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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 12 (c) of the provisional agenda

**HARMONIZATION WITH THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION
AND LABELLING OF CHEMICALS**

Physical hazards

Physical hazards requirements for organic peroxides and self-reactive substances
and comments on ST/SG/AC.10/C.3/2004/21

Transmitted by the expert from the United States of America

1. The expert from the United States received a technical paper from the Organic Peroxide Producers Safety Division (OPPSD) of the Society for the Plastics Industry (SPI) concerning the labelling and classification of organic peroxides and self reactive substances. OPPSD does not have observer status on either the TDG or GHS Sub-Committee and is not able to submit papers for consideration by the Sub-Committees. The OPPSD paper provides information and identifies issues that are relevant to the labelling and classification of organic peroxides and self reactive substances. The paper also provides comments on the proposal from Norway (ST/SG/AC.10/C.3/2004/21) and suggests alternative labelling options. The paper identifies other problems associated with the current classification of organic peroxides and self-reactive substances and suggests actions that should be considered by the Sub-Committees. The OPPSD paper is submitted for consideration by both the GHS and TDG Sub-Committees so that these views can be taken into account when considering the Norwegian proposal (see Annexes 1 and 2). While we are grateful for the work that Norway has undertaken to try to enhance the hazard communication requirements for organic peroxides, the expert from the United States suggests that the issue raised by Norway requires careful consideration and urges the Sub-Committees not to take a decision without allowing sufficient time to adequately consider all possible alternatives. It is necessary to welcome the involvement of the safety organizations such as OPPSD because they can provide valuable information necessary to reach a solution that will benefit all concerned.

Annex 1

Re: Proposal to Reclassify Organic Peroxides

Attached is a proposal to Reclassify Organic Peroxides by removing them from class 5 oxidizing substances and combining them more closely with self-reactive substances. Organic peroxides are generally not compatible oxidizers and their hazard characteristics are not similar. This information is provided in part as a response to the proposal by Norway to change the label for organic peroxides. It is also however a subject that has been of both concern and study for several years by the Organic Peroxide Producers Safety Division (OPPSD) of the Society for the Plastics Industry (SPI) and has been discussed with the international community and the subject of papers presented at IGUS-EOS meetings.

The OPPSD was formed in 1962 to organize and promote the development of a classification system for organic peroxides together with the supporting tests. Previously, the manufacturing companies conducted OPPSD activities, individually, since the US did not have a national laboratory for such studies. OPPSD is also the coordinator of safety issues relating to organic peroxides. The OPPSD was an active participant in the early development of the UN classification scheme for organic peroxides and in the tests currently used therefore. Working with the National Fire Protection Association (NFPA) the first national storage code for the storage of organic peroxides was developed and is currently in the process of being upgraded.

The OPPSD is submitting the attached proposal, which recommends removing organic peroxides from Class 5 – oxidizing materials, with which organic peroxides are not compatible, and combine them more closely with self-reactive compounds.

Annex 2

Introduction

1. In the United Nations' *Recommendations on the Transport of Dangerous Goods*, organic peroxides were placed in Class 5 with oxidizing substances, evidently because they are formally derivatives of hydrogen peroxide. They therefore have an oxygen-oxygen group and, thus, an available oxygen (O). However, organic peroxides are weak oxidizers. Their properties, in fact, are dramatically different from that of oxidizing substances in Division 5.1. For instance:

- Organic peroxides are phlegmatized, or stabilized (desensitized), by organic materials. This includes even the organic peroxyacids, which are the strongest oxidizers in Division 5.2. The reverse is true of the oxidizing substances in Division 5.1^{1, 2} which are not compatible with, and are sensitized by, organic materials.
- Organic peroxides, in general, are not compatible with the oxidizing substances in Division 5.1 since they are organic in composition and provide fuel for oxidizers.

Organic peroxides, however, are generally similar in properties and are thus classified by the same tests and flow chart as self-reactive substances.³ While it is agreed that there are sufficient differences to justify a separate division, the current grouping places them in completely separate classes. It is recommended that self-reactive substances and organic peroxides be assigned to separate divisions within Class 4.

2. The transfer of organic peroxides to the same class as self-reactive substances is consistent with the general principles of the United Nations' *Recommendations on the Transport of Dangerous Goods Model Regulations* (13th Revised Edition). It is stated under the heading "Principles Underlying the Transport of Dangerous Goods", paragraph 4, that "With this exception, the aim of regulations is to make transport feasible by eliminating risks or reducing them to a minimum. It is a matter therefore of safety no less than one of facilitating transport." Further, under the heading "Consignment Procedures", it states: "Whenever dangerous goods are offered for transport, certain measures should be taken to ensure that the potential risks of the dangerous goods offered are adequately communicated to all who may come in contact with the goods in the course of transport. This has traditionally been accomplished through special marking and labelling of packages to indicate the hazards."

3. The labels required in 5.2.2.2 of the Model Regulations should be affixed on goods or packages. The labelling system is based on the classification of dangerous goods and was established with the following aims in mind:

- to make dangerous goods easily recognizable from a distance by the general appearance (symbol, colour and shape) of the labels they bear;
- to provide, by means of colours on the labels, a useful first guide for handling, stowage and segregation.

¹ Section 2.5.1, p 81, *Model Regulations - Recommendations on the Transport of Dangerous Goods, 13th revised edition, United Nations* (see also 2.5.3.2.4 p 85-94 and 2.5.3.5, p 99).

² *Swern, Organic Peroxides Vol III, Wiley-Interscience, 1972, p 360.*

³ *Figures 20.1 (a) & (b), p 188 and 189, Manual of Tests and Criteria - Recommendations on the Transport of Dangerous Goods, Third Edition, United Nations.*

One of the primary requirements of the transport document for dangerous goods is to communicate information relative to the hazard of the goods being offered for transport . . . individual national authorities or international organizations may consider it necessary to require additional information”

4. The communication of the information relative to the hazards of organic peroxides, can be significantly improved by removing organic peroxides from the same class as oxidizing substances, Class 5, and by modifying the label to more properly represent the true hazard posed, which is flammability, combustibility, and thermal stability. The current colour and symbol (icon) of Division 5.2, which is identical to that used for Division 5.1, falsely implies that organic peroxides are similar to, and compatible with, oxidizers. In reality, organic peroxides and oxidizers should be segregated from one another. For example, the International Maritime Dangerous Goods Code requires that organic peroxides be separated from oxidizers during transport.

Problem

5. In the interest of safety and to comply with the consignment procedures as set forth in the UN Model Regulations, it is necessary to correlate the inherent hazards with the labeling for purposes of ensuring compatibility, easy recognition, and appropriate emergency response in the event of an incident. The proposal submitted by Norway (see ST/SG/AC.10/C.3/2004/21) recognizes that organic peroxides and oxidizing materials, which are both currently in Class 5, are fundamentally different and that there is a need to change the shipping label for organic peroxides, to differentiate them from oxidizers. The proposal also sets forth the importance of having a shipping label that is recognized from a distance. We agree with Norway that it is important to effectively communicate the hazards of organic peroxides to emergency responders. The paper also recognizes the difference in burning hazard between oxidizers and organic peroxides. However, we do not feel that the proposal by Norway adequately resolves all of the problems that have been identified. We believe that fundamental changes to both the classification and hazard communication for organic peroxides are warranted in order to:

- minimize the potential for incidents in transport involving incompatible materials such as oxidizers, and;
- reduce the likelihood of improper emergency response procedures being used in the event of an incident.

6. The common opinion that organic peroxides are strong oxidizers is incorrect but difficult to change, even among some chemists (who have not worked with them). The organic peroxyacids are the strongest organic peroxide oxidizers, yet they are phlegmatized by diluting them with organic solids or liquids (also water). Di-tert-butyl peroxide (DTBP) is so weak an oxidizer that it releases only a trace of iodine from a solution of potassium iodide. Analysis is carried out by chromatography. The extent of the misconception is obvious from the following quotation from a highly respected technical journal: “Di-tert-butyl peroxide (DTBP) is a clear, colourless to yellow liquid. Like other organic peroxides, it is a powerful oxidizer---”.⁴ The Norwegian proposal presumes what is generally assumed, that commercial organic peroxides supply much of their own oxygen for combustion. Contrary to common belief, organic peroxides contribute very little internal oxygen for combustion. DTBP, common organic peroxide manufactured in considerable volume, contributes internally only 1/24th of the oxygen required for combustion. The oxygen-oxygen bond however is energetic, and thus energy is released when the oxygen-oxygen bond is broken.

⁴

Antrim et.al., Process Safety Progress, 17, 3 (Fall) 225.

7. The Norwegian proposal retains the oxidizing symbol while acknowledging that flammability is the real hazard. We believe that since flammability is the real hazard that the symbol should be that of a flame. The solid red top on the label suggested by Norway was discussed extensively by the OPPSD but it was agreed that a striped top more accurately represents the hazard. Organic peroxides have a broad range of burning properties⁵ and only a few have the properties of a “flammable liquid”, which employs a solid red label. “Flammable” as used in the sense of a “flammable liquid”, has distinct properties other than burning. Flammable liquids have low temperature flash points, low ignition energy, often a broad vapor explosive range, and a heavy vapor density, which makes them especially hazardous compared to combustible liquids.

8. As Organic Peroxide formulations are fuels, mixing them with oxidizers is the major hazard to be avoided in storage, handling, and transport. Mixing in certain critical ratios can, in fact, produce an explosive. The proper handling of spills is also very critical. Since the peroxide bond is energetic, commercial organic peroxide formulations are commonly phlegmatized by dilution (mass per-peroxy group), usually by high boiling organic solvents, water, or by inert solids. Internal dilution by employing a high molecular weight molecule is also used to increase stability. When an instability problem occurs, dilution by a high boiling solvent (e.g. plasticizer) is usually the best treatment for stabilizing (desensitizing) organic peroxides, while this would be the worst treatment for an oxidizer.

9. Self-reactive substances currently are assigned to Division 4.1, which places them in a division with other dangerous goods with which they are not readily compatible (powdered metals which require exactly opposite treatment in fire control). A study of the options concluded that placing organic peroxides in Class 4, Division 4 and self-reactives in Division 4.5 would enhance transport safety.

Hazard Communication

10. The Organic Peroxide Producers Safety Division (OPPSD) of the Society of the Plastic Industry (SPI) has been studying several shipping label options including the one proposed by Norway and their ease of recognition in addition to their identification of the hazards of the goods (organic peroxides) being transported.

Since organic peroxides pose no hazard as oxidizers, but are a hazard when combined with oxidizers, it is considered an essential safety issue that the oxidizing symbols on the currently required labels be replaced by the flame symbol. The striped red and white on the upper half of the label conveys the burning characteristics of most of the organic peroxide formulations, while the bottom yellow retains the relationship to the old label and makes the name readily readable as well. It is also proposed that Class 4 labels indicate the Division numbers at the bottom of the label as opposed to simply indicating 4. This would further enhance the ability of emergency responders to differentiate between hazards.

5 The UN separates organic peroxides into 7 classes, the first being too hazardous to be shipped and the last being so low in hazard that it is exempted from hazards labelling. The US storage code NFPA 432 separates the organic peroxides into 5 classes, which does not include the UN. Class A, if included, would make this 6 classes. Note the considerable similarity. The primary difference is the US emphasis on the burning characteristics and fire suppression requirements, which includes packaging standards other than physical integrity. The UN does not recognize the flammable or combustible character of organic peroxide formulations in their classification, even for the few organic peroxides with low flash points.

11. A label similar to that suggested by Norway has been under consideration by the OPPSD as a combination organic peroxide-flammable liquid label for those few organic peroxides that are also flammable liquids. Adopting such a label would eliminate the need for a subsidiary label but would also make the label selection and recognition of the burning characteristics more complex. This approach also would not address the compatibility issue or take into account that organic peroxides are more closely aligned with self-reactive substances than oxidizers.

12. The labels that are recommended by the OPPSD for organic peroxides and for self-reactive substances are shown below.



(No. 4.4)
Division 4.4
Organic Peroxides
Symbol (flame); black
Background: upper half:
white with seven vertical red stripes;
lower half: yellow;
Figure: '4.4' in bottom corner



(No. 4.5)
Division 4.5
Self-reactive Substances
Symbol (flame); black;
Background: upper half:
white with seven vertical red stripes;
lower half: yellow;
Figure: '4.5' in bottom corner

Proposal

13. It is proposed that the organic peroxides be removed from Class 5, Division 2 and assigned to a new Class 4, Division 4 and that the self-reactive substances be moved from Division 4.1 to a new Division 4.5. It is further proposed that a new label be employed in which the upper half of the label be striped red and white and the lower half be yellow, and that the flame replace the oxidizer symbol. All Class 4 labels should include the division number at the bottom of the label.

14. The Norwegian proposal identifies the problem and provides a means for addressing the hazard communication shortfall, however it is our goal to encourage the Sub-Committee to adopt a comprehensive and appropriate solution that will address all of the shortfalls in order to preclude the need for future incremental changes to the Model Regulations while enhancing safety.

Justification

15. The changes proposed will substantially increase safety during transport and storage and place the regulatory requirements on a scientifically sound basis.
