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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 Globally Harmonized System of Classification and Labelling of Chemicals

Eighth session, 7-9 December 2004
Item 2 (a) of the provisional agenda

UPDATING OF THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS (GHS)

Physical hazards

Note by the secretariat

The document ST/SG/AC.10/C.3/2004/106 submitted to the TDG Sub-Committee for its twenty-sixth session (29 November-7 December 2004) may be of interest to the GHS Sub-Committee for the discussion of the above agenda item. It is reproduced hereafter.

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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-sixth session, 29 November-3 December 2004
Item 2 of the provisional agenda

TEXTS ADOPTED BY THE SUB-COMMITTEE AT ITS TWENTY-THIRD, TWENTY-FOURTH AND TWENTY-FIFTH SESSIONS AND RELATED PROPOSALS

Hazard Communication for Organic Peroxides

Transmitted by the expert from the United States of America

Introduction

1. At its 25th session, the Sub-Committee provisionally adopted a proposal from Norway (see ST/SG/AC.10/C.3/2004/21) to amend the label for organic peroxides. The Sub-Committee recognized 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 label and placard for organic peroxides, to more effectively differentiate them from oxidizers. The Sub-Committee retained the oxidizing symbol even though several experts acknowledged and agreed that the hazard associated with organic peroxides is more of a flammability hazard since organic peroxide formulations are fuels and the primary hazard is fire and burning rate. Organic peroxides are generally weak oxidizers. The expert from the United States of America believes that the symbol for organic peroxides should be a flame and that requiring different symbols for oxidizers and organic peroxides would improve recognition of the hazards of these dangerous goods in transport and the workplace. Since organic peroxides pose only minor oxidizing hazards, but are a hazard when combined with oxidizers, it is considered that replacing the oxidizing symbols on organic peroxide labels with the flame symbol would enhance safety. This paper requests that the Sub-Committee consider:

- changing the symbol used for organic peroxides from a burning O to a flame to better represent the true hazards associated with organic peroxides and to better differentiate the oxidizer and organic peroxide labels;

- authorizing either black or white symbols consistent with other labels in 5.2.2.2.2.

Flame versus Oxidizer Symbol on Labels and Placards

2. Organic peroxides were originally placed in Class 5 with oxidizing substances, evidently because they are formally derivatives of hydrogen peroxide. They 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 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 are not strong oxidizers. They 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. Since organic peroxides, in general, burn rapidly and are incompatible with most oxidizers and considering the extraordinary hazard of a fuel-oxidizer mixture. It is most important that the properties of oxidizers and organic peroxides be readily identified and that these materials be properly segregated in transport and storage.

3. In the interest of safety and to comply with the consignment procedures in the UN Model Regulations, it is necessary to correlate the inherent hazards with the labelling for purposes of ensuring compatibility, easy recognition, and appropriate emergency response in the event of an incident. The purpose of labels and placards is to make dangerous goods easily recognizable from a distance by the general appearance (symbol, colour and shape) of labels and to provide, by means of colours, symbols and numbers on the labels, a useful first guide for handling, stowage and segregation.

4. The communication of the information relative to the hazards of organic peroxides, can be significantly improved by better differentiating the organic peroxide label from the oxidizer label. The label colour change that was adopted in July will improve the current situation but additionally requiring different symbols on the oxidizer and organic peroxide labels will enhance the ability of individuals to distinguish between the two labels more efficiently for purposes of emergency response, transport and workplace safety. This is particularly critical for individuals that are unable to recognize colour differences or in situations where smoke, smog or other factors make colour recognition difficult. It is considered that improved differentiation using more than one variable (colour and symbol) will minimize the potential for incidents involving incompatible materials such as oxidizers, and reduce the likelihood of improper emergency response procedures being used in the event of an incident.

5. Since GHS pictograms do not use colour as a distinguishing hazard communication variable the symbol used is particularly important. Currently the GHS pictograms for oxidizing substances and organic peroxides are the same while the symbol for self-reactive substances which have similar hazards as organic peroxides is a flame. If it is important from a transport safety perspective to differentiate organic peroxide formulations from oxidizing materials for compatibility concerns in storage and transport and because different emergency response procedures are necessary then it is equally a concern

in the workplace. Using the same symbol for both oxidizers and organic peroxides falsely implies that organic peroxides are similar to, and compatible with, oxidizers. The GHS Sub-Committee should be consulted to request their views on whether the same pictograms for oxidizers and organic peroxides should be used or whether there is a preference to change the pictogram for organic peroxides. Currently the hazard statement for organic peroxides states "Heating may cause a fire" This hazard statement is more consistent with a flame symbol than with a burning O. Considering the 2011 implementation date proposed by Norway, it appears there is certainly time to consider this matter to ensure that an appropriate level of safety is afforded for all sectors.

Proposals

6. The TDG Sub-Committee is requested to consider whether the labels should be shown with two alternatives (black on dark background or white on dark background) consistent with other labels in 5.2.2.2.2 (see models No. 2.1, No. 2.2, No.3 and No. 4.3 for instance). The following are examples of the proposed organic peroxide labels as they would appear in 5.2.2.2.2 of the Model Regulations:

(No. 5.2)
Division 5.2
Organic Peroxides
Symbol (flame): black or white
Background: upper half red, lower half yellow
Figure '5.2' in the bottom corner