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**COMITÉ D'EXPERTS DU TRANSPORT
DES MARCHANDISES DANGEREUSES
ET DU SYSTÈME GÉNÉRAL HARMONISÉ
DE CLASSIFICATION ET D'ÉTIQUETAGE
DES PRODUITS CHIMIQUES**

**Sous -Comité d'experts du transport
des marchandises dangereuses**

**(Vingt deuxième session, 2-6 décembre 2002,
point 8 c) de l'ordre du jour)**

INSCRIPTION ET CLASSEMENT

Propositions de modification diverses (Parties 2 et 3)

Hydrogène dans un dispositif de stockage à hydrure métallique

Communication de l'experte du Canada

Exposé de la situation/Généralités

1. À la vingt et unième session du Sous-Comité, l'experte du Canada proposait le document informel INF. 35 sollicitant des commentaires concernant l'hydrogène dans un dispositif de stockage à hydrure métallique.
2. L'expert des États-Unis d'Amérique, dans le document informel INF. 56, a présenté certains commentaires et d'autres délégations ont également fait part de commentaires pendant la discussion.
3. Depuis la vingt et unième session du Sous-Comité, l'experte du Canada a bénéficié d'autres observations de la part des experts des États-Unis d'Amérique et de l'Allemagne, ainsi que de l'industrie.

* Il ne doit pas être tenu compte des exemplaires du présent document publié par erreur sous la cote ST/SG/AC.10/C.3/82, daté du 21 octobre 2002.

4. La discussion se poursuit quant à la nécessité de prévoir un risque subsidiaire pour de tels systèmes. Une lettre du Dr. Ned T. Stetson, Texaco Ovonix Hydrogen Systems, L.L.C., est jointe au présent document, qui explique, à la demande de l'experte du Canada, les aspects techniques des systèmes de stockage d'hydrogène à hydrure métallique et examine l'affectation de risques subsidiaires. Selon les observations du Dr. Stetson et d'autres intervenants, l'affectation d'un risque subsidiaire est fonction de l'état et de la composition de l'hydrure métallique.

5. Bien qu'il soit attrayant d'éviter la mention de risques subsidiaires, l'experte du Canada est d'avis que l'expéditeur devrait avoir l'option de mentionner un risque subsidiaire, selon l'état et la composition de l'hydrure métallique, option qui fait déjà partie des obligations de l'expéditeur qui doit effectuer la classification des matières. En outre, si un expéditeur pense qu'un risque subsidiaire est approprié, il ne fait que remplir ses obligations de fournir les renseignements nécessaires au personnel d'urgence en cas d'incident.

Propositions

1. Le Sous-Comité est prié de prendre en considération l'adjonction, dans la Liste des marchandises dangereuses, d'une nouvelle rubrique applicable à l'hydrogène dans des systèmes de stockage à hydrure métallique :

No ONU	Nom et description	Classe ou division	Risque Subsi- diaire	Groupe d'embal- lage	Dispo- sitions spécia- les	Quantités limitées	Emballages et GRV		Citernes mobiles	
							Instructions d'emballage	Dispositions spéciales	Instructions de transport	Dispositions spéciales
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
3AAA	HYDROGÈNE DANS UN SYSTÈME DE STOCKAGE À HYDRURE MÉTALLIQUE	2.1				AUCUNE	P099	BBB CCC		

2. Il est à noter que la désignation officielle de transport, HYDROGÈNE DANS UN SYSTÈME DE STOCKAGE À HYDRURE MÉTALLIQUE, serait également applicable à un tel système contenu dans un équipement; en tel cas, une désignation officielle pour l'équipement semble être superflue.

3. À noter également que, dans la colonne 8, l'instruction d'emballage P099 est suggérée pour cette rubrique, réservant ainsi l'approbation de l'emballage à l'autorité compétente.

4. Deux dispositions spéciales sont également suggérées dans la colonne 9 en regard de cette désignation officielle :

« BBB. Ces systèmes de stockage doivent toujours être considérés contenir de l'hydrogène. »

« CCC. Selon l'état et la composition de l'hydrure métallique, l'expéditeur, s'il le juge à propos, affectera un risque subsidiaire de la division 4.1, 4.2 ou 4.3. »

Ms. Linda Hume-Sastre
Director, Legislation and Regulations
Transport Canada
Place de Ville
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 H_2), 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, TiH_2 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 preceeding 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