

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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Sub-Committee of Experts on the Transport of Dangerous Goods

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Item 3 of the provisional agenda

Listing, classification and packing

Exemptions for polymerizing substances

Transmitted by the European Chemical Industry Council (CEFIC)

Introduction

1. In the last biennium, the Sub-Committee of Experts on the Transport of Dangerous Goods had decided to introduce polymerizing substances in Division 4.1.
2. The definition of section 2.4.2.5.1 describes polymerizing substances as “substances which, without stabilization, are liable to undergo a strongly exothermic reaction resulting in the formation of larger molecules or resulting in the formation of polymers under conditions normally encountered in transport.”
3. However, the text does not contain any provisions about exemptions.
4. Industry believes it would be helpful to introduce some criteria for exemptions in analogy to self-reactive substances of Division 4.1 and organic peroxides of Division 5.2.
5. The proposal of these exemption was discussed during the meeting in June / July 2016 by the Sub-Committee. During the review of the paper there was the request to provide more details on the proposed exemptions, including data.
6. In this paper CEFIC has included some data that has already been obtained and some pictures of the packages that should be exempted.
7. Regarding the request to test these products to determine the sensitiveness to the effect of intense heat under high confinement using the Koenen-Test, CEFIC thinks that this test cannot be applied, as the products would polymerize in the test apparatus and with that the test apparatus would no longer be usable.
8. We suggest the described proposal in analogy to 2.1.3.6.4 of the UN Model Regulations (see Annex I) to include an exemption based on the temperature on the surface and non-disruptor and fragmentation of the packaging.
9. In addition, to meet the concerns of some delegations, the new proposal is limited to packages, so IBCs and tanks are excluded from the exemption in the first step, to gain experience. The packages are tested as used for the transport and not combined to a certain amount.
10. Besides, another alternative proposal is added to just exempt the small packages from temperature control and not totally exempt them from the transport provisions.

Proposal

11. In the Model Regulations, insert a new section 2.4.2.5.3 to read:

“Any substance packed in packages shall be exempted from classification as a polymerizing substance of Division 4.1 in the package to be used, provided that upon initiation of the polymerization from a temperature 5 K above the SAPT of the tested package:

- (a) The temperature on the surface of the package does not exceed 100 °C, and
- (b) There is no effect outside the package, except that the packages might open without release of its contents.
- (c) no health or physical hazards arise from the emitted gases, especially concerning toxic or flammable gases.

The assessment shall be based on evidence obtained either by experiment in a 1:1 scale on the package size used for transport or by a model derived from experimental kinetic data in consideration of the heat loss of the package.”

12. An alternative wording could be:

“Any substance packed in packages shall be exempted from the requirement of temperature control when classified as a polymerizing substance of Division 4.1 provided that upon initiation of the polymerization from a temperature 5 K above the SAPT of the relevant package

- (a) The temperature on the surface of the package does not exceed 100 °C, and
- (b) There is no effect outside the package, except that the packages might open without release of its contents.
- (c) no health or physical hazards arise from the emitted gases, especially concerning toxic or flammable gases.

The assessment shall be based on evidence obtained either by experiment in a 1:1 scale on the package size used for transport or by a model derived from experimental kinetic data in consideration of the heat loss of the package.”

Justification

13. For self-reactive substances of Division 4.1, the following provisions apply according to 2.4.2.3.3.2 (g): “Any substance which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power shall be exempted from classification as a self-reactive substance ... provided that the formulation is thermally stable ... and any diluent meets the requirements of 2.4.2.3.5 ...”.

14. Similar wording can be found in 2.5.3.3.2 (g) for organic peroxides of Division 5.2.

15. Polymerizing substances do not detonate nor do they deflagrate. They have no explosive power and show no effects when heated under confinement. Their only hazard is a thermal runaway reaction and a possible pressure-buildup.

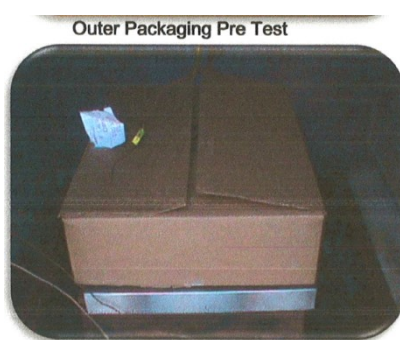
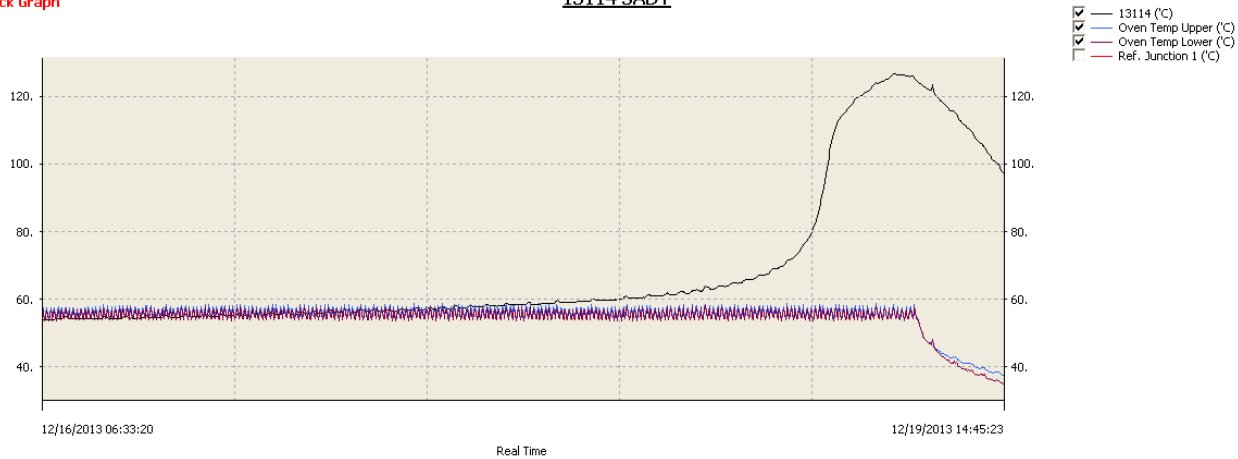
16. Therefore, the remaining applicable criteria are a tolerable temperature rise and the integrity of the package. This is supported by the following test:

17. A one part epoxy adhesive classified as UN3240, Self-Reactive Solid Type F, Temperature Controlled, packaged in sheet form with 80 individual sheets with a net weight

of 14.56 kg, exhibiting a heat of polymerization of 345J/g determined by DSC, was tested per the UN Manual of Tests and Criteria at 55°C. The internal temperature of the package was monitored. The temperature of sample ascended for approximately 97 hours from the start of the test to 53°C, and then continued to rise to >61°C approximately 94 hours later. The sample reached a maximum temperature of 126.6°C 102 hours after reaching 53°C. After the temperature plateaued the test was terminated. The package exhibited swelling due to the product design which is intended to expand upon curing.

Quick Graph

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18. Prior to the test the package has been opened to place the thermocouples into the middle of the material. But although the package has been opened due to this, no product ~~has~~ could escape, as it is now polymerized. The package is not damaged by the heat that developed during the test. Therefore the 2 criteria that are proposed are fulfilled:

- (a) The temperature on the surface of the package does not exceed 100 °C, and
- (b) There is no effect outside the package except that the packages might open without release of its contents, *there is no effect like spillage outside the package and the package itself is not damaged, just open.*

19. There was also a package tested with only 7 sheets of the above described product. The 7 sheet package configuration was also tested at 55C and that package passed the test. The package never exceeded a 6C rise in temperature. There was no change in the package after testing. Therefore, it makes sense for these products, to test the package used for transport instead of a 50 kg package.

Annex I

Text of paragraph 2.1.3.6.4 in the Model Regulations:

2.1.3.6.4 An article may be excluded from Class 1 when three unpacked articles, each individually activated by its own means of initiation or ignition or external means to function in the designed mode, meet the following test criteria:

- (a) **No external surface shall have a temperature of more than 65°C. A momentary spike in temperature up to 200°C is acceptable.**
 - (b) **No rupture or fragmentation of the external casing or movement of the article or detached parts thereof of more than one metre in any direction.**
 - (c) No audible report exceeding 135 dB (C) peak at a distance of one metre
 - (d) No flash or flame capable of igniting a material such as a sheet of 80 ± 10 g/m² paper in contact with the article; and
 - (e) No production of smoke, fumes or dust in such quantities that the visibility in a one cubic metre chamber equipped with appropriately sized blow out panels is reduced more than 50% as measured by a calibrated light (lux) meter or radiometer located in one metre from a constant light source located at the midpoint on the opposite walls. [...].”
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