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**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-second session, 2-6 December 2002,
agenda item 8(c))**

LISTING AND CLASSIFICATION

**Miscellaneous amendment proposals (Parts 2 and 3)
Hydrogen in a Metal Hydride Storage System**

Transmitted by the Expert from Canada

Introduction

1. At the twenty-first session of the Sub-Committee of Experts on the Transport of Dangerous Goods, the Expert from Canada submitted Informal Paper 35 to request comments on the proposals for hydrogen in a metal hydride storage system.
2. The Expert from the United States submitted comments in Informal Paper 56 and a number of delegations provided comments during debate.
3. Since the twenty-first session of the Sub-Committee, the Expert from Canada has benefitted from additional comments provided by the Experts from the United States and Germany as well as by industry.

4. There is still some discussion as to whether or not there should be a subsidiary risk assigned to these storage systems. Attached to this paper is a letter from Dr. Ned T. Stetson, Texaco Ovonic Hydrogen Systems, L.L.C., who, at the request of the Expert from Canada, has explained the technical aspects of the metal hydride storage systems and discusses the assignment of subsidiary risks. According to Dr. Stetson's comments and comments from others, the assignment of a subsidiary risk depends on the state and composition of the hydridable metal.

5. While it may be attractive not to mention subsidiary risks, the Expert from Canada believes that the consignor should have the option of assigning a subsidiary risk, depending on the state and composition of the hydridable metal, and this option is in keeping with the onus that is already on the consignor to classify substances. In addition, if a consignor believes that a subsidiary risk is appropriate, the consignor is fulfilling his or her obligations to provide the appropriate information for emergency response personnel should there be an incident.

Proposal

1. Consequently, the Sub-Committee is requested to consider the addition to the Dangerous Goods List of the following entry that would be applied to hydrogen in metal hydride storage systems:

UN No.	Name and description	Class or division	Subsidiary risk	UN packing group	Special provisions	Limited quantities	Packagings and IBCs		Portable tanks	
							Packing Instruction	Special provisions	Portable tank instruction	Portable tank special provisions
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
3AAA	HYDROGEN IN A METAL HYDRIDE STORAGE SYSTEM	2.1				None	P099	BBB CCC		

2. It is noted that the proposed shipping name, HYDROGEN IN A METAL HYDRIDE STORAGE SYSTEM, would also apply to such a system transported in equipment, therefore, an additional shipping name for equipment does not seem necessary.

3. It is noted that in column 8, P099 is suggested for this entry so that the competent authority approves the packaging.

4. It is suggested that the following two special provisions be assigned to this entry as noted in column 9:

"BBB. These storage systems shall always be considered as containing hydrogen."

"CCC. Depending on the state and composition of the hydridable metal, the consignor shall, if appropriate, assign a subsidiary risk of Division 4.1, Division 4.2 or Division 4.3.

Ms. Linda Hume-Sastre
Director, Legislation and Regulations
Transport Canada
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330 Sparks Street
Ottawa, Ontario, Canada K1A 0N5

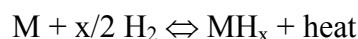
6 September 2002

Dear Ms. Hume-Sastre:

I am writing regarding to your efforts to establish unique listings and classifications of hydrogen absorbed in reversible metal hydrides within the UN Dangerous Goods List. First I would like to thank you for leading this effort, I believe that having a unique and appropriate classification for hydrogen absorbed in reversible metal hydride systems is needed and very important.

Storage of hydrogen utilizing reversible metal hydrides is actually a system composed of a pressure vessel filled with a finely divided metal powder and components for heat and gas conduction. The system must also include valving and safety devices such as pressure relief devices. The fine metal powder is a metallic alloy capable of absorbing hydrogen and forming a metal hydride. The physical properties of the material will change depending on the amount of hydrogen absorbed within the alloy. With this letter I will try to explain the chemistry behind the hydriding/dehydriding reactions of metal hydride materials and how it relates to the UN and US DOT material classifications.

The mechanism of hydrogen storage with metal hydrides is based on the following reversible equilibrium reaction:



where M is a hydridable metal; MH_x is the metal hydride where the hydrogen is bonded within the metal matrix and the heat (ΔH) is the enthalpy of the reaction and relates to the strength or stability of the metal-hydrogen bond. In designing materials for hydrogen storage for specific applications, the composition is modified to maximize x, the quantity of hydrogen which can be stored and to adjust the enthalpy (heat) so that the material absorbs and desorbs under the temperature and pressure constraints of the application. The other phenomenon which occurs with this reversible reaction is that the material will break down into fine (micron-sized) powders, due to the stress on the metal lattice in expanding/contracting between the reversible hydride/non-hydride phases.

Many of the traditional hydrogen storage materials, such as classical AB, AB_2 and AB_5 -type materials, are made by high-temperature melt processes and can be formed either directly as a coarse powder or crushed to a coarse powder. It is this initial coarse powder material that is filled into the storage cylinders. At this stage, the material has not undergone any activation process and will not readily absorb hydrogen. The material in this state may be non-flammable and might **NOT** be appropriately classified as a Class 4, Division 4.1, 4.2 or 4.3 material.

After filling the pressure vessel with the hydrogen storage material and sealing it with a valve assembly, the material is put through an activation process. The objective of the activation process is to prepare the material to readily absorb hydrogen. One of the processes in the activation is the

removal of the oxides that have formed on the metal surfaces, thereby forming a reduced metal. The final part of the activation is the absorption of hydrogen by the metal alloy. In this forward reaction to the hydrided phase, the heat term is positive, meaning that heat is released. The reason for this is that the hydrided material is in a lower potential energy state, i.e. more stable. In this lower energy state the material is fairly unreactive, especially with respect to oxidation. In this stage the material would be a flammable solid (4.1), but not pyrophoric (4.2).

Normally, to be useful as a hydrogen storage material in these applications, the material is tailored to release hydrogen at above atmospheric pressures and at ambient temperatures. If this hydrided material is removed from its container (and its overpressure of H₂), it will absorb ambient heat and undergo the reverse reaction to the non-hydrided metal powder. In the pure metal state, especially as fine micron-sized powders, the activated material will readily undergo re-oxidation. It will therefore react with air to form a metal oxide and produce heat. It is thus a 4.2 class material in the activated, non-hydrided state. The metal-oxygen bond strengths tend to be much higher than the metal hydrogen bond strengths, therefore even more heat is liberated by the oxidation reaction than the hydriding reaction.

As an example, TiH₂ is classified as a 4.1 flammable solid (UN1871)*, Ti powder is classified as a 4.2 substance capable of spontaneous combustion (UN2546)*. Unlike the alloys used in the storage system, titanium hydride will not spontaneously undergo the reverse dehydriding reaction except at elevated temperatures of 450°C or greater. This is due to the high Ti-H bond energy of ~159 kJ/mol versus ~30 kJ/mol for the alloys used in the storage systems. The Ti-O bond energy is ~662 kJ/mol, more than four times higher Ti-H bond energy. This oxidation would be observed with any micron-sized, very clean, reduced transition metal powder, including iron (UN1383)*. (*Note all UN numbers are taken from the Alfa Aesar catalog for Research Chemicals, Metals and Materials.)

The 4.2 classification of many reversible metal hydride materials arises from the UN and US DOT material classification tests being performed on fine, very clean, reduced metallic powders. The way the tests are designed and written, they cannot be carried out with an overpressure of hydrogen, if they could and the hydrided phases were tested, it is my opinion that they would be in the 4.1 class. In the real world, if the materials are removed from the containment and suddenly exposed, they would release hydrogen as designed, revert to the non-hydrided state and undergo oxidation. However in this real-life situation, the rapid release of hydrogen would cool the material and slow the oxidation process. In this case the oxidation might be slow enough to prevent the possible ignition of nearby combustible materials. In rupture tests in which storage systems with hydrided material have been ruptured without the spreading of alloy, the canisters rapidly vented hydrogen and cooled sufficiently to form ice on the vessel surface. The cooling and ice formation slowed the hydrogen release and no effects from the oxidation of the alloy were observed. The UN and US DOT material classification tests are carried out on samples which represent the “worst case” scenario of fully non-hydrided, activated, fine powders at ambient temperature being spread out on exposure.

It is my opinion that hydrogen storage systems utilizing reversible metal hydrides should be viewed as total systems whose critical component is the pressure vessel. As long as the pressure vessel integrity is not compromised, no problems should arise either with the gaseous hydrogen contained within the cylinder or with the activated storage alloy in either the hydrided or non-hydrided state. While the activated non-hydrided material may belong to the 4.2 class according to the current

classification system and testing, in a real world situation, the material within the storage system will not behave the same as other 4.2 class materials when exposed due to the dehydriding reaction which will occur.

The preceding discussion is generally valid for most of the classical AB, AB₂ and AB₅-type reversible metal hydrides. There are other types of potentially reversible metal hydrides, some of which fall into the 4.3, water reactive, classification, such as many of the magnesium-based hydrides and the alanate-type materials. However, again, due to changes in material properties while undergoing the hydriding/dehydriding reaction, the appropriate material classification may change depending on the state the material is in.

I am hopeful that this answers any questions you had regarding hydrogen storage systems using reversible metal hydrides and the material classification.

Sincerely,



Ned T. Stetson, Ph.D.
Senior Research Scientist