COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS AND ON THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS

Sub-Committee of Experts on the Transport of Dangerous Goods

Twenty-ninth session
Geneva, 3-12 (a.m.) July 2006
Item 3 of the provisional agenda

TRANSPORT OF GASES

P200 Special Provision "d"

Transmitted by the expert from the United States of America

Addendum to ST/SG/AC.10/C.3/2006/39

Discussion

1. In SC/SG/AC.10/C.3/2006/39, the expert from the United States of America proposed to amend P200 by deleting special provision "d" from the entries for Arsine (UN2188), Germane (UN2192), Phosphine (UN2199), and Silane (UN2203). The intent of this paper is to provide the technical justification necessary for the Sub-Committee to consider the proposal.

2. This document presents test data relevant to the compatibility of silane with high strength steel alloys at ultimate tensile strength levels up to 1100 MPA. High strength steels have been shown to have an increased susceptibility to hydrogen embrittlement in hydrogen gas service. However, silane does not affect high strength steels in this manner. Although hydrogen is a component of the silane molecule, silane and the reaction of silane with steels produces a negligible amount of atomic (diffusible) hydrogen. In addition to stress, a significant amount of atomic hydrogen must be present for hydrogen embrittlement to occur. It is the atomic hydrogen, not the total hydrogen that includes molecular hydrogen that causes the embrittlement hazard. Due to the similar molecular structures, the expert from the United States proposes that arsine, germane and phosphine also produce a negligible amount of atomic hydrogen and will not cause hydrogen embrittlement.

3. Paragraph 6.2.2.2 of the UN Model Regulations identifies applicable standards for material compatibility. In the ISO standard 11114 – 1 "Transportable gas cylinders – Compatibility of cylinder and valve materials with gas contents – Part 1: Metallic materials", the gases arsine, germane, phosphine, and silane are identified as gases that contribute to hydrogen embrittlement. This is also reflected by the assignment of Special Provision "d" to these four gases in P200. The expert from the United States has been unable to locate data to show that silane at pressures as high as 200 Bar will cause hydrogen embrittlement in chromium-molybdenum type alloy steels, such as AISI 4145 steel alloys, with ultimate tensile strength levels up to 1100 MPa.

4. Chromium-molybdenum type alloy steels, such as AISI 4145 steel alloys, with ultimate tensile strength levels up to 1100 MPa have been used successfully for many years to manufacture high pressure cylinders for the transport of silane gas at pressures up to 200 Bar. These cylinders are made to the U.S. DOT 3T specification and to the current ISO 9809-1 standard. No incidents of failure of such cylinders in silane service at these strength levels and at these operating pressures have occurred. Export shipments from the United States for 2006 are expected in excess of 1000 metric tons. These world-wide shipments will utilize DOT 3T cylinders/tubes that are made from steel alloys that have tensile strength higher that those values that are considered to be not compatible with silane in ISO 11114 -1. However, these DOT 3T cylinders and tubes have been accepted world-wide for over 20 years without any failure that are related to hydrogen embrittlement. This market is being driven largely by the increase in LCD or flat panel display fabrication. These large area substrates are used for computer displays as well as monitors to replace the standard CRT used for television. Silane is a critical material in the fabrication of these types of electronic components as well as many others. While the majority of the shipments from the U.S. are to the Far East, - Korea, Taiwan, Japan and now China, the demand is growing from European Union countries.

5. To support this position, the expert from the United States submits to the Sub-Committee test data from an U.S. laboratory (see attachment). These tests were performed in order to evaluate the compatibility of silane gas with high strength steel alloys at ultimate tensile strength levels up to 1100 MPA. The procedure used in these tests satisfy the requirements of ISO standard 11114 – 4 “Transportable gas cylinders – Compatibility of cylinder and valve materials with gas contents – Part 4: Test methods for selecting metallic materials resistant to hydrogen embrittlement”. The results of these tests did not show any embrittlement of these steels alloys in the presence of silane.

6. ISO 11114-4 provides three different test methods. Any of these three test methods (A, B or C) will determine compatibility of materials related to hydrogen embrittlement. Based on the above test results, the current ISO 11114-1 and special provision of P200 are in conflict with ISO 11114-4.

7. In addition to the proposed amendment to delete the assignment of special provision “d” to these four gases in P200, the expert from the United States also proposes to add a note under 6.2.2.2 to indicate these gases are not subject to the limitations on hydrogen embrittlement for high strength steel alloys at ultimate tensile strength levels up to 1100 MPA. The expert from the United States is working within ISO/TC58/SC4 to modify the ISO 11114-1 based on the test data and results which were performed in accordance with method “C” of the ISO 11114-4.

Proposal

8. As proposed in ST/SG/AC.10/C.3/2006/39, delete references to special provision “d” in the special packing provision column of Packing Instruction P200, for the entries Arsine (UN2188), Germane (UN2192), Phosphine (UN2199), and Silane (UN2203).

9. Add a note to the end of 6.2.2.2:

Note: The limitations imposed in ISO 11114-1 on high strength steel alloys at ultimate tensile strength levels up to 1100 MPA do not apply to Arsine (UN2188), Germane (UN2192), Phosphine (UN2199), and Silane (UN2203).

JUSTIFICATION FOR THE CONTINUED USE OF CHROMIUM-MOLYBDENUM TYPE ALLOY STEELS WITH ULTIMATE TENSILE STRENGTHS UP TO 1100 MPa. (US DOT 3T) MATERIAL IN SILANE TRANSPORT

September 12, 2004

INTRODUCTION

The safe handling and storage of silane is not compromised by the use of DOT-3T / AISI 4145 material at 1600-1700 psig and ambient temperatures. While it is proven that high strength materials such as DOT-3T / AISI 4145 have an increased susceptibility to hydrogen embrittlement in hydrogen gas service, the same concept does not hold true for these materials in silane (SiH_4) service. Although hydrogen is a component of the silane molecule, silane and the reaction of silane with steels produces a negligible amount of atomic (diffusible) hydrogen. In addition to a sufficient stress, a significant source of atomic hydrogen must be present or hydrogen embrittlement will not occur. It is the atomic hydrogen, not the total hydrogen that includes molecular hydrogen (H_2) that causes problems.

The small amounts of hydrogen that is present in silane cannot be considered to have an effect on DOT-3T / AISI 4145 steels. The VLSI grade silane specification allows only 20 ppm hydrogen in silane maximum and more relaxed specifications allow 200 ppm hydrogen. Even at 200 ppm hydrogen, the partial pressure of hydrogen exerted on the steel is negligible.

As proof that the atomic hydrogen generated by the interaction of silane and its carbon steel container is not enough to cause hydrogen embrittlement or hydrogen assisted stress corrosion cracking, Advanced Silicon Materials, LLC (ASiMI) participated in a study of DOT-3T / AISI 4145 material in silane service in 1999.

In this study, 23 DOT-3T / AISI 4145 bolt-loaded compact specimens were prepared in accordance with ASTM standard E1681, "Standard Test Method for Determining Threshold Stress Intensity Factor for Environment-Assisted Cracking of Metallic Materials". Twenty-two of these samples were placed inside four tubes in a new DOT-3AAX ISO module. The silane was then allowed to interact with the surface of the module tubes and coupons for 6 months. In addition, supplemental hydrogen or increased silane pressure was also added to some tubes. After the samples were removed from their silane/hydrogen environment, they were examined for cracking. Additionally, several samples were analyzed for hydrogen content.

EXPERIMENTAL PROCEDURES

Samples of DOT-3T / AISI 4145 material provided by CP Industries (CPI) underwent constant displacement testing in order to examine the material for evidence of environment-assisted crack growth. Materials Engineering Associates (MEA) prepared twenty-three bolt-loaded compact specimens in accordance with ASTM standard E1681 "Standard Test Method for Determining Threshold Stress Intensity Factor for Environment-Assisted Cracking of Metallic Materials." Advanced Silicon Materials, LLC (ASiMI) exposed twenty-two of these samples to a silane atmosphere with varying pressures and hydrogen contents. After exposing the specimens to silane for approximately 6 months, MEA performed post-test evaluation of the samples. Durkee Testing Laboratories analyzed several samples for hydrogen content.

CPI provided 24 coupons from three heats (8 coupons each) of DOT-3T / AISI 4145 steel. Each sample is approximately 0.5 inch thick. The heat designations are T38H, T04R, and T27P. The tensile properties of the three heats as provided by MEA are listed in Table 1.

Table 1. Tensile Properties of DOT-3T AISI 4145 Steel Samples

Heat Code	Yield Strength (ksi)	Ultimate Tensile Strength (ksi)
T38H	133.9	150.6
T04R	135.0	151.9
T27P	135.1	153.7

The specimens were machined as a bolt loaded compact specimen of the MC(W) design, commonly known as a WOL specimen. The specimen configuration is dictated by ASTM E1681 and is presented as Figure 1 of the MEA report "Preparation of Specimens for Environmentally Assisted Cracking Tests." The width (w) and notch depth (a) is machined into each specimen. The width of 2 inches and notch depth of 0.6 inch are chosen in part to maintain a normalized crack size ($^a/_w$) within the specified limits of 0.3 - 1. The specimens are then precracked by fatigue approximately 0.1 inch.

The specimens are then loaded by widening the crack mouth a specified amount. This Crack Mouth Opening Displacement (CMOD) is measured by a displacement gage placed across the crack mouth. The CMOD for the samples is chosen so that a predetermined stress intensity factor (K_I) will be achieved. In choosing a stress intensity factor, it must not be so high that crack extension occurs during the loading process. It is important to use a stress intensity factor below that which would cause plastic deformation of the sample to occur. A maximum stress intensity factor (K_Q) was determined by loading one specimen to failure. All remaining specimens were loaded to achieve a stress intensity factor of $0.85K_Q$ (70 ksi-$\sqrt{\text{in}}$).

After the samples had been prepared, they were sent to Advanced Silicon Materials, LLC (ASiMI) to be placed in the test atmosphere. Bolt loaded specimens from each material heat were placed inside new, ISO module tubes as described in Table 2. The tubes were filled with high or low-pressure silane. Hydrogen was also added to two of the tubes to simulate elevated hydrogen. One sample was not placed in the module tubes to act as a control specimen for hydrogen measurement later on in the study.

Table 2. Design of Hydrogen Induced Cracking Study

Tube Number	Hydrogen	Pressure	Specimens
1	Low Hydrogen	Low Pressure	TO4R-6, T38H-6, T27P-1, T27P-4
2	High Hydrogen	Low Pressure	TO4R-5, T38H-4, T27P-5, T27P-8
3	Low Hydrogen	High Pressure	TO4R-4, TO4R-7, TO4R-8, T38H-5, T38H-8, T27P-2, T27P-3
4	High Hydrogen	High Pressure	TO4R-1, TO4R-2, TO4R-3, T38H-1, T38H-3, T27P-6, T27P-7
5-8	Low Hydrogen	Low Pressure	None
Control Sample	No Exposure	No Exposure	T38H-2

Tubes 1 and 2 were filled with approximately 100 psig silane and tubes 3 and 4 were filled to approximately 1200 psig. In addition to varying pressure, tubes 2 and 4 were supplemented with hydrogen in levels above what is generated by silane in service or during passivation. The levels of hydrogen in each tube were examined three times during the six-month test. The hydrogen level in tubes 2 and 4 was increased after the second evaluation.

A new, ISO module tube filled with silane will "passivate" over time. Passivation is the partial decomposition of silane by reduction with the carbon steel container. As silane reacts with active sites on the container, disilane and atomic hydrogen are generated. At first, the rate of disilane and hydrogen generation is fast, but over time, as the number of active sites on the container are reduced, the rate slows. The reaction slows until the rate is no longer changing. At this point, silane can be given a certain shelf life for which it will not decompose and generate disilane or hydrogen above specified levels.

The bolt-loaded compact specimens were removed from the module in early August 1999. Durkee Testing Laboratory analyzed the control specimen and one specimen from each tube for hydrogen content. Materials Engineering Associates (MEA) performed a post-test evaluation for hydrogen induced stress corrosion cracking on all 23 samples.

RESULTS

The details of the specimen preparation at Materials Engineering Associates (MEA) are presented in the report "Preparation of Specimens for Environmentally Assisted Cracking Tests."

The analytical data obtained by Advanced Silicon Materials, LLC (ASiMI) regarding hydrogen level are presented in Tables 3-5 below. The amount of hydrogen generated naturally by passivation in tubes 1 and 3 increases over time as expected. The rate of hydrogen generation cannot be determined from so few data points. Additionally, the passivation process requires removing the contaminated silane and replacing it with new silane which was not done in this experiment in order to keep hydrogen levels high.

Table 3. Analytical Data (3/20/99)

Tube Number	Hydrogen (ppm)	Pressure (psig)
1	95.2	109
2	225.2	100
3	16.4	1222
4	493.4	1243

Table 4. Analytical Data (4/3/99)

Tube Number	Hydrogen (ppm)	Pressure (psig)
1	108.3	N/A
2	99.6	80
3	17.5	1176
4	142	1200

Table 5. Analytical Data (6/28/99)

Tube Number	Hydrogen (ppm)	Pressure (psig)
1	144	98

2	>535	N/A
3	21.5	1159
4	>497	N/A

When analyzed for hydrogen content by the inert gas fusion method, not one sample showed hydrogen levels greater than 1 ppm. The results are shown in Table 6 below.

Table 6. Hydrogen Analysis Test Report

Sample	**Tube Represented**	**Results**
T27P4	1	0.8 ppm
T27P8	2	0.7 ppm
T04R2	4	0.3 ppm
T04R4	3	0.8 ppm
T38H2	Control	0.2 ppm

During the post-test evaluation at MEA, the samples were visually examined for cracking. The samples were broken apart to obtain a more clear view of the fracture faces. No evidence of hydrogen assisted stress corrosion cracking was found on any of the samples. The final values of load and stress intensity factor are given in Table 1 of the MEA report titled “Post-Test Evaluation of Environmentally-Assisted Cracking Tests.”

DISCUSSION

The ISO standard 11114-4 “Transportable Gas Cylinders Compatibility of Cylinder and Valve Materials with Gas Contents – Part 4: Test Methods for Selecting Metallic Materials Resistant to Hydrogen Embrittlement” specifies test methods required to qualify steels suitable for use in the manufacture of gas cylinders for embrittling gasses. This document applies to seemless gas cylinders where the working pressure of the filled embrittling gas is greater than 20% of the test pressure of the cylinder and where the partial pressure of the filled embrittling gas of a gas mixture is greater than 5 MPa (725 psi). If these conditions are not met, the cylinders may be designed as for ordinary (non embrittling) gases.

While it could be argued that the hydrogen in silane is less than 5MPa and therefore considered a non embrittling gas by this ISO standard, the test results obtained in this study are proof that silane does not cause hydrogen induced cracking for normal operating conditions or in instances of elevated hydrogen. While the ISO 11114-4 standard suggests following the procedure of ISO standard 7539-6 for the testing required, the test performed by Materials Engineering Associates (MEA) and Advanced Silicon Materials, LLC (ASiMI) was based on the ASTM version of the ISO 7539-6 standard. ASTM E1681, “Standard Test Method for Determining Threshold Stress Intensity Factor for Environment-Assisted Cracking of Metallic Materials.” The intent of test method (method C) described by ISO 11114-4 was realized through the use of ASTM standard E1681.

Both standards require that the bolt-loaded specimens be examined after being exposed to embrittling gas to determine whether or not the initial fatigue crack did or did not grow. The standards concur that absence of cracking constitutes a pass for the specimen. They also concur that if all specimens pass, the material is qualified for use with tubes of the tensile strength examined.

CONCLUSION

The concern over hydrogen embrittlement of 3T steel in silane service seems to be unsubstantiated. In addition to a sufficient stress, a significant source of atomic hydrogen must be present or hydrogen embrittlement will not occur. Although hydrogen is a component of the silane molecule, silane and the reaction of silane with steels produces a negligible amount of atomic (diffusible) hydrogen.

While hydrogen does cause embrittlement in high strength steels, the small amounts of hydrogen that is present in silane cannot be considered to have an effect on DOT-3T / AISI 4145 steels. Even at elevated levels of hydrogen, such as those examined in this study (500 ppm hydrogen), the partial pressure of hydrogen exerted on the steel is negligible.

This study was performed in accordance with new ISO standard 11114-4 that describes test methods for qualifying steels resistant to hydrogen embrittlement. This study offers proof that the atomic hydrogen generated by the interaction of silane and its carbon steel container is not enough to cause hydrogen embrittlement or hydrogen assisted stress corrosion cracking of DOT-3T / AISI 4145 material.

During the post-test evaluation, when analyzed for hydrogen content, not one sample showed hydrogen levels greater than 1ppm. Most importantly, no hydrogen assisted stress corrosion cracking was found on the samples. Thus, DOT-3T / AISI 4145 material should be qualified for use with silane under standard operating conditions.