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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-fifth session, 5-14 July 2004
Item 4 (c) of the provisional agenda

PACKAGINGS (including IBCs and large packagings)

Proposal to amend the Packing Instruction for Thionyl Chloride (UN 1836)

Submitted by the International Council of Chemical Associations (ICCA)

1. Introduction

For several decades European manufacturers of Thionyl Chloride (UN 1836) have used drums manufactured from galvanized, unalloyed steel, with a non-removable head (1A1), for its transport. The use of this type of packaging has proven to be a safe practice over time.

The restructuring of the dangerous goods regulations and the introduction of packing instructions has led to a change in these packing instructions in the UN Recommendations and consequentially in a number of the modal regulations (IMDG Code and ADR/RID).

Indeed, whereas till then ADR/RID and IMDG allowed the transport of Thionyl Chloride in "steel drums", the 11th revised edition of the UN Recommendations introduced Packing Instruction P802 including paragraph (4), whereby only drums of austenitic steel (1A1), with a maximum capacity of 250 liters, may be used as individual packaging for the transport of Thionyl Chloride.

As these requirements were taken over by the modal regulations, European manufacturers affected by this change have submitted, as an interim solution, applications to be exempted from this rule for the transport of Thionyl Chloride within national boundaries and by sea,. These exemptions have been granted by the competent authorities of Germany and Switzerland.(see Annex).

The purpose of this proposal is to include the use of galvanized unalloyed steel drums for UN 1836 in the UN recommendations, since such drums have been found to be suitable for safe use in the past, and have been approved for continued use by two different competent authorities.

2. Proposal

- Create a new Special Packing Provision "PPxy" to be included in subsection 4.1.4.1 in Packing Instruction P802

"PPxy For UN 1836 the following applies: Deviating from paragraph (4), drums of galvanized, unalloyed steel may also be used, provided that they satisfy the following additional requirements:
- The Thionyl Chloride must be free of water;
- The zinc layer must have a thickness of not less than 15 µm (before filling);
- Only new drums may be filled."

- Add the new Special Packing Provision "PPxy" in column 9 of In the Dangerous Goods List in Chapter 3.2, for UN 1836 THIONYL CHLORIDE.

3. Justification

Thionyl Chloride has been transported in galvanized drums of unalloyed steel, both overland and by sea, for more than 35 years. To date there have been no reports of any adverse incidents with this type of drums. The proposed supplement to P802 is intended to allow the continued use of this type of packaging, proven in practice to be adequate, in order not to have to replace them by other packagings that would lead to a substantial increase in expenditure, without any increase in safety.

Evidence that the use of drums of austenitic steel, currently required by P802, does not bring any additional safety, can be found in the BAM* technical safety Expert Report, which compares the corrosion resistance of both materials.

Thionyl Chloride, in anhydrous form, attacks metallic materials to only a very minor degree. If water is present, corrosive hydrochloric acid is formed and this will result in pitting corrosion, which however is identical for galvanized, unalloyed steel and for austenitic CrNi and CrNiMo steel. Both materials are indeed nearly equally susceptible to corrosion.

Also the characteristics of the deformation of the materials do not make the use of austenitic steels essential in any way. Drums manufactured from austenitic steel may have lower wall thickness values as a result of the more favorable deformation characteristics than drums fabricated from unalloyed steel but the requirements placed on such drums are maintained at the same level through the continued use of type testing.

In summary, the use of galvanized drums of unalloyed steel, under the conditions defined in the proposed Special Packing Provision "PPxy", offers a level of safety that is at least equal to that obtained through the use of the packaging required under the current P802 paragraph (4).

*BAM = Federal Institute for Materials Research and Testing, Berlin / Germany

Attachment: BAM Expert Report (incl. Annex 1 and 2)

Annex (in ENGLISH only)

BAM
Bundesanstalt für Materialforschung und –prüfung
[Federal Institute for Materials Research and Testing]
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Expert Report

File reference No. III.12/100674

Expert Report on the use of drums of unalloyed steel, with a non-removable head (1A1) and inner coating of zinc, for the transport of UN1836 Thionyl chloride by road and rail

On behalf of: **Bayer Chemicals AG**
PCH-SC-SY
Building K10
51368 Leverkusen

- 4th duplicate -

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1. Introduction and background

The company Bayer Chemicals AG, Leverkusen, Germany, applied in its letter of October 7, 2003 to the Federal Institute for Materials Research and Testing, BAM, for the issue of an Expert Report in accordance with § 5, paragraph 5 of the GGVSE for the granting of a national exemption to allow the use of drums of unalloyed steel with a non-removable head (1A1), with an inner coating of zinc, for the transport of UN1836 Thionyl chloride by road and rail.

2. Applicable regulations

Paragraph (4) of ADR/RID Packing Instruction P802 specifies drums of austenitic steel (1A1) for the transport of UN1836 Thionyl chloride.

Under § 5, paragraph 4, sentence 1 of the valid GGVSE, exceptions to this rule are permitted if adherence to a requirement cannot be expected. Bayer Chemicals AG regards this requirement as unreasonable since the packaging in use for decades for Thionyl chloride can no longer be used as a result of the changes to the regulations through the restructuring.

In addition, an exception in accordance with § 5, paragraph 4, sentence 2 of the GGVSE is permissible if it can be demonstrated that the safety precautions reflect the state of the art.

In concrete terms this means that the packaging in use for decades (galvanized, unalloyed steel drums) must be at least equivalent to the drums of austenitic steel required under paragraph (4) of Packing Instruction P802 in terms of safety engineering, to justify exemption under § 5 of GGVSE.

3. Characteristics of steels

a) Deformation characteristics

It is generally known that austenitic steel has a more favorable deformation behavior than unalloyed steel. Nevertheless, packaging forms manufactured from austenitic steel do not offer any intrinsic safety advantages over corresponding designs manufactured from an unalloyed steel, since the main criterion for the approval of packaging is the type testing. To meet UN requirements, drums manufactured from an austenitic steel can have a lower wall thickness compared to drums manufactured from an unalloyed steel – for the same performance values – because of the more favorable deformation characteristics of austenitic steel. Consequently, on the basis of requirements, drums manufactured from an austenitic steel will not necessarily have more favorable characteristics.

b) Corrosion resistance

The corrosion resistance of galvanized unalloyed steel, compared to austenitic CrNi and CrNiMo steels, upon exposure to Thionyl chloride, was recently investigated. The studies were conducted on the premises of Bayer Chemicals AG under the direction and supervision of the BAM.

As is evident from the attached report of the BAM (Annex 1), Thionyl chloride that is free of water attacks metallic materials to only a minor degree. However, corrosive hydrochloric acid is formed in the presence of water and pitting corrosion can then be expected to an equal degree with both galvanized, unalloyed steels and austenitic CrNi and CrNiMo steels.

With the exception of austenitic special higher-grade steels, nickel-based alloys and tantalum, all other metallic drum materials – including austenitic CrNi and CrNiMo steels – are susceptible to corrosion in the presence of Thionyl chloride containing water. Thionyl chloride is manufactured in the absence of air because of its hygroscopic properties. In addition, the product is filled by Bayer Chemicals AG in a nitrogen atmosphere.

No differences were seen in terms of corrosion characteristics between galvanized, unalloyed steels and austenitic CrNi or CrNiMo steels in the studies carried out. All the materials exhibited identical corrosion properties.

4 Assessment

On the basis of the conclusions drawn on the deformation characteristics and the studies of corrosion resistance, the BAM as the competent authority, granted Bayer Chemicals AG in Leverkusen approval on July 22, 2003 to use galvanized, unalloyed steel as an alternative packaging. This approval was granted under the GGVSee with reference to subsection 4.1.3.7 of the IMDG Code and has been assigned the file reference No. III.12/100242 (Annex 2). The BAM thereby expressly confirms that this alternative packaging in accordance with Section 4.1.3.7.3 of the IMDG Code represents a level of safety that is at least equivalent to that which would be attained if the substance UN1836 Thionyl chloride were packed in accordance with the Packing Instruction P802, provided that the following requirements are satisfied:

- the Thionyl chloride must be free of water
- the layer of zinc must be at least 15 µm (before filling)
- only new drums may be filled
- the drums must reach their final destination within 18 months of filling.

In our estimation, from a safety engineering perspective, the transport of Thionyl chloride in accordance with the approval we have granted under adherence to the above requirements is to be viewed as equivalent to transport in accordance with the applicable Packing Instruction P802. P802 does not limit the period over which the austenitic steel drums can be used, so that there is a greater risk that such drums will leak Thionyl chloride, for instance because of pitting corrosion which is difficult to detect in advance. By comparison, general corrosion of unalloyed steel upon entry of moisture is apparent in its early stages (through rust formation), so that such drums can be withdrawn from use long before they start to leak.

This holds equally for the transport of the substance by road or rail, since the requirements for marine transportation are on the whole more stringent.

5. Summary

On the basis of the documentation, the BAM has no reservations in terms of safety engineering about the transport of UN1836 Thionyl chloride in galvanized, unalloyed steel drums by road or rail, provided that the aforementioned conditions are met.

This packing form (galvanized drums of unalloyed steel) is at least equivalent in safety terms so that, provided the above conditions are met, in an exception under § 5 of the GGVSE it is ensured that the necessary safety precautions to limit the dangers that Thionyl chloride presents meet current technical safety requirements.

12200 Berlin, 15 January 2004

Specialist Group III.1 Dangerous goods packing	Department III.12 Dangerous goods packing Approval and Usage
On behalf of the BAM	On behalf of the BAM
[Stamp]	
Dr. P. Blümel	Dipl.-Ing. U. Körner

Annex 1

BAM-III.23 Berlin, 06.08.03

To Department III.12
Dr. Blümel

Comparison of corrosion resistance of galvanized unalloyed steel as a drum material with that of austenitic CrNi and CrNiMo steels for the transport of Thionyl chloride

Thionyl chloride ($SOCl_2$) that is free of water attacks metallic materials to only a minor degree. In the presence of water the metals are converted to their chlorides through the formation of corrosive hydrochloric acid and pitting corrosion is likely to result. With the exception of austenitic special higher-grade steels, nickel-based alloys and tantalum, all other metallic drum materials are not resistant to water-containing Thionyl chloride. The common commercial austenitic CrNi and CrNiMo steels are susceptible to the development of local pitting corrosion that can result in sudden leakages of the contents. Unalloyed steels that come into contact with hydrochloric acid are much more likely to exhibit increased general corrosion.

There is no data on the corrosion of metallic materials by Thionyl chloride in the Corrosion Data Survey, a NACE publication from 1985.

The DECHEMA Materials Table: Sulfur chloride and oxychlorides, drawn up in 1974, gives a general corrosion rate of < 0.5 mm per annum on exposure to Thionyl chloride that is free of water at 25 ºC. The corrosion rate increases as the temperature rises. The corrosion rates for the austenitic steels AISI 304 (1.4301) and AISI 316 (1.4401), upon exposure to water-free Thionyl chloride at 25 ºC, are between 0.02 and 0.5 mm per annum. It was stated for zinc that it exhibits mild corrosion when exposed to water-free Thionyl chloride at cold temperatures.

To derive concrete corrosion data on galvanized, unalloyed steel, we requested that Bayer Technology Services carry out corrosion studies in the laboratory at 55 ºC over a period of 7 and 21 days for galvanized steel (with test specimens derived from drums) and for zinc in water-free Thionyl chloride in an atmosphere of nitrogen. The test specimens were either immersed fully in the test medium, immersed to 50 % in the medium or suspended in the gas phase. The corrosion rates found after 7 and 21 days at 55 ºC were markedly below 0.1 mm per annum. The values for galvanized metal were 0.028 mm per annum after 21 days of immersion in the liquid phase. The corresponding value for the vapor phase was 0.032 mm per annum. Pure zinc exhibited a corrosion value of 0.021 mm per annum within 7 days of immersion in water-free Thionyl chloride.
Earlier studies with unalloyed steel in water-free Thionyl chloride revealed a corrosion rate of 0.03 mm per annum after immersion in the liquid and vapor phase for 34 days at room temperature. A value of 0.1 mm per annum was obtained after immersion in the liquid phase at 75 ºC for the same period. This temperature is not relevant for the transport of Thionyl chloride in galvanized drums.

The studies show that the use of galvanized drums for the transport of water-free Thionyl chloride is acceptable from a corrosion chemistry perspective. The use of stainless steel drums would not bring any advantages. It is absolutely essential that the Thionyl chloride be filled into the drums under a nitrogen atmosphere to fully rule out the entry of moisture.

[Signature]
Weltschev

Annex 2

Zulassung einer alternativen Verpackung
Approval of an alternative packaging

BAM
Bundesanstalt für Materialforschung und -prüfung

Zulassung einer alternativen Verpackung

Approval of an alternative packaging

Zulassung nach Kapitel 7.9 des IMDG Code
Approval according to chapter 9.7 of the IMDG Code

Aktenzeichen Nr. III.12/100 242

Rechtsverbindlich ist ausschließlich der deutsche Text
The German version is the only legally binding text

1. **Rechtsgrundlage** */ Legal basis*
Gefahrgutverordnung See - GGVSee vom 4. März 1998 (BGBl. I S. 419), zuletzt geändert durch die GGVSeeÄndV vom 31. Oktober 2001 (BGBl. I S. 2878) in Verbindung mit Unterabschnitt 4.1.3.7 des IMDG Code vom 5. Juni 2001 (Bundesanzeiger Nr. 123a vom 6. Juli 2001)
(Reference to the german regulation concerning the carriage of dangerous goods by seagoing vessels, in particular 4.1.3.7 of the IMDG Code)

2. **Antragsteller** */ Applicant*
Bayer AG
Chemicals
BU Performance Chemicals
51368 Leverkusen

3. **Spezifikation der Verpackung** */ Specification of the packaging*
Folgende Verpackung ist erlaubt, wenn die Vorschriften nach 4.1.1, 4.1.3 und Verpackungsanweisung P802 Nr. 4 des IMDG Code erfüllt sind. Die unter 5. genannten Auflagen sind einzuhalten.
The following packaging is authorized, provided the general packing provisions of 4.1.1, 4.1.3 and Packing Instruction P 802 (4) of the IMDG-Code are met. Requirements, named in No 5 must be met.
Fass aus Stahl mit nichtabnehmbarem Deckel (1A1) (unlegierter Stahl) mit einer inneren Beschichtung aus Zink
steel drum with non-removable head (1A1)(mild steel) with a inner coating of zinc

4. **Geeignete gefährliche Stoffe** */ Suitable dangerous goods*
THIONYLCHLORID, UN 1836, Verpackungsgruppe I
THIONYL CHLORIDE, UN 1836, Packing group I

5. **Auflagen** */ requirements*
Folgende Auflagen sind einzuhalten:
- das Thionylchlorid muss wasserfrei sein
- die Zinkschicht muss min. 15µm betragen (vor der Befüllung)
- es dürfen nur neue Fässer befüllt werden
- die Beförderung muss innerhalb 18 Monate nach der erfolgten Befüllung abgeschlossen sein

following requirements must be met:
- *the Thionyl chloride must be anhydrous*
- *the thickness of the zinc layer must be at least 15µm (prior filling)*
- *new drums shall be used only*
- *the transport shall be finished within 18 month*

Bundesanstalt für Materialforschung und -prüfung (BAM) in 12205 Berlin
Zuständige Behörde der Bundesrepublik Deutschland gem. 7.9 des internationalen Codes für die Beförderung mit Seeschiffen (IMDG Code), autorisiert durch das Bundesministerium für Verkehr am 01. August 1991
Competent authority of Germany according to 7.9 of the International Maritime Dangerous Goods Code (IMDG Code), authorized by the Ministry of Transport on 1. August 1991

6. Zulassung ***/ approval***

Es wird bescheinigt, daß die in Ziffer 3 spezifizierte Verpackung bei Beförderung des unter Ziffer 4 bezeichneten Stoffes im Seeverkehr unter Einhaltung der in Ziffer 5 genannten Auflagen mit den unter 4. der Verpackungsanweisung P 802 des IMDG Codes genannten Verpackungen gleichwertig und zur Verwendung zugelassen ist.

This is to certify that the packaging specified in No. 3 at least the same level of safety as packagings, which are described in Packing Instruction P 802 (4)of the IMDG Code, provided the requirements in No 5 are met. Under these conditions the packagings are approved for the transport by seagoing vessels for the substance specified in No. 4.

7. Widerruf ***/ Revocation***

Diese Zulassung wird unter dem Vorbehalt des jederzeitigen Widerrufes erteilt

This approval is declared revocable at any time

8. Befristungen ***/ Limitations***

Diese Gleichwertigkeitsbescheinigung ist bis zum 31. Dezember 2009 befristet.

This approval is valid until 31st December 2009.

9. Hinweise ***/ Notices***

Eine Kopie dieser Gleichwertigkeitsbescheinigung ist bei jeder Sendung mitzuführen, oder das Beförderungspapier enthält einen Hinweis, dass diese alternativen Verpackungen durch die zuständige Behörde zugelassen wurden.

A copy of this Approval for the equivalence of a packaging shall accompany each consignment or the transport document shall include an indication that alternative packagings were approved by the competent authority.

10. Rechtsbehelfsbelehrung ***/ Rights of legal appeal***

Gegen diesen Bescheid kann innerhalb eines Monats nach Bekanntgabe Widerspruch erhoben werden. Der Widerspruch ist bei dem Präsidenten der Bundesanstalt für Materialforschung und -prüfung (BAM), 12205 Berlin, Unter den Eichen 87, schriftlich oder zur Niederschrift, einzulegen.

Legal appeal may be raised against this approval within one month after the issue date. The appeal shall be submitted to the President of the Federal Institute for Materials Research and Testing (BAM), 12205 Berlin, Unter den Eichen 87, in writing or on record.

Berlin, 22. Juli 2003

Fachgruppe III.1
Gefahrgutverpackungen
Im Auftrag

Dr.rer.nat. P. Blümel
Oberregierungsrat

Referat III.12
Gefahrgutverpackungen
Zulassung und Verwendung
Im Auftrag

Dipl.- Ing. B.-U. Wienecke

(Diese Zulassung einer alternativen Verpackung besteht aus 2 Seiten)
(This Approval of an alternative packaging covers 2 pages)