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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-cinquième session, 5-14 juillet 2004
Point 4 c) de l'ordre du jour provisoire

EMBALLAGES (y compris GRV et grands emballages)

Proposition d'amendement à l'instruction d'emballage pour
le chlorure de thionyle (n° ONU 1836)

Communication du Conseil international des associations chimiques (ICCA)

1. Introduction

Pendant plusieurs dizaines d'années, les fabricants européens de chlorure de thionyle (n° ONU 1386) ont employé pour le transport de celui-ci des fûts en acier galvanisé non allié, à dessus non amovible (1A1). L'utilisation de ce type d'emballage s'est avérée dans le temps être une pratique sûre.

La restructuration des règlements relatifs au transport des marchandises dangereuses et l'introduction de nouvelles instructions d'emballage a conduit à modifier les instructions d'emballage dans les Recommandations de l'ONU et, en conséquence, dans un certain nombre de règlements modaux (Code IMDG et ADR/RID).

En effet, tandis que l'ADR/RID et le Code IMDG autorisaient jusqu'alors le transport du chlorure de thionyle dans des «fûts en acier», on a introduit dans la onzième édition révisée des Recommandations de l'ONU l'instruction d'emballage P802 avec son paragraphe 4, qui stipulait que seuls les fûts en acier austénitique (1A1) d'une contenance maximale de 250 litres pouvaient être employés comme emballages individuels pour un tel transport.

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Lorsque ces prescriptions ont été reprises dans les règlements modaux, les fabricants européens, concernés par ce changement, ont soumis, à titre de solution provisoire, des cas où il devrait être dérogé à cette règle, notamment lors du transport du chlorure de thionyle à l'intérieur des frontières nationales et par mer. Ces dérogations ont été accordées par les autorités compétentes de l'Allemagne et de la Suisse (voir l'annexe).

Puisque les fûts en acier galvanisé non allié se sont avérés dans le passé être d'un emploi sûr et que deux autorités compétentes différentes ont approuvé leur utilisation continue, il est proposé, dans le présent document, d'inclure leur emploi pour le n° ONU 1386 dans les Recommandations de l'ONU.

2. Proposition

- Créer une nouvelle disposition spéciale d'emballage «PPxy» à insérer dans l'instruction d'emballage P802 à la sous-section 4.1.4.1, ainsi conçue:

«PPxy Pour le n° 1386, par dérogation au paragraphe 4, les fûts en acier galvanisé non allié peuvent aussi être employés, à condition que soient respectées les prescriptions supplémentaires suivantes:
 - Le chlorure de thionyle ne doit pas contenir d'eau;
 - L'épaisseur de la couche de zinc ne doit pas être inférieure à 15 µm (avant remplissage);
 - Seuls de nouveaux fûts peuvent être remplis.».
- Ajouter dans la colonne 9 de la Liste des marchandises dangereuses au chapitre 3.2, en regard du n° ONU 1386 CHLORURE DE THIONYLE, la nouvelle disposition spéciale d'emballage «PPxy».

3. Motifs

Le transport du chlorure de thionyle s'est fait pendant plus de 35 ans, tant par la voie terrestre que maritime, dans des fûts galvanisés en acier non allié. À ce jour, aucun accident impliquant ce type de fûts n'a été signalé. La proposition d'adjonction à l'instruction P802 vise à autoriser l'emploi continu de ce type d'emballage qui a concrètement fait ses preuves, afin de ne pas avoir à le remplacer par d'autres emballages qui impliqueraient une augmentation importante des dépenses, sans renforcer aucunement la sécurité.

Le rapport technique d'expert sur la sécurité du BAM* contient des éléments témoignant du fait que l'emploi des fûts en acier austénitique, actuellement exigés par l'instruction d'emballage P802, ne contribue nullement à accroître la sécurité. Il y est aussi donné une comparaison de la résistance à la corrosion des deux matériaux.

* BAM = Institut fédéral de recherche et d'essai sur les matériaux, Berlin (Allemagne).

Le chlorure de thionyle, sous sa forme anhydre, n'attaque que très faiblement les matériaux métalliques. Si de l'eau est présente, il se forme de l'acide chlorhydrique corrosif provoquant des piqûres, qui sont toutefois les mêmes, qu'il s'agisse de l'acier galvanisé non allié ou de l'acier CrNi et CrNiMo austénitique. Les deux matériaux sont en effet presque également sensibles à la corrosion.

Par ailleurs, les caractéristiques de déformation des matériaux n'obligent en aucune façon à employer l'acier austénitique. Des fûts en acier austénitique peuvent avoir une épaisseur des parois moindre en raison de leurs caractéristiques de déformation plus favorables que celles de fûts en acier non allié, mais les prescriptions qui s'appliquent à ces fûts sont maintenues au même niveau au moyen de l'emploi continu des essais de type.

En résumé, l'emploi de fûts galvanisés en acier non allié, soumis aux conditions définies dans la disposition spéciale d'emballage «PPxy» proposée, offre un niveau de sécurité au moins égal à celui qui est obtenu en employant l'emballage exigé en application du paragraphe 4 de l'instruction d'emballage P802 en vigueur.

Pièce jointe: Rapport d'expert du BAM (y compris les annexes 1 et 2)

Annexe (en ANGLAIS seulement)

BAM
Bundesanstalt für Materialforschung
und –prüfung
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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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Annex 1: 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

Report issued by BAM department III.23 – Tanks for dangerous goods and accident mechanics – transport technology, transport tanks and pressure vessels

Annex 2: Approval of alternative packaging, file reference No. III 12/100242

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

On behalf of the BAM

Dr. P. Blümel

[Stamp]

Department III.12
Dangerous goods packing
Approval and Usage

On behalf of the BAM

Dipl.-Ing. U. Körner

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°C . 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°C , 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°C 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°C 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°C 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



**Bundesanstalt für
Materialforschung
und -prüfung**

Unter den Eichen 87
D-12205 Berlin
Telefon: 030/81 04-0

**Zulassung einer alternativen
Verpackung**

Approval of an alternative packaging

Zulassung nach Kapitel 7.9 des IMDG Code
Approval according to chapter 7.9 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

Schematische Darstellung der Chemie- und Materialtechnik

Seite:page 2

zur Zulassung einer alternativen Verpackung/Approval of an alternative packaging

vom 22. Juli 2003
Nr. III.12/100 242

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 Widerrufs 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)