Lies of Omission in Safety Data Sheets

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The absence of a specific hazard on a safety data sheet does not necessarily indicate the hazard's nonexistence. Assessing chemical hazards via alternative methods is imperative.

The safety data sheet (SDS, formerly Material Safety Data Sheet) is essential for modern chemical hazard assessments. Efforts by safety professionals, educators, regulatory agencies, and people across the chemistry and chemical engineering disciplines have made consulting an SDS the basic expectation when assessing a chemical's potential hazards. Under the Globally Harmonized System for Hazard Communication (GHS), these documents and their classifications are relatively standardized. Although variations exist between jurisdictions, the minimum information present, hazard codes and phrases, and corresponding hazard pictograms are typically managed according to clear guidance published by the United Nations (UN) *(1)*.

The ubiquity of the SDS, however, can have unintended consequences. Over-reliance on simplified and standardized documents may lead individuals to incorrectly assume a material is safer than it actually is. When SDS documentation is incomplete or inaccurate, serious accidents can result. For instance, an explosion and fire at Optima Belle LLC (Belle, WV) in December 2020 led to one fatality and two serious injuries. The U.S. Chemical Safety and Hazard Investigation Board (CSB) cited failure of an SDS to include all known hazards as a contributing cause, emphasizing the importance of performing hazard analyses beyond just reviewing the SDS *(2)*.

Failures in SDS communication are not new, with recent publications addressing these risks by providing best practices and technical advice *(3)*. Examples of such failures can range from omitting well-known hazards to failing to identify potential explosive formation through evaporation or side reactions *(4)*. Many common laboratory solvents are prone to slow formation of potentially explosive peroxides *(5, 6)*, but no corresponding GHS hazard statement exists for this risk. Other chemicals pose risks well-known to reactive hazard experts that are not necessarily in an SDS. For example, the potentially explosive decomposition of dimethyl sulfoxide, a common solvent, is well-documented in the literature but not usually mentioned in an SDS *(7)*.

Many professionals and students are aware that GHS hazard phrases and codes exist to describe explosive hazards, such as those in Table 1. It is natural to assume that the absence of a hazard statement indicates the absence of a hazard. After all, a material that is not flammable would normally not carry any hazard statement about flammability or combustibility, and no flame pictogram would be included. Why not conclude the same for chemicals that pose a risk of explosion?

This assumption can be dangerously misleading, even when the SDS is accurate. It may be easy to blame chemical suppliers when an SDS does not mention a chemical's potential for deflagration or detonation. However, the SDS's "lies of omission" result from multiple factors: common misconceptions about the term "explosive" in hazard

classification, a lack of chemical process information in standard SDSs, and an oversimplification of the reactive hazard assessment.
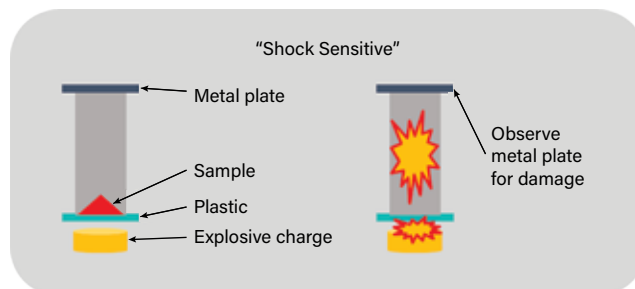
"Explosive" may not mean what you think

While most chemical engineering professionals, academics, and students have read an SDS, few have delved into the "UN Manual of Tests and Criteria" which outlines how these hazard codes are assigned (8). Even fewer have conducted related tests. Terms like "shock sensitive" might be commonly used — particularly when discussing the risks associated with isolating peroxides from parent peroxide-forming solvents (5) — but their meanings are not commonly understood. What, then, do terms such as "shock sensitive," "impact sensitive," "friction sensitive," and "thermal stability" mean?

Regardless of common perceptions, "shock sensitive" has a specific definition under GHS. Sensitivity to "shock" is determined by the UN gap test, illustrated in Figure 1. A sample is placed atop a sheet of plastic at one end of a carbon steel pipe. A metal watch plate is positioned at the other end with an explosive charge situated beneath the test specimen. The proximity of the explosive charge depends on whether the test aims to assess shock sensitivity or the specimen's ability to propagate an explosion. After the explosive charge is activated, damage to the metal watch plate or to the metal pipe is viewed as evidence of a positive result.

The conditions of the shock sensitivity test are fairly

extreme. As a result, detonable but relatively insensitive materials may yield a positive result on a shock sensitivity test but fail to exhibit other explosive properties. The common understanding of "shock sensitive" often corresponds to "impact sensitive" instead, illustrated in Figure 2. Impact sensitivity refers to whether striking a material initiates or causes a chemical reaction or explosion. In practice, this is usually evaluated by dropping a weight with a controlled amount of force onto a sample and checking for evidence of initiation. Quantitative impact sensitivity tests yield a limiting impact energy — below which initiation is not observed — and a material may be deemed non-explosive if this limiting energy is above a threshold for the chosen test method (8).

By contrast, "friction sensitive" is usually correctly understood. The friction sensitivity test subjects a potentially sensitive sample to friction, as illustrated in Figure 3. Mul-

Table 1. Selected hazard classes, hazard statement codes, and hazard statements mentioning explosive risks, from the Globally Harmonized System for Hazard Communication (GHS), Rev. 10 are listed below (1).		
GHS Hazard Class	H-code	Hazard Statement
Explosives	H204	Fire or projection hazard
Desensitized Explosives	H206	Fire, blast, or projection hazard; increased risk of explosion if desensitizing agent is reduced
	H207	Fire or projection hazard; increased risk of explosion if desensitizing agent is reduced
	H208	Fire hazard; increased risk of explosion if desensitizing agent is reduced
Explosives	H209	Explosive
	H210	Very sensitive
	H211	Maybe sensitive
Self-Reactive Substances and Mixtures; Organic Peroxides	H240	Heating may cause an explosion
	H241	Heating may cause a fire or an explosion

▲ **Figure 1.** Shock sensitivity testing can be conducted through the United Nations (UN) gap test as illustrated.
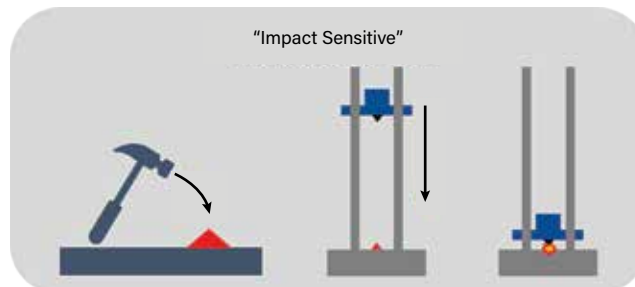
▲ **Figure 2.** Impact sensitivity testing involves striking a sample. While this might be thought of as hitting a sample with a hammer (left), it is usually conducted with a controlled amount of force such as by a drop-weight or fall-hammer test.
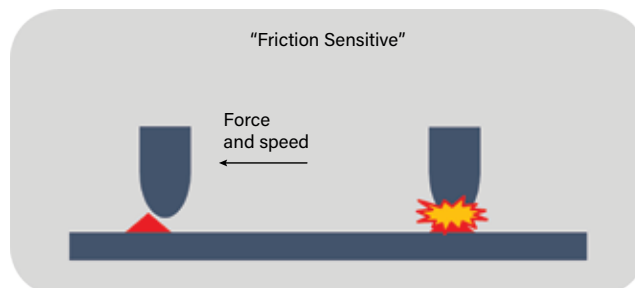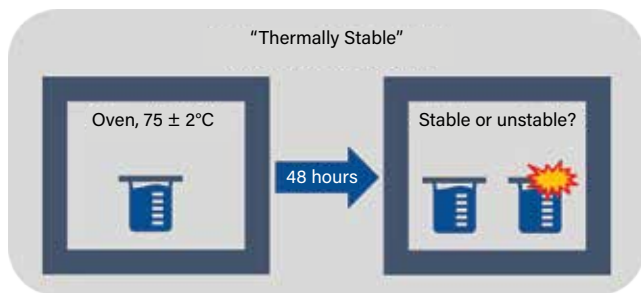

▲ **Figure 3.** Friction sensitivity testing can quantify the friction load, velocity, or pressure below which a sensitive material will not react.
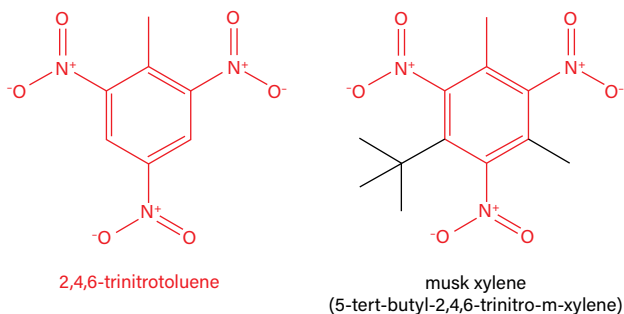
tiple test methods to assess friction sensitivity are permitted under GHS. For a material to be classified as friction-sensitive, it must exhibit a certain sensitivity to friction, with the threshold defined according to the specific method. For example, 2,4,6-trinitrotoluene (TNT) is generally not friction-sensitive under any of these classifications, whereas dry lead azide is *(8)*.

Finally, the "thermal stability" of a material can be defined in a variety of ways (Figure 4). To an experienced chemical process engineer or reactive safety expert, the concept often considers factors beyond temperature, such as data acquisition methods and operating conditions of the corresponding chemical processes *(9)*. Standard hazard classifications for an SDS, however, lack insight into specific chemical processes and focus instead on hazards associated with general handling and transport. Under GHS, an explosive's thermal stability is determined based on its behavior at 75°C. The simplest version of this test *(8)* involves heating a covered beaker containing 50 g of material to 75°C for 48 hours. If no explosion occurs and no signs of a reaction are observed, the material is considered thermally stable. Additional testing is indicated when there is some evidence of reactivity without explosion, though this will not necessarily mean it is classified as explosive.

In addition to these methods, other factors are considered in the classification of chemicals as explosive or not, according to flow charts outlined in the "UN Manual of Tests and Criteria" *(8)*. These tests primarily consider transportation, storage, and general handling hazards rather than the application of chemicals in processes. A material capable of explosion under temperature conditions relevant in chemical processes (*e.g.,* >100 °C) might still exhibit thermal stability and relative insensitivity to shock, friction, and impact under these tests.

Ideally, such potential dangers would be identified early during process development and avoided by the time commercial production was achieved. However, in academic and industrial research settings where novel reactions and processes are continually explored, even a small quantity of an explosive material can pose a significant hazard. In general, 1 g of a high explosive can cause serious injury to a person holding it, 10 g can cause serious injury to those nearby, and 100 g can result in almost certain death *(10)*. Such quantities are ubiquitous in early research, and quantities on the scale of 100 g to 1,000 g are relevant in process development and in fine chemicals manufacturing. The following examples will explore how a material's explosive risks during processing can be identified if they are not defined in an SDS.

Example 1. Can you spot the explosive?

It is easy to make sweeping alarmist claims without concrete examples. Therefore, illustrative cases are necessary. Musk xylene, illustrated in Figure 5, bears a close structural resemblance to TNT, a high explosive sensitive to initiation by shock and impact. Intuitively, musk xylene would exhibit a similar sensitivity based on its structural similarity. Indeed, one variant of the UN gap test has demonstrated that it can propagate detonation. However, tests for thermal stability, limiting impact energy, friction sensitivity, and the tendency to explode when ignited all yield results classifying it as non-explosive according to the "UN Manual of Tests and Criteria" *(8)*. Section 10 specifically lists all these test outcomes for musk xylene, as well as its non-explosive classification. Despite this, musk xylene can detonate and might still represent an explosive reactivity risk in some situations due to its high energy release potential.

To further illustrate, consider four other compounds, with their structures given in Figure 6. Two of these materials — 3,5-dinitrobenzoyl chloride (DNBC) and 2,4-dinitrophenylhydrazine (DNPH) — are commonly used as derivatizing agents in analytical laboratories. All four share varying degrees of structural similarity to TNT, but only one is classified as an explosive: DNPH, which is typically sold wetted with ≥30% water, classifying it as an H206 desensitized explosive.

We assume all four materials underwent proper tests during initial SDS generation, and we can presume negative results on at least some of the explosive tests for all but DNPH. However, calorimetric screening tests demonstrate

▲ **Figure 4.** Thermal stability testing for explosives classification involves temperatures well below those relevant to chemical engineering processes.

2,4,6-trinitrotoluene

musk xylene
(5-tert-butyl-2,4,6-trinitro-m-xylene)

▲ **Figure 5.** On the left is 2,4,6-trinitrotoluene (TNT), a known and widely recognized high explosive. On the right is its structural relative, musk xylene.

why the other three materials pose hazards due to energetic exothermic decomposition reactions.

Differential scanning calorimetry (DSC) allows for the screening of milligram-scale samples in hermetically sealed environments, yielding heat flow data that correspond to exothermic and endothermic processes. When used appropriately, DSC can help identify and predict reactive hazards *(11)*. All data herein were acquired using flame-sealed glass capillaries, using methods comparable to those by Sheng *et al. (12)*. Unlike traditional high-pressure DSC pans, glass containers offer a significant advantage: When they rupture due to explosive over-pressure, they are not as likely to damage the calorimeter, as has been reported to occur with pans *(13)*.

DSC thermograms corresponding to the four chemicals are shown in Figure 7. The curves are labeled with letters to permit consideration of which species might relate to which curve. Which one is the explosive? It is not (a), which has the highest peak and is one of the most energetic. That is 3,5-dinitro-2-methylphenylboronic acid, which is not classified as an explosive. Nor is it (b), another energetic curve belonging to DNBC despite its energy release exceeding –3,000 J/g. It is also not (c), which is 4-nitrocatechol. The explosive is (d), DNPH wetted with 30% water, with an exothermic decomposition initiating almost immediately after its observed melting point. Even the classification of explosives by a quantitative calorimetric method is not straightforward.

Derivatives and relatives of these chemicals have been indicated in reactivity incidents *(14)*, and synthesizing novel species from these reagents may pose hazards. However, safe handling might be possible under low-temperature or low-concentration applications.

DSC testing can be more relevant to practicing engineers than explosive classification testing because it more closely mimics process conditions. The presence or absence of an explosive classification in the SDS does not convey the full story.
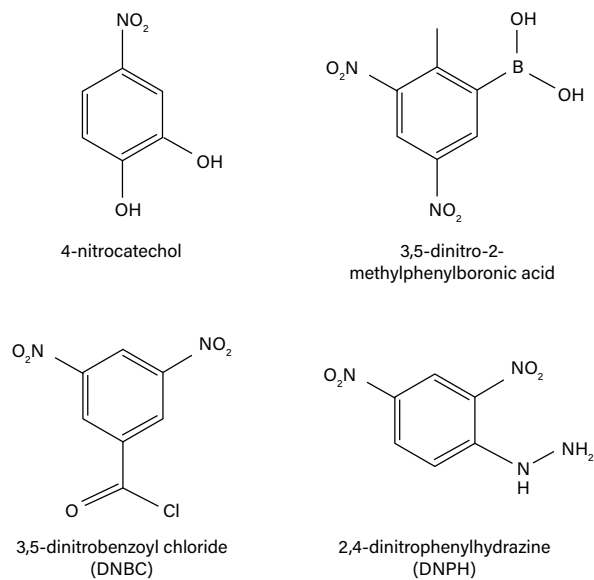
Example 2. Triallyl phosphate

The chemicals in Example 1 contained the classic explosive functional group, $-NO_2$. A review of potentially explosive functional groups might facilitate the identification of these as reactive hazards *(10)*. However, what about substances not immediately associated with an explosive?

A researcher approached their reactive safety expert for assistance evaluating several new materials proposed for an approximate 160–180°C experimental application. One material was triallyl phosphate, which is generally classified as non-hazardous. The only obvious safety concern was some sensitivity to generating allyl alcohol in the presence of water, a risk primarily related to toxicity.

However, "Bretherick's Handbook of Reactive Chemical Hazards" warned of triallyl phosphate's potential for explosion during heating, particularly during distillation *(14)*. It referenced a 1950 *Chemical & Engineering News* article describing how the explosion of triallyl phosphate reduced its distillation apparatus to pieces *(15)*. With this information available in the chemical safety literature, how was it that triallyl phosphate was not classified as an explosive?

The material, a liquid, was evaluated by DSC. A first attempt to screen the material resulted in the violent over-pressure of the sample capillary, which did not lead to equipment damage. Successive tests using isothermal DSC

4-nitrocatechol

3,5-dinitro-2-methylphenylboronic acid

3,5-dinitrobenzoyl chloride (DNBC)

2,4-dinitrophenylhydrazine (DNPH)

▲ **Figure 6.** Illustrated are four compounds that are structurally similar to TNT: 4-nitrocatechol, 3,5-dinitro-2-methylphenylboronic acid, DNBC, and DNPH.
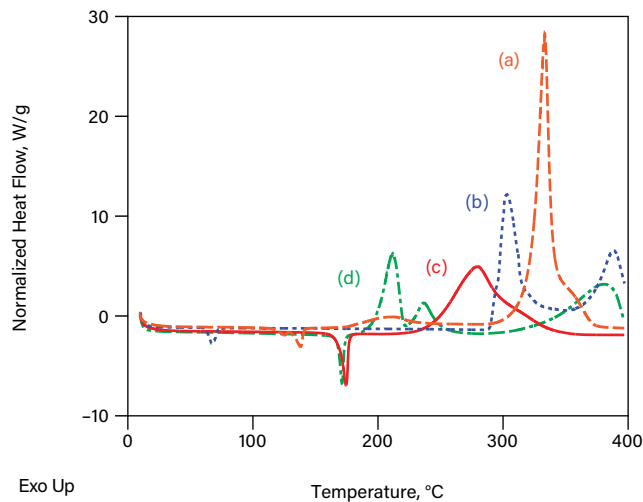
▲ **Figure 7.** The differential scanning calorimetry (DSC) thermograms for the four chemicals in Figure 6 (with exotherms pointing up) do not obviously indicate the explosive material.

experiments confirmed that a highly exothermic reaction was to blame, as illustrated in Figure 8. Here, maintaining an elevated-temperature environment for an extended time yielded an energy release between –1,000 J/g and –2,000 J/g, which overpressure events in the DSC suggested was significantly gas-generating.

The reaction, however, did not occur quickly. Sustained high-temperature, closed-system conditions were required. This was consistent with an autocatalytic decomposition mechanism, theorized to result from acidic contaminants catalyzing the formation of additional acids over time. Such reactions can be particularly pernicious, since the thermal history and purity of a chemical can be strong determining factors for safe handling. However, one abnormality was observed: The induction time at 165°C was somehow longer than the induction time at 160°C. Further testing identified that the age of the sample and the exact headspace volume of the container in which it was tested could change the induction time. Safe handling at elevated temperatures requires a strong understanding of the material's purity, age, and specific processing conditions.

Curiously, a 1950 follow-up letter to *Chemical & Engineering News* argued that triallyl phosphate and other allyl esters of inorganic acids could, if handled properly, "be kept docile as kittens!" *(16)*. The letter provided recommendations on specific processing conditions, purity requirements, and the use of base inhibitors to mitigate decomposition risks. The letter highlights the importance of how specific handling procedures ensure safety, and these procedures might include information that would not necessarily be present in an SDS.

Overall, the hazard classification for triallyl phosphate was likely the result of its physical properties and overall thermal stability. While heating to a temperature range of 160°C to 180°C could initiate an explosion, a 75°C thermal stability test might show no decomposition. Moreover, triallyl phosphate could also evaporate, complicating results. Could it be an explosive hazard in certain chemical processing applications? Yes. Was its SDS lying about its reactive hazards? Not under GHS.

## Example 3. Graphene oxide

Not all SDSs commit lies of omission. In this example, a researcher was interested in using a graphene oxide paste, which is not classified as reactively hazardous under GHS. However, upon reviewing the SDS, they found a non-standard warning on its final page:

"The only known safety issue is related to the well-known 'flashing' when dry graphene oxide is heated rapidly to temperatures in the range of 100°C or higher. In the flashing process, approximately half a liter of gas is released by one gram of graphene oxide in an explosion-like reaction…"

Intrigued by this warning, the researcher consulted a reactive safety expert and requested a hazard evaluation specific to their intended use case. A search of the literature confirmed the "flashing" behavior, which was reported to have an exothermic energy release between –1,400 J/g and –1,700 J/g *(13)*.

This example highlights the importance of both reading the SDS and considering the specific application. The graphene oxide paste contained only 10 wt% graphene oxide, reducing its overall hazard potential. Additionally, the researcher's application involved a ventilated system capable of handling sudden gas evolution.

A DSC screening of the graphene oxide paste (Figure 9)
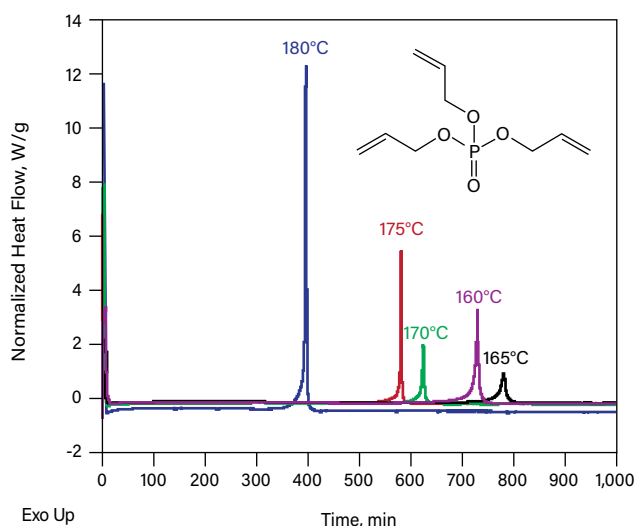
▲ **Figure 8.** Isothermal DSC thermograms for triallyl phosphate illustrate the "induction time" phenomenon consistent with autocatalytic decomposition.
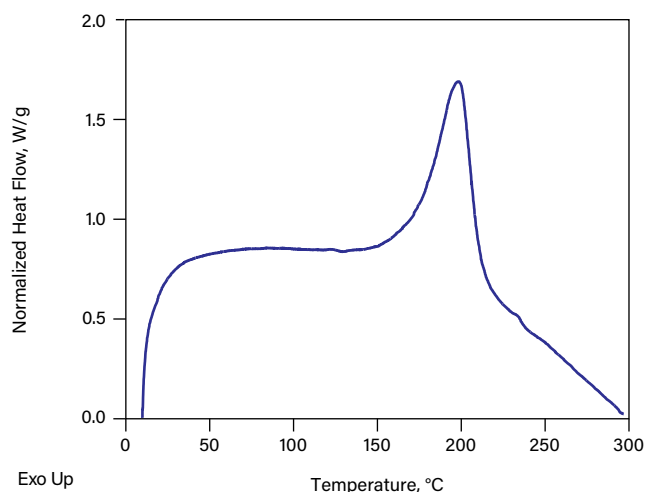
▲ **Figure 9.** The DSC thermogram for 10 wt% graphene oxide paste's reaction above 150°C is shown. The significant sloping of the baseline above 200°C was attributed to heat capacity changes of the volatile components as they were heated beyond their boiling points.

showed that the reaction would still occur even in a wetted paste, with an energy release consistent with the expected –140 J/g to –170 J/g based on mass dilution effects. The material was appropriately identified, the risk was assessed, and research proceeded safely with the hazard mitigated by engineering controls inherent to the experimental design.

Closing thoughts

Explosive reactivity hazards can be identified in an SDS, but other hazards may be concealed within chemical processing details. SDSs and the GHS were developed with the intention of harmonizing chemical hazard communication, not to communicate every possible hazard. Based on these stories and the context of the GHS classification criteria, the following practices are recommended:

• Review the supplier's SDS. Critical safety information is often accurately reported. Go beyond the SDS and review competing suppliers' SDSs, relevant literature, and reactive safety reference texts. Consult lists of highly reactive functional groups and assess the chemical for their presence *(10)*. Take advantage of reference texts available to AIChE members, such as Bretherick's in the Knovel eLibrary.

• Consider hazards identified in the context of the chemical process. Where needed, consult the corresponding GHS manual to understand how that classification was assigned and whether it is relevant to the process.

• Rely on engineering controls that improve safety and practice the principles of inherently safer design: limit scale, quantity, or concentration to minimize the hazard.

• If any step of the review identifies a potential significant reactive hazard, consider consulting a reactivity or process safety expert.

Overall, the "lies of omission" in an SDS are not necessarily any one person or organization's fault. They emerge from the assumptions we make about chemical safety, and they can be eliminated through good engineering practice, critical thinking, and scientific due diligence. **CEP**

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Literature Cited

1. **United Nations,** "Globally Harmonized System of Classification and Labelling of Chemicals (GHS Rev. 10, 2023)," UNECE, unece.org/transport/dangerous-goods/ghs-rev10-2023 (July 27, 2023).

2. **U.S. Chemical Safety and Hazard Investigation Board,** "Fatal Chemical Decomposition Reaction and Explosion at Optima Belle LLC: Investigation Report," U.S. CSB, Washington, DC (2023).

3. **DeMasi, A., *et al.,*** "Safety Data Sheets: Challenges for Authors, Expectations for End-Users," *ACS Chemical Health & Safety,* **29** (4), pp. 369–377 (May 2022).

4. **Kolchinski, A. G.,** "When Safety Data Sheets are a Safety Hazard," *Organic Process Research & Development,* **26** (2), pp. 263–266 (2022).

5. **Clark, D. E.,** "Peroxides and Peroxide-Forming Compounds," *Chemical Health and Safety,* **8** (5), pp. 12–22 (2001).

6. **Kelly, R. J.,** "Review of Safety Guidelines for Peroxidizable Organic Chemicals," *Chemical Health & Safety,* **3** (5), pp. 28–36 (1996).

7. **Deguchi, Y., *et al.,*** "Study on Autocatalytic Decomposition of Dimethyl Sulfoxide (DMSO)," *Organic Process Research & Development,* **24** (9), pp. 1614–1620 (2020).

8. **United Nations,** "UN Manual of Tests and Criteria Rev.8 (2023)," UNECE, https://unece.org/info/publications/pub/387256 (Jan. 2024).

9. **Dutta, S., and R. J. Bellair,** "Losing Your Heat Balance: Insights into Thermal Hazard Assessments," *Chemical Engineering Progress,* **119** (3), pp. 27–33 (Mar. 2022).

10. **Carson, P. A., and C. J. Mumford,** "Hazardous Chemicals Handbook," 2nd ed., Butterworth-Heinemann, Woburn, MA (2002).

11. **Stoessel, F.,** "Thermal Safety of Chemical Processes: Risk Assessment and Process Design," Wiley VCH, Weinheim, Germany (2020).

12. **Sheng, M., *et al.,*** "Practical Use of Differential Scanning Calorimetry for Thermal Stability Hazard Evaluation," *Organic Process Research & Development,* **23** (10), pp. 2200–2209 (2019).

13. **Qiu, Y., *et al.,*** "Explosive Thermal Reduction of Graphene Oxide-Based Materials: Mechanism and Safety Implications," *Carbon,* **72,** pp. 215–223 (2014).

14. **Urben, P. G., and M. J. Pitt, eds.,** "Bretherick's Handbook of Reactive Chemical Hazards (8th Edition)," Elsevier, Cambridge, MA (2017).

15. "Safety Forum: Explosions are Described Involving Allyl Esters of Strong Acids, and Preventive Procedures are Recommended . . . Use of Safety Shield Is Mandatory," *Chemical & Engineering News Archive,* **28** (40), p. 3452 (1950).

16. **Steinberg, G. M.,** "Letter to the Editor: Allyl and Benzyl Esters," *Chemical & Engineering News Archive,* **28** (44), p. 3755 (1950).