

Solstice® Propellant

Alternate Name(s): Solstice®1234ze, HFO-1234ze, 1234ze Flammability Assessment

Solstice® Propellant (trans-1,3,3,3-tetrafluoroprop-1-ene) is an ultra-low GWP liquefied gas propellant developed by Honeywell. It boils at -2.2° F (-19° C) and exerts a vapor pressure of 47 PSIG (3.2 bars gauge) at 70° F (21° C). Solstice® Propellant is designated as a Class 2.2 (nonflammable) Liquefied Gas N.O.S.

1. Flammability of Gases – Definition and Measurement

The Globally Harmonized System of Classification and Labeling of Chemicals (GHS) defines a flammable gas as a gas having a flammable range in air at 20°C (68° F) and at a standard pressure of 101.3 kPa (1 atmosphere). Similar definitions of a flammable gas are found in DOT, IATA and IMDG regulations as well as in the Aerosol Dispensers Directive (2008/47/EC).

Gases are considered to have a flammable range if they exhibit vapor flame limits, i.e., a lower flame limit (LFL) and an upper flame limit (UFL). The LFL is the leanest concentration of the gas in air that will support combustion and the UFL is the richest concentration in air that will support combustion.

Two of the commonly-used tests to determine vapor flame limits are ASTM E-681 and International Standard ISO 10156. A brief description of those methods appears below. Solstice® Propellant was tested according to both methods and found not to have a flammable range under the prescribed test conditions of 20°C and one atmosphere. It was also tested under EC Testing Method A11: Flammability of Gases (E.U.) and did not have a flammable range. Solstice® Propellant is, therefore, classified as a nonflammable liquefied gas by GHS, DOT, IATA and IMDG criteria.

In ASTM E-681 the test gas is metered into a 12-liter spherical glass flask. Pressure is adjusted up to one atmosphere with air. The gas is mixed to ensure homogeneity and a spark is applied. A composition is considered to be flammable if it produces a flame which reaches the wall and exhibits an angle of greater than 90 degrees. Composition is varied to determine the lower and upper flammability limits at 50% relative humidity.

The ISO 10156 test procedure is similar except that the test vessel is a vertical glass tube 5 centimeters in diameter by 100 centimeters in height. A composition is considered to be flammable if it produces a flame which detaches from the source and moves up the tube.

Although classified as nonflammable by GHS, DOT, IATA and IMDG and as measured by ASTM E-681 and ISO 10156, Solstice[®] Propellant has a very narrow flammable range (LFL-UFL) of 8.0-8.5 volume percent in air at one atmosphere under the following conditions:

- Temperature is 86°F (30°C), (and)
- Relative Humidity $\geq 50\%$, (and)
- High energy ignition source or open flame is present

To further understand the high energy ignition source, the minimum ignition energy (MIE) of Solstice® propellant was measured by an outside laboratory.



2. Minimum Ignition Energy and Auto ignition Temperature

The minimum ignition energy (MIE) of a substance is the lowest spark energy capable of igniting that substance. The test is run in a 5-liter glass flask fitted with electrodes capable of generating electrostatic discharges of varying energy. Results are usually reported in joules or millijoules. Compositions ranging from 6 volume percent of Solstice® Propellant in air to greater than 13 volume percent were tested. At the normal test temperature of 68°F (20°C), there is no measurable MIE for Solstice® Propellant. It does not ignite. At 130°F (54°C), the MIE was determined to be between 61,000 millijoules and 64,000 millijoules. For comparison, the MIE of propane is 0.25 millijoules, HFC-152a is 0.38 millijoules and methane is 0.47 millijoules. This shows that Solstice® Propellant is very difficult to ignite even at the conditions listed in the prior section. For reference a typical static discharge from a human body is < 10 millijoules which is not sufficient to ignite Solstice® Propellant.

Auto ignition temperature is the lowest temperature at which a substance will spontaneously ignite without an external source of ignition. The auto ignition temperature of Solstice[®] Propellant was determined to be $694^{\circ}F$ ($368^{\circ}C$).

3. Aerosol Flammability Tests

The primary aerosol flammability test used in Honeywell's laboratory is the ASTM D 3065-01 flame extension test. That test involves spraying an aerosol product through a candle flame from a fixed distance of six inches (15 cm) and recording the length of the flame projection, if any. A product is considered flammable if a flame extends 18 inches (46 cm) or more, or if the flame flashes back to the actuator, sometimes called "the button". For this test, 100% Solstice® Propellant was charged into an aerosol can containing a dip tube (for a liquid spray). Two different actuators were used. One gave a stream-like spray and the other gave more of a misty spray. Regardless of the actuator, Solstice® Propellant exhibited no flame enhancement whatsoever in this test. In fact, it usually extinguished the flame. This is exactly the same behavior we observe with HFC-134a.

ASTM D 3065-01 also describes a "closed drum test" which is, essentially, the same as the enclosed space ignition test called for in the Aerosol Dispensers Directive (2008/47/EC) and the GHS. In this test, the entire contents of an aerosol can are sprayed into a 55-gallon (208 liter) drum that is lying on its side. A lighted candle is positioned inside the drum, mid-way along the length of the drum. The (spraying) time to ignition, if any, is recorded. The test is repeated three times with three separate cans. Solstice[®] Propellant was tested in aerosol cans with and without dip tubes to evaluate liquid versus vapor sprays. No ignition was observed in any of the tests.

Based on suggestions from a representative of a European aerosol association, the following "non-standard", aerosol flammability tests were conducted.

- The enclosed space ignition test was repeated with aerosol cans that had been preconditioned to a temperature of 113°F (45°C) prior to testing. The test is normally done at room temperature. Again Solstice[®] Propellant was determined to be nonflammable.
- The *ignition distance test* was run, also with pre-heated cans instead of at room temperature as called for in the method. That test is similar to the flame projection test except that the cans are sprayed at varying distances from the flame. Spray distances vary from ~36 inches (90 cm.) down to 6 inches (15 cm.) in 6-inch increments. (Figure 4) Solstice® Propellant was determined to be nonflammable in this test.



• To study the effect of spraying onto a hot surface, two non-traditional tests were run. In one, Solstice® Propellant was sprayed from an aerosol can directly onto a hotplate that registered a temperature of 392°F (200°C). It was sprayed both as a liquid (from an aerosol can with a dip tube) and as a vapor (from a can without a dip-tube). No ignition, flash or other "activity" was observed. In an even more extreme test, Solstice® Propellant (again liquid and vapor) was sprayed into a heated crucible over a range of temperatures up to 1166° F (630°C). No ignition, flash or other activity was observed at any of the test temperatures.

Conclusions

Solstice[®] Propellant is classified as a nonflammable liquefied gas by GHS, DOT, IATA and IMDG. The flame projection and ignition distance tests evaluate the flammability of an aerosol product sprayed directly into a flame source. In both the flame projection and the ignition distance tests, Solstice[®] Propellant was nonflammable. The enclosed space ignition test mimics a situation in which an aerosol is sprayed into a confined space where the vapors are allowed to accumulate in the presence of a flame source and Solstice[®] Propellant was nonflammable in this test. Finally, the "hotplate" and "crucible" tests simulate a situation in which an aerosol is sprayed directly onto an extremely hot surface. Solstice[®] Propellant was nonflammable in both of those tests. In all of the aerosol flammability testing we have conducted, Solstice[®] Propellant is non-flammable..

Testing Notes:

- 1. ASTM E-681 (flame limit determination) described in section 1 and ASTM D-3065-01 (flame projection test) described in section 3 were run at Honeywell's Buffalo Research Laboratory, as were the "hotplate" and "crucible" tests described in section 3.
- 2. ISO 10156, EC Testing Method A11: Flammability of Gases (section 1), Minimum Ignition Energy and Auto ignition Temperature (section 2) were all run by Chilworth Technology Ltd. Copies of the test reports can be made available upon request.
- 3. The Ignition Distance and Enclosed Space Ignition tests (section 3) were conducted by Stresau Laboratory, Inc. Copies of the test reports can be made available upon request.