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SPECIAL FEATURE SECTION: SAFETY OF CHEMICAL PROCESSES

Editorial

Are MSDs Safe? Reflections at the MSDS's 20th Birthday[1]

OSHA estimates that 32 million Americans are exposed at their workplaces to 650,000 dangerous materials.[2] Until the 1970s, trade-named and internal material codes "concealed" the information on the identity of the materials that were in use. OSHA's Hazard Communication Standard 29 CFR Part 1910 became effective on November 25, 1983. It was based on the constitutional right to know. Seven years later, the International Labor Organisation (ILO) followed suit, requiring that producers will mark their products in a manner that will indicate their identity, and that manufacturers will provide Material Safety Data Sheets (MSDSs) that will contain vital information on the chemicals. That is, a producer of a dangerous material must provide an MSDS to protect its workers and its users.

The MSDS should contain the following 16 chapters of information:[3]

- Substance identity and company contact information
- Chemical composition and data on components
- Hazards identification
- First aid measures
- Fire-fighting measures
- Accidental release measures
- Handling and storage
- Exposure controls and personal protection
- Physical and chemical properties
- Stability and reactivity
- Toxicological information
- Ecological information
- Disposal considerations
- Transport information
- Regulations
- Other information

MSDS for the same material can be different from one producer to another, but nature requires that the information will be basically identical, or at least very similar: same material—same information. The information must be **complete**, **accurate**, and **updated**. If some information is not known (to the manufacturer? to the world?), it should be explicitly stated, and no omissions are allowed.

Things get complicated when the dangerous materials are mixtures. Regulations demand that, if the product is evaluated as a single product, the dangerous materials included should be named. If the product was not evaluated as a whole, toxic materials present in concentrations above 1% have to be detailed (and carcinogenic substances above 0.1%). A manufacturer may declare the presence of a dangerous material, the identity of which is a trade secret. Degreasing agents, for example, typically consist of saturated hydrocarbons, cyclic hydrocarbons, aromatics, and halogenated hydrocarbons. A survey published in Korea in 2000[4] on MSDSs of 21 degreasing agents communicates that (1) Most MSDSs were incorrect regarding the formulation ingredients. A third of them did not provide any detail regarding composition. (2) In most cases, safety information (classification, exposure levels, toxicity, etc.) was erroneous. Sixty-two percent stated wrong classification: 67%, wrong TLV and 67%, wrong LD_{50}. (3) In some cases, the presence of carcinogenic materials was not declared. The authors conclude: "The MSDS regulation relating to the confidential business information may need to be revised to ensure reliability of MSDS".

A well-known report by Kolp, Williams, and Burtan[5] on the Assessment of the accuracy of Material Safety Data Sheets studied 150 MSDSs. The study found that 11% misidentified the dangerous materials, 63% of the MDSDs had **missing or wrong information** on reported health effects, 53% were inaccurate with regards to standard exposure levels, the same amount provided wrong instructions for safety equipment, and 24% indicated wrong first-aid measures. Only 11% of the 150 MSDSs were satisfactory in all the information details!

In addition to missing or wrong information there is the **problem of understanding** the document. A study done in 2000 in Japan, by sending questionnaires to more than 422 workplaces, shows the extent of this problem in 393 plants[2] 9 years after MSDSs became mandatory in Japan: Thirteen percent of the workplaces claimed MSDSs were unsatisfactory due to missing information, and 49.9% complained that the documents contained sentences or words which were difficult to understand. Only 29.5% were satisfied with the MSDSs. Another study, made at the University of Maryland[6] in 1997 concluded that literate workers could understand only 60% of the information given in MSDSs.

(1) All opinions expressed in this article are those of the author and not of the American Chemical Society.
(2) Seki, A.; Takehara, H.; Takigawa, T.; Hidehira, T.; Nakayama, S.; Usami, M.; Uchida, G.; Kira, S. *J. Occup. Health* **2001**, *43*, 95−100 (http://www.nap.edu/issues/19.2/fagotto.htm).
(3) (a) Commission Directive 91/155/EEC. (b) *ANSI Standard Z400.1-1998*; American National Standards Institute: New York, NY, 1998.
(4) Yoon, C. G.; Jeon, T.-W.; Chung, C.-K.; Lee, M.-H.; Lee, S.-i.; Cha, S.-E.; Yu, I.-J. *Korean Ind. Hyg. Assoc. J.* **2000**, *10*, 18.
(5) Kolp, P. W.; Williams, P. L.; Burtan, R. C. *Am. Ind. Hyg. Assoc. J.* **1995**, *178A*, 183.
(6) Sutler, B. *Second Draft Report on Hazard Communication*; University of Maryland Medical School, 1997.

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Improvement was clearly needed, and a new standard, ANSI Z400.1-2003, was implemented by the American National Standards Institute (ANSI) to overcome the problems. It details 16 headlines that have to be addressed in an MSDS and adds guidelines for the author of the MSDS document. As yet, no study to investigate the extent of improvement that has been achieved can be found.

The disclaimer found in almost each MSDS[7] and stating that "the information is provided without any warranty" should be regarded very seriously by the users of the dangerous materials.

Clearly, a responsible employer cannot rely upon (some of the) MSDSs he receives from his suppliers. One should supplement the information that is given there with internal Standard Operating Procedures that fill in the blanks and take into account the specific conditions and processes under which the materials will be used. Thus, if the MSDS says that "spills should be treated according to the municipal regulations", an SOP should say "do not wet the spill. Sweep it and collect it in the green solid waste container located by the eastern gate of warehouse #2".

Most readers know the Internet joke about DHMO (dihydrogen monoxide).[8] Unfortunately, a study of 10 MSDSs[9] of deionized water proved the joke is serious. All but one call the product either "deionized water" or "water - deionized". One (#10) suggests the name dihydrogen oxide. In the section on first aid for the eyes, the following recommendations were given: "Dry with soft cloth of tissue" (#1), "First aid: obtain medical attention in all cases" (#2), "Irrigate with water" (#10).

All but two MSDSs addressed the issue of water solubility in water. Terms such as "soluble", "miscible", "complete", "infinite" were used. Three MSDSs reported this information as not determined, or not available. Two documents advised that the flash point of water is above 200 °F...!

Other interesting citations from the MSDSs of deionized water are:

"Store at room temperature", "Keep container tightly closed, store in cool dry, well-ventilated area. Keep from ignition source", "Eyewash and safety showers should be immediately available", "Protective gloves - recommended. Minimize contact and wash thoroughly after handling", "Prolonged immersion in large quantities may produce death".

The role of MSDS reliability was discussed in the investigations of at least two severe accidents.

An explosion occurred at Napp Technologies, Lodi, New Jersey, U.S.A., on April 21, 1995, causing the death of five workers and extensive damage. It occurred during the production of a gold-precipitating agent by toll manufacturing for Technip. The process is mainly the mixing of four components (total weight 3688 kg) in a Patterson-Kelly mixer.

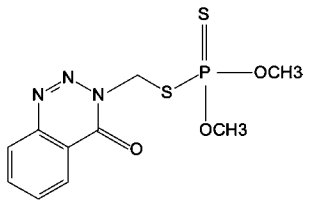
The ingredients are sodium hydrosulfite (or dithionite, $Na_2S_2O_4$), aluminum powder, potassium carbonate, and a small amount of benzaldehyde. The accident investigation committee concluded that the ingress of a small amount of water to the mixer that was loaded with the three powders caused the explosion.[10]

The MSDSs of the ingredients and product contained inaccuracies and contradictions. For example, regarding fire extinguishing: MSDS for the aluminum powder says "avoid water", but the product's MSDS says "use water spray". The latter also says that a small amount of water will cause a chemical reaction, but to control the auto-ignition process once it has started, the material should be flooded by water.

Some information was missing: Aluminum powder may explode in contact with SO_2; sodium hydrosulfite decomposition process cannot be quenched by flooding with water.

The investigating committee regarded the deficient MSDSs as a secondary cause for the accident. They claimed the MSDSs were not detailed enough, they provided information on chemical hazard (but not on process hazard), and they related to a package unit (a drum) but not a full reactor load.

Another accident occurred at Bartlo Packaging Incorporated (BPS),[11] an agricultural chemical packaging facility of West Helena, Arkansas, U.S.A. On May 8, 1997, a massive explosion and fire caused the death of three firefighters, and 17 people required medical attention. Decomposition of a sack containing the pesticide azinphos methyl (AZM) 50W which had been placed close to a hot compressor discharge pipe caused the release of flammable vapors and consequently the fatal explosion.



Azinphos methyl

BPS was about to repackage the AZM for MicroFlow Company (MFC). On January 29, 1996, BPS wrote to MFC

(7) Two random examples: (a) "Some of the information presented and conclusions drawn herein are from sources other than direct test data on the product itself. The information in this MSDS was obtained from sources which we believe are reliable. However, the information is provided **without any warranty**, express or implied, **regarding its correctness**. This MSDS has been prepared in accordance with the requirements of the OSHA Hazard Communication System (29 CFR 1200)". (b) "The information in this MSDS was obtained from current and reliable sources. However, the data is provided **without any warranty**, **expressed or implied**, **regarding its correctness or accuracy**. Since the conditions for use, handling, storage and disposal of this product are beyond the control of TRECE Inc., **it is the responsibility of the user both to determine safe conditions for use of this product** and to assume liability for loss, damage, or expense arising out of the improper use of this product. No warranty expressed or implied regarding the product described herein shall be created by or inferred from any statement or omission in this MSDS".

(8) DHMO: that dangerous material that may cause death when inhaled. Contact with its solid form may damage human tissues, and contact with its vapors causes burns. It is a major constituent in acid rain and a primary factor in corrosion. It was also found in large amounts in tumor cells of terminally ill patients.

(9) The MSDSs were numbered as follows: (1) BSI, (2) Industrial Municipal Equipment, (3) Betz, (4) Betz Dearborn, (5) Caroline Biological Supply, (6) Medical Chemical, (7) Vauchem Canada, (8) Little Chemical, (9) Ricca Chemical, (10) U.S. Chem.

(10) EPA/OSHA Joint Accident Investigation Report - Napp Technologies, Inc., Lodi, New Jersey, (Issued: October 1997).

(11) See: http://yosemite.epa.gov/oswer/ceppoweb.nsf/vwResourcesByFilename/bpsrpt.pdf/$File/bpsrpt.pdf

with concern about the reactivity/flammability of AZM 50W (Bayer had experienced incidents of thermal decomposition or fires involving Guthion, which is Bayer's AZM). BPS asked why the MSDS provided by MFC did not have information similar to Bayer's MSDS on Guthion. Both companies discussed the inconsistency on the AZM hazards and concluded with MFC making a safety presentation to BPS workers. Shortly after that, MFC added that AZM will begin to smolder and smoke at approximately 170 °F. When the material was unloaded at BPS, one of the sacks was leaning against the compressor pipes. Heavy smoke developed. The yellow smoke was too thick for the firefighter to enter. The firefighters received an MSDS from BPS and reported back to the Fire Chief. The Fire Chief then asked about the danger of an explosion, and the reply was that there was none. Unfortunately, an explosion occurred a while later, causing the wall to collapse. Four firefighters were struck. Three of them were killed, and the remaining one was seriously injured.

The MSDS for AZM used by BPS included the following information:

- HMIS flammability rating of 0 (noncombustible).
- HMIS reactivity rating of 0.
- Stable under normal conditions.
- High temperatures may cause hazardous vapors.
- Do not place near heat or open flame.

The MSDS did not mention any 167 °F (75 °C) decomposition temperature.

For comparison, the MSDS for Bayer's Guthion includes the following information:

- NFPA flammability rating of 2. (Must be moderately heated before ignition can occur.)
- NFPA reactivity rating of 2. (Normally unstable and readily undergoes violent chemical change. Not capable of detonation.)
- Stable material. Unstable in sustained temperature above 100 °F (38 °C).
- Store in cool, dry area away from heat source.

The investigation committee said: "EPA and OSHA should facilitate a workshop to make recommendations on how to improve the quality of hazardous materials information available during response actions. It should review appropriate uses of MSDS by local emergency response groups and how to provide these groups information describing the behavior of hazardous materials when they begin to react or decompose and what responders should look for during a chemical emergency."

It is clear that users of hazardous chemicals cannot rely on MSDSs provided by suppliers without cross-checking and without issuing their own standard operation procedures which will take into account the specific usage of the materials, and the conditions in place where they are used.

"The man who thinks he knows something does not yet know as he ought to know." (I Corinthians 8:1−2)

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