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An evaluation of engineered nanomaterial safety data sheets for safety and health information post implementation of the revised hazard communication standard

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Abstract

In 2012, the Occupational Safety and Health Administration issued the revised Hazard Communication Standard to bring the US in closer alignment with the Globally Harmonized System of Classification and Labeling of Chemicals, and make the exchange of health and safety information more effective. To evaluate the impact of this change on the reliability and accuracy of safety data sheets, a sample of safety data sheets specific to engineered nanomaterials was obtained by using an internet search engine and subsequently evaluated. These safety data sheets were evaluated using a modified Kimlisch et al. (1997) criteria for ranking the quality of data into categories of reliability and the Eastlake et al. (2012) ranking scheme for scoring four categories. While 86 safety data sheets for nanomaterials were obtained during 2016–2017, 19 of these had no date of completion or revision and could not be evaluated since it was impossible to determine if they were pre or post 2012, when the revised OSHA Hazard Communication Standard was issued. The remaining 67 safety data sheets were ranked by the Kimlisch et al. criteria, and 28.4% (19) were found to be reliable without restrictions (excellent), 35.8% (24) were reliable with restrictions (good), and 35.8% (24) were determined to be unreliable. Evaluating the SDSs using the Eastlake et al. ranking scheme resulted in 3% (2) as satisfactory, 17.9% (12) as being in need of improvement, and 79% (53) in need of significant improvement. It is noteworthy that out of the 79% in need of significant improvement, 25.4% (17) did not have enough data to be evaluated. This evaluation of nanomaterial safety data sheets revealed that the quality of information on many still cannot be relied upon to offer adequate information on the inherent health and safety hazards, including handling and storage of engineered nanomaterials.

Keywords

Safety data sheets; engineered nanomaterial; GHS; HazCom standard

Disclaimer

The findings and conclusions in this report are those of the author(s) and do not necessarily represent the official position of the National Institute for Occupational Safety and Health.

Introduction

Since 1985, the Occupational Safety and Health Administration (OSHA) has required chemical manufacturers and importers to create Material Safety Data Sheets (MSDSs) on chemicals determined to be hazardous [OSHA Hazard Communication Standard (HazCom standard) (29 CFR 1910.1200)].¹ In 2012, OSHA issued a final rule to revise the HazCom standard to align with the United Nations Globally Harmonized System of Classification and Labeling of Chemicals (GHS).¹ In addition to new labeling requirements, the updated rule changed the name of a MSDS to Safety Data Sheet (SDS). The purpose of the SDS is to communicate information on the inherent health and safety hazards of a chemical, and precautions and protections during the handling and storage of hazardous chemicals. The format of the SDS contains 16 sections to address these hazards; however, only 12 of the 16 sections are legally mandatory and 4 sections (ecological information, disposal considerations, transport information, and regulatory information) deal with information beyond exposure hazards.

Engineered nanomaterials (ENMs) are one type of chemical that would require a SDS. The small size of ENMs, approximately 1 to 100 nm, can have novel chemical and physical properties. Development and commercialization of nanomaterial-based products and applications are occurring at a rapid rate, making it imperative to communicate sufficient information about the potential hazards from exposure to ENMs. The number of workers exposed to ENMs is not known, but market reports indicate that large and growing quantities of ENMs are being used in commerce; and workers are involved throughout the manufacture, formulation and use of these nanomaterial products.²

There is evidence that nanoscale materials tend to be more hazardous than the same material in a non-nanoscale form. Nanoparticles can be inhaled and deposited in all sections of the respiratory tract, including the gas-exchange (alveolar) region.³ Nanoparticles have also been observed to reach the interstitium and the blood, which may represent a path for the translocation of inhaled nanoparticles from the lung to secondary organs.^{4, 5, 6, 7, 8} Carbon nanotubes (CNTs) also appear to promote interstitial fibrosis, and specific multi-walled CNTs (MWCNTs) have been shown to promote lung cancer.^{8, 9} Inhalation of certain types of nanoparticles have also been linked to cardiovascular effects.^{10, 11} At present, there are no enforceable national or international occupational exposure limits (OELs) or standards specific to engineered nanomaterials, however, recommended exposure limits (RELs) have been published for two types of nanomaterials. NIOSH published a REL of 0.3 mg/m³ for ultrafine (nano) titanium dioxide (TiO₂) and a REL of 1 µg/m³ for CNTs and carbon nanofibers (CNF), measured as elemental carbon, for an 8-hour respirable-mass airborne concentration.^{12,13}

In 2012, NIOSH authors (Eastlake et al.) published a review of engineered nanomaterial MSDSs using four questions to determine quality, and concluded that only 17–33% of those published during 2007–2011 provided sufficient data for communicating the potential hazards to employers and workers.¹⁴ The range of results come from grouping MSDS by the publication years of 2007–2008 and 2010–2011. The purpose of this current evaluation is to

determine if the revised 2012 OSHA HazCom standard has impacted the reliability of ENM safety and health information provided on nanomaterial SDSs.

METHODS

Obtaining Safety Data Sheets

A sample of SDSs specific to ENMs was obtained by using internet search engines and online nanomaterial databases. The Nanowerk database of commercially available nanomaterials <http://nanowerk.com/nanocatalog> and a database that is maintained by CPWR - The Center for Construction Research and Training (CPWR) in their Electronic Library of Construction Occupational Safety and Health (eLCOSH) Nano database <http://nano.elcosh.org> (of nano-containing construction materials) were both used as starting points for obtaining publically available SDSs. Both databases identified various nanomaterial manufacturers, and then the manufacturers' website was subsequently visited to download the SDS. In instances where multiple SDSs from a single manufacturer (as was frequently the case) were located, the SDS with the latest date was selected for review since SDSs produced by the same manufacturer are likely to have similar information. Only SDSs that included "nano" in the product name or on Section 3 of the SDS (chemical composition) and those with a date of 2012 or later were evaluated. A total of 86 unique SDSs were obtained from 86 manufacturers. Of the SDSs collected, 19 had no date of completion or revision and could not be evaluated since it was impossible to determine if they were pre or post 2012, when the revised OSHA HazCom standard was issued. This left 67 SDSs for the evaluation. The ENM SDSs in this study included CNT, CNF, graphene, fullerene, alumina, boron nitride, cadmium selenide, cadmium telluride, cellulose nanocrystals, quantum dots, copper, nickel, gold, silver, TiO₂, composites, treated lumber, paints, coatings, lubricants and greases. Construction materials that contained nanomaterials made up 19 of the SDSs evaluated. All of the SDSs were written in English.

Technical specification sheets were also collected for the materials, when available. Technical specification sheets were available online from the manufacturers for 38 of the 67 SDSs. These technical specification sheets were reviewed to determine if information on size was provided if that information was not available on the SDS.

Reviewing Safety Data Sheets

The SDSs were evaluated using both a modified Kimlisch et al. (1997) criteria on 11 SDS categories and the Eastlake et al. ranking scheme that utilized four questions.^{14,15} The Kimlisch et al. criteria for ranking the quality of toxicological and ecotoxicological data into categories of reliability, relevance and adequacy was used as a basis for developing categories and a numerical code for each of the quality factors.¹⁵ Eleven of the 12 mandatory sections of the SDS were evaluated on the basis of the ranking scheme (Table 1). Section 16 of the SDS is for "other information" including the revision date, which is mandatory, but was omitted from this evaluation since the purpose was to evaluate only SDS published in 2012 or later. It is noteworthy that the 2012 HazCom standard did allow a phase-in period until June 1, 2015 for manufacturers to comply with the new requirements, and the SDSs in this evaluation were collected during 2016–2017.

The Kimlisch et al. criteria suggest assigning individual “codes or points” for each category. For this study the following numerical coding was utilized for each section and then the total number of points was assigned for each SDS (Table 2). The highest score a SDS could achieve would be 44 (4 times the 11 categories) and the lowest possible score would be 22 (2 times the 11 categories). The total scores were then classified as excellent (scores 41–44), good (scores 37–40) and unreliable (22–36). The SDSs were independently scored by the co-authors and then a consensus was utilized to create the final score.

SDSs were also scored using the criteria described by Eastlake et al., which utilizes four questions: “1) Did the MSDS indicate that the material is in the nanometer size range (<100 nm) by using numerical references or ranges? 2) Did the MSDS contain an OEL for the larger or bulk form (macroscale) of the material, and was there any guidance given on whether this OEL may or may not be protective for the nanomaterial? 3) Did the MSDS include specific toxicological data or information on the nanomaterial or indicate that nanomaterials may have different toxicities than larger particles of the same material? and, 4) Did the MSDS advise the use of protective measures, such as engineering controls, appropriate respiratory protection, and non-permeable gloves, when there is the potential for exposure?”¹⁴ The following paradigm was then used to evaluate the collected MSDSs:

- If the MSDS was deficient in only one of the above categories, it was classified as satisfactory.
- If it was deficient in two categories, it was classified as in need of improvement.
- If it was deficient in more than two categories, it was classified as in need of significant improvement.

Since this ranking scheme depended on asking if toxicological information was provided and the updated HazCom standard in Appendix A.02.1 clarifies that “there is no requirement for testing chemicals”, using the Eastlake et al. ranking scheme alone was deemed to be inadequate for the evaluation, hence the Kimlisch et al. evaluation was the primary focus.

Results

A total of 67 unique SDSs for nanomaterials were obtained from 67 manufacturers and ranked using the Kimlisch et al. criteria. The results of the evaluation were 28.4% (19) reliable without restrictions (excellent), 35.8% (24) reliable with restrictions (good), and 35.8% (24) unreliable (Figure 1).

The lowest ranked categories were Section 11, Toxicological information, followed by Section 4, First aid measures and Section 5, Firefighting measures. The highest ranked sections were Section 9, Physical and chemicals properties, followed by Section 7, Handling and storage, and Section 3, Composition information.

There was only 1 SDS that scored a perfect 44 with thorough and complete information. There were 2 SDSs that scored 43, but both were missing toxicological information. While having toxicological information on the ENMs would be helpful to some end users, the updated HazCom Standard specifically states that “there is no requirement for testing

chemicals”.¹ These scores of 43 represent that a SDS only missing toxicological data is still considered “excellent”.

The lowest score for a SDS was 31 and this nanomaterial solution SDS (deemed unreliable), contained very general statements such as follow “general industrial hygiene practice,” “respiratory protection not required,” and that there is “no data available”.

A subset of nano-containing construction materials (treated lumber, paints, coatings, lubricants and greases) was evaluated and compared to the total set since one of the databases used for gathering the SDSs was the CPWR database of nano containing construction materials. Of the 19 construction materials SDSs, 26.3% (5) were found to be reliable without restrictions (excellent), 47.4% (9) were reliable with restrictions (good), and 26.3% (5) were determined to be unreliable. Figure 2 shows data for 48 ENM SDSs as compared to 19 SDSs for nano containing construction materials.

Applying the Eastlake et al. ranking scheme to the 67 ENM SDSs collected for this evaluation resulted in 3% (2) as satisfactory, 17.9% (12) as being in need of improvement, and 79% (53) in need of significant improvement. It is noteworthy that out of the 79% in need of significant improvement, 25.4% (17) did not have data that answered any of the four posed questions.

Technical specification sheets are increasingly used to communicate physical and chemical properties specific to the material. Out of the 67 SDSs obtained, 56.7% (38) had technical specification sheets available. The technical specification sheets were a good source of particle size information and while only 10 SDS out of 67 contained information on size, an additional 16 technical specification sheets contained the information. This led to an increase in the percent of positive answers for the Eastlake et al. criterion 2 (specified that material is nanometer range, using numbers) to go from 14.9% (10) to 38.3% (26). No other information on the technical specification sheets provided information to the proposed ranking questions. The only difference noted was in the availability of size in the SDS in combination with the technical specification sheet versus that of the SDS alone. This indicates that it may be necessary to supplement the information from a SDS with information found on the technical specification sheet. A summary of the data obtained using the Eastlake et al. 2012 method on the 67 SDSs is shown in Table 3.

The SDSs were evaluated to determine if they included the NIOSH RELs for two types of ENMs. The NIOSH REL for CNT and CNF was included on 23.1% (3/13) of the SDSs for CNT and CNF containing materials. Of 24 SDSs for all carbon-based materials (such as graphene, fullerene, CNT, CNF), 29.2% (7/24) referenced the OSHA PEL for graphite. None of the three SDSs that indicated that they contained nano TiO₂ provided the NIOSH REL for ultrafine TiO₂, but the bulk size TiO₂ REL was listed on 66.7% (2/3) of the SDS.

Discussion

The evaluation of a SDS can be subjective. To quantify the quality of information on the SDS, a ranking scheme was developed to evaluate Sections 1–11 and then create a summary score. This was done independently by the co-authors and then a consensus score created.

For the 67 SDSs for ENMs and nano-containing construction products evaluated, 28.4% were determined to be of excellent quality and clearly communicated the potential hazards of engineered nanoparticles in a way that was informative and protective. There were 35.8% that were reliable with restrictions (good) which meant that they relied on generic protection statements (e.g. avoid inhalation, use adequate ventilation, use adequate protective clothing, handle in accordance with good industrial hygiene and safety practice) without any specifics or any attention to the material being nanoscale. This left 35.8% of SDSs that did a poor (unreliable) job of communicating potential hazards.

Other researchers (Lee et al. 2012, Safework Australia 2010, Nayer et al. 2015), have examined nanomaterial-related and other MSDSs for quality.^{16, 17, 18} They found that the majority of the MSDS did not include sufficient information on the safety of nanomaterials or on how to appropriately inform an occupational risk assessment.

Lee et al. evaluated 97 nanomaterial-related MSDS as either describing or not describing the information in each of 8 categories (identification of substance, hazard identification, composition information of ingredients, first-aid measures, firefighting measures, accidental release measures, handling and storage, and exposure control/personal protective equipment). Lee et al. found that the majority of the SDS did not include sufficient information on the safety of nanomaterials. Most products (85%) did not include any nanomaterial specific data, and 76% had no information on accidental release measures. Engineering controls were not mentioned in 36% of the SDS, and 65% did not recommend the use of PPE to avoid nanomaterial exposure.¹⁶ The results of this study were used to inform the International Standards Organization Technical Committee 229 (ISO TC 229) report, ISO/TR 13329:2012, Nanomaterials – Preparation of Material Safety Data Sheet (MSDS).¹⁹

Safe Work Australia evaluated 50 ENM MSDS authored prior to 2009 using a similar criteria to the one used here. They ranked the MSDS accuracy using a scale of 1 (inaccurate), 2 (partially accurate), and 3 (accurate). They determined that only 18% (9/50) MSDS provided reliable information to appropriately inform an occupational risk assessment. That left 82% as not providing reliable information.¹⁷

Nayar et al. evaluated the efficiency of 200 SDSs from 89 suppliers used in the aerospace industry (not nanomaterial specific) using the same Klimisch et al. categorical approach described herein, for Sections 2, 6, 7, 8, and 13 (hazard identification, accidental release measures, handling and storage, exposure controls/PPE and waste disposal). They grouped SDSs into pre and post 2010, yet found no statistical differences between the groups. Human health hazard information was good or acceptable on 58% of the SDSs, and safety hazards were good or acceptable on 50% of the SDSs. This left 42% of the SDS as lacking acceptable human health information and 50% lacking acceptable safety information.¹⁸

This evaluation of ENM SDS authored since 2012 (and collected during 2016–2017) revealed that the quality of information on many SDSs still cannot be relied upon to offer adequate information on the inherent health and safety hazards, including handling and storage of ENMs. It is concerning that according to our evaluation, many SDSs remain

unreliable, thus making it difficult for end users to know if they can trust the information, or even how to interpret the limited information made available. It is also concerning that SDSs do not always provide technical information (such as particle size) even though this information can often be found in separate technical specification sheets. One positive finding was that several SDSs advised using engineering controls and/or PPE.

Conclusions

This evaluation of nanomaterial safety data sheets revealed that the quality of SDS information on many of the ENM SDSs still cannot be relied upon to offer adequate information on the potential health and safety hazards, including handling and storage of engineered nanomaterials. Chemical manufacturers should consult the recommendations issued in the International Standards Organization Technical Committee 29 (ISO TC 229) report ISO/TR 13329:2012, Nanomaterials – Preparation of Material Safety Data Sheet (MSDS) when developing SDSs.¹⁹ An additional resource for chemical manufacturers is the SDS and Label Authoring Registry program, which recognizes chemical hazard communication and environmental health professionals who specialize in authoring SDS and labels. This registry program was developed through a partnership between the American Industrial Hygiene Association (AIHA) and the Society for Chemical Hazard Communication (SCHC) to assure the recognition of competent professionals to author SDSs. To obtain the Registered Professional: SDS and Label Author credential, an individual must meet the established qualifications and must demonstrate competency in the skills and knowledge defined by the program's Body of Knowledge. This AIHA Registry Program is the first EHS Specialty Credential that provides recognition for individuals who have expertise in this area. Learn more at <http://bit.ly/sdsregistry>.

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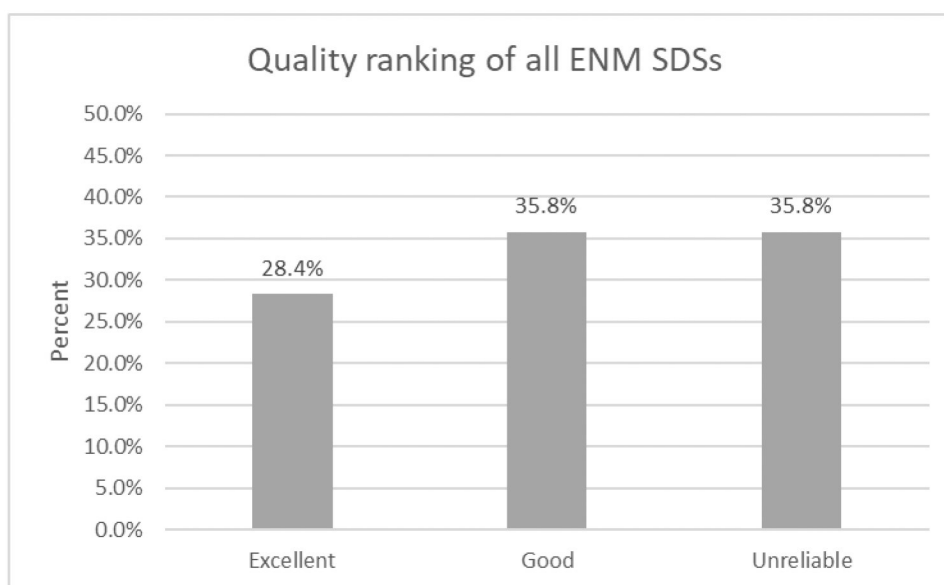


Figure 1. Total scores of all 67 safety data sheets ranked using the Kimlisch et al. criteria. Scores above 41 are excellent, scores between 37–40 are good and scores below 36 are unreliable.

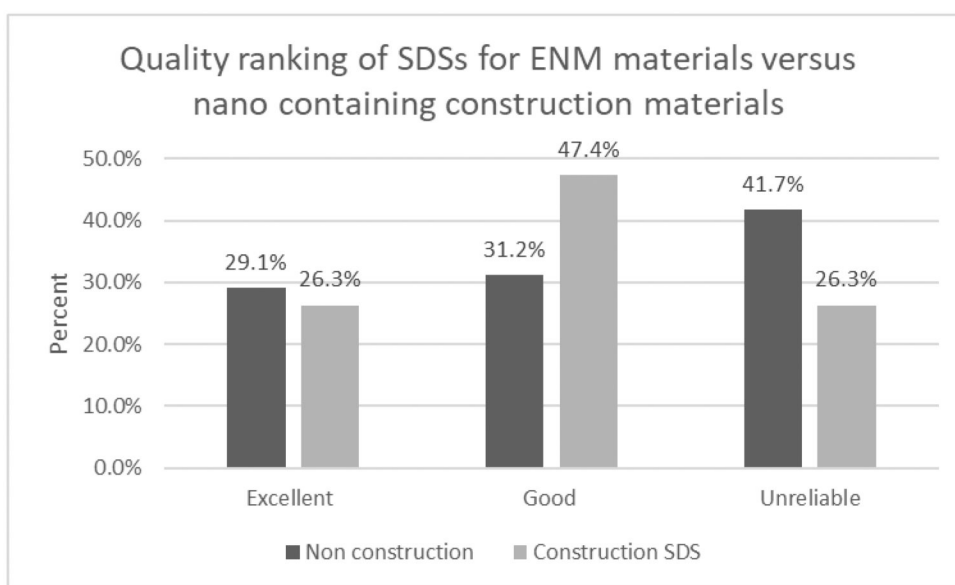


Figure 2. Summary of the total scores of ENM SDS data (n=48) versus nano-containing construction nanomaterials (n=19) ranked using the Kimlisch et al. criteria.

Table 1.

Scoring criteria for the SDS collection.

SDS Section/Scoring Criteria	Reliable without restrictions (score of 4)	Reliable with restrictions (score of 3)	Unreliable (score of 2)
Section 1, Identification includes product identifier; manufacturer or distributor name, address, phone number; emergency phone number; recommended use; restrictions on use.	All information provided	Missing one of the required pieces of identification	Missing two or more of the required pieces of identification
Section 2, Hazard(s) identification includes all hazards regarding the chemical; required label elements.	Identifies chemical composition and specific hazards. Includes pictograms and H statements	Missing a precautionary H statement.	Vague statements
Section 3, Composition/information on ingredients includes information on chemical ingredients; trade secret claims.	Complete information	Missing one of the required pieces (e.g. the ingredient concentrations)	Missing two or more pieces of the required information
Section 4, First-aid measures includes important symptoms/effects, acute, delayed; required treatment.	Complete information for eye, skin, ingestion and inhalation exposure	Missing one of the required pieces	No or poorly written first aid measures
Section 5, Fire-fighting measures lists suitable extinguishing techniques, equipment; chemical hazards from fire.	States if there are any combustion/explosion concerns	Generic firefighting statement, no specifics to nanomaterials	No information
Section 6, Accidental release measures lists emergency procedures; protective equipment; proper methods of containment and cleanup.	Advises the use of HEPA vacuums and to avoid creating dusts or aerosol	No detailed guidance, only generic statements	No information
Section 7, Handling and storage lists precautions for safe handling and storage, including incompatibilities.	Includes information on safe handling and storage	Missing either handling or storage information	No information
Section 8, Exposure controls/personal protection lists OSHA's Permissible Exposure Limits (PELs); ACGIH Threshold Limit Values (TLVs); and any other exposure limit used or recommended by the chemical manufacturer, importer, or employer preparing the SDS where available as well as appropriate engineering controls; personal protective equipment (PPE).	OEL/REL provided for bulk or nanomaterial. Includes specific information on engineering controls and PPE	No OEL/REL and generic engineering control and PPE information without specifics	No information on OELs or engineering controls or PPE
Section 9, Physical and chemical properties lists the chemical's characteristics.	Complete information	General information without specifics	No information
Section 10, Stability and reactivity lists chemical stability and possibility of hazardous reactions.	Lists conditions to avoid	General information without specifics	No information
Section 11, Toxicological information includes routes of exposure; related symptoms, acute and chronic effects; numerical measures of toxicity.	Referenced toxicological data provided for both acute and chronic exposure	General toxicological data with no specifics	No information
Section 12, Ecological information *	Not evaluated	Not evaluated	Not evaluated
Section 13, Disposal considerations *	Not evaluated	Not evaluated	Not evaluated
Section 14, Transport information *	Not evaluated	Not evaluated	Not evaluated
Section 15, Regulatory information *	Not evaluated	Not evaluated	Not evaluated
Section 16, Other information, includes the date of preparation or last revision.	Date included		No date, excluded from evaluation

* not regulated by the OSHA Hazard Communication Standard

Table 2.

Scoring codes

Category	Scoring Code	Total score for 11 sections
Reliable without restrictions (excellent)	4	41–44
Reliable with restrictions (good)	3	37–40
Unreliable	2	22–36

Table 3.

Summary of SDS evaluation using Eastlake et al. 2012 method

	SDS only		SDS & Technical data	
	#	%	#	%
Contain bulk OEL (macroscale)	5	7.5%	5	7.5%
Specified that material is nanometer range, using numbers	10	14.9%	26	38.8%
Specified nanomaterial toxicological data for product	4	6.0%	4	6.0%
Advised using engineering controls and/or PPE	47	70.1%	47	70.1%