended, due to the possibility of hydrogen pressure build-up without a visual indication of the glass container's high pressure prior to failure.

Drums that have contained other materials should not be reused to store SiH siloxanes due to the potential for contamination and resulting unwanted chemical reactions. Similarly, repackaging of poly(methylhydrogen)siloxanes is strongly discouraged to reduce possible contamination.

Fire Protection

By definition, 1107 Fluid, is classified as a class IIIA combustible liquid. Normal precautions for storing and handling combustible liquids should be followed, with additional focus on controlling the fire hazards that may arise from the generation of hydrogen, Me3SiH or Me2SiH2.

Normal safety procedures include isolating the material from ignition sources such as open flames, sparks and hot surfaces. Additional measures include adequate mechanical ventilation to minimize the concentration of any fugitive emissions of hydrogen gas that may form, adequate bonding/grounding measures, and the use of dry, inert gases (e.g. nitrogen) in equipment and containers. When purging and inerting are carried out, it is critical that levels of oxygen be kept low. The minimum oxygen concentrations required for hydrogen combustion are approximately 5 vol % (which is less than half that of typical hydrocarbons), and an adequate safety factor should be applied.

Adequate high level ventilation should be provided where hydrogen gas generating materials are stored or handled. It is important to ventilate the upper areas of buildings or storage facilities using or storing hydrogen-liberating materials, to avoid the generation of concentrated pockets of flammable hydrogen gas.

Note: The flammability characteristics of other similar polysiloxanes will vary and some poly(methylhydrogen) siloxanes are classified as flammable (Class I or II) liquids. Therefore, each product and each source of supply should be evaluated on its own particular properties as stated by the supplier or determined by the user.

Poly(methylhydrogen)siloxanes, such as 1107 Fluid, may pose a fire hazard through spontaneous combustion if in contact with absorbent material such as open cell insulation. This is a phenomenon exhibited by certain other polysiloxanes and many organic materials. Although 1107 Fluid has an autoignition temperature of 311°C, spontaneous combustion can occur as low as 50°C when in contact with open cell pipe or oven insulation. Care should be taken to prevent leaks and spills from contacting such materials, or by installing closed cell insulation in areas of anticipated liquid leaks or spillage.

The autoignition temperature of Me₂SiH₂ is 230°C and its boiling point is -20°C. The autoignition temperature of MeSiH₃ is 130°C and the boiling point is -57°C. Appropriate measures must be taken if these by-products are produced. Both materials are very flammable gases that will ignite in low oxygen containing atmospheres with low energy ignition sources (e.g. static sparks).

Fire Extinguishment

Fires involving SiH polysiloxane materials can be difficult to extinguish. Control can be accomplished with most extinguishing agents such as water fog, foam or carbon dioxide. The use of dry chemical or dry powder extinguishing agents is not recommended.

Fire testing has shown that fire extinguishment, particularly for well-developed fires, is best done with AFFF alcohol compatible foam. As with all burning liquids, straight water streams should be avoided as they can agitate and disperse the burning liquid and increase the intensity of a fire. Automatic fire sprinkler systems discharge water similar to a water fog nozzle, and have been shown to be effective in controlling fires involving 1107 fluid.

Care should be taken when using water based extinguishing agents as hydrogen can be liberated and, once the fire is put out, accumulate in poorly ventilated or confined areas and result in flash fire or explosion if ignited. Foam blankets may also trap hydrogen or flammable vapors, with the possibility of subsurface explosions.

Dry chemical extinguishers should not be used because they are typically very alkaline or acidic. If used on SiH materials, they will cause hydrogen evolution.

The products of combustion of poly(methylhydrogen) siloxanes are silicon dioxide, carbon dioxide, water vapor and various partially burned compounds of silicon and carbon. The products of combustion should be avoided and the appropriate personal protective equipment should be worn when fighting fires involving these materials.

Spill Control

Spills of poly(methylhydrogen)siloxanes should be cleaned up promptly to avoid a slipping hazard and to minimize the potential for fire. Neutral, non-combustible absorbent materials such as sand should be used to collect spilled SiH containing materials. The absorbed material should either be disposed of immediately or provided with adequate air circulation to prevent spontaneous ignition. No other waste should be added to the absorbed material. Suction equipment may also be used for spill removal, but such equipment should be designed and operated in a manner similar to those used for flammable materials due to the potential for hydrogen evolution. Equipment used for collection of waste should be dedicated for this use, or it should be thoroughly cleaned before use in another application. Collected materials should be disposed of in accordance with all federal, state and local regulations.

Environmental Issues & Disposal

The Material Safety Data Sheet should be referenced for the proper characterization of poly(methylhydrogen)siloxane wastes for disposal. Because the reaction produces gels, generates heat, and liberates flammable gases (e.g. hydrogen); waste storage, collection, treatment, and disposal methods should not be used that involve the potential for co-mingling of silicon-hydride containing streams with other wastes. Thermal destruction in a licensed hazardous waste incinerator is the recommended disposal method.

Note: The information in this brochure is offered in good faith as typical practice and not as specific recommendations for particular situations. The recommended procedures are believed to be generally applicable. However, each user should review these recommendations in the specific context of the intended use and determine whether they are appropriate.

References

Additional information regarding the safe handling of SiH containing products can be found on the Internet sites of the silicone producers associations:

- o Centre Européen des Silicones, Safe Handling of SiH Products (http://www.silicones-safety.com/files/SiH_manuel_22b.PDF)
- o The Silicones Environmental, Health and Safety Council of North America, Materials Handling Guide: Hydrogen-Bonded Silicon Compounds(http://www.sehsc.com/PDFs/SiH_Manual_Revised_01_Aug_07.pdf)

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