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

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MISCELLANEOUS PROPOSALS OF AMENDMENTS TO THE MODEL REGULATIONS ON THE TRANSPORT OF DANGEROUS GOODS

Further information concerning paper ST/SG/AC.10/C.3/2009/30

Transmitted by the expert from the United Kingdom

Introduction

1. The accident described in paragraph 2 of paper 2009/30 appeared at first sight to have resulted from filling the aluminium cylinder with ethyl chloride, a practice forbidden in P200. However, this did not seem to be the complete answer, because the cylinder failed only 14 days after filling, whereas in previous known accidents involving ethyl chloride it had taken several years for the reaction between the aluminium alloy and ethyl chloride to result in cylinder failure.

2. The manufacturer of the cylinder has undertaken detailed research to gain a better understanding of the nature of the reaction between the cylinder contents and the material of the cylinder. This research has demonstrated a plausible explanation of how cylinder contents could have caused a vigorous exothermic reaction with the aluminium, leading to a pneumatic burst of the cylinder.

3. Known compatibility issues with aluminium have already been addressed in the Model Regulations and the standard ISO 11114-1. The mechanism described below, however, is the first known incident of its kind, and it was caused by a rare combination of factors.

4. The purpose of this paper is to present a summary of the information known to date and to propose action that should be initiated to prevent repetitions of this accident.

The Research Findings

5. Metallurgical study of the incident cylinder showed that it had been exposed for some time to a temperature of about 200^{o} C. Such a high temperature can only have been caused by a vigorous exothermic chemical reaction inside the cylinder.

6. The 10-litre cylinder was filled with 4 litres of ethyl chloride containing 20 ppm 1,1,1 trichloroethane (TCA) and 30 ppm trichloroethylene (TCE). A literature study showed that chlorinated hydrocarbons such as 1,1,1 trichloroethane and trichloroethylene have the property of reacting with aluminium alloy. Because this has been known for more than 40 years, inhibitors are added to these chlorinated hydrocarbons to prevent reactions with aluminium alloys. The ASTM Test Method D-2943-96 is used to assess whether the chosen inhibitor additions provide sufficient protection; BAM (Bundesanstalt für Materialforschung und –prüfung) also has a test method.

7. Further study showed three reasons to believe that inhibitors in this mixture were ineffective:

(i) A freshly scribed scratch on an aluminium surface immersed in uninhibited 1,1,1 trichloroethane produces a blood-red reaction product. A red deposit was found inside the incident cylinder. Red-coloured substances containing aluminium are rare;

(ii) Mixing these two hydrocarbons together is known to compromise the effectiveness of their respective inhibitors. Indeed, for this reason the Industry Best Practice advises that mixtures of chlorinated solvents should never be used;

(iii) Large-scale dilution of an aluminium-stable 1,1,1 trichloroethane with another solvent such as ethyl chloride is known to render the normal inhibitor ineffective against aluminium, and the same can be expected with trichloroethylene.

8. Having established that 1,1,1 trichloroethane and trichloroethylene can activate the aluminium surface, the researchers identified from the literature various reactions that would raise the temperature and generate gas so as to cause the pneumatic burst of the cylinder.

9. Substances potentially capable of initiating the sequence of chemical reactions outlined above will be limited to a small subset of halogenated hydrocarbons, with the vast majority of these substances being impotent.

Suggested Further Work

10. It is clearly necessary to ensure that information about the risks described above be made widely available to gas cylinder fillers. We foresee the following steps in that process:

(i) Identify the small subset of halogenated hydrocarbons that potentially could lead to the observed service failure;

(ii) Formulate advice in a way acceptable to the Industrial Gas Industry;

(iii) Publish the advice and consider any necessary changes to the Model Regulations.

11. An obvious place to publish advice on the compatibility of these hydrocarbons with aluminium alloy would be in the standard ISO 11114-1 “Transportable gas cylinders – Compatibility of cylinder and valve materials with gas contents – Part 1: Metallic materials”. This standard is currently under revision by ISO/TC58/Working Group 7, which has a total of 30 participants, including experts from CGA, EIGA, ECMA, US DOT and BAM. It is therefore

proposed that all information on this subject be given to ISO/TC58/WG7, where after due expert consideration, suitable advice to industry can be developed.

12. It is recognised that not all parties with a contribution to make will want to participate in this ISO working group. Therefore Dr Chris Jubb, the Chairman of ISO/TC58, has agreed to act as a focus for transmission of information to the working group and back to this Sub Committee. His e-mail address is chrisjubb42@tiscali.co.uk. We would particularly like to receive information from the Chemical Industry as to which halogenated hydrocarbons require inhibitors to prevent reaction with aluminium and its alloys.

13. The ISO working group next meets in week commencing 8th March 2010, so we expect to be able to report progress to the next session of the Sub Committee.
