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Heat transfer fluids by Eastman

EXECUTIVE SUMMARY

Operating a heat transfer fluid system safely

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Many industrial processes require heating or cooling with precise temperature control. Maintaining this temperature control can be achieved through several industrial practices but is most often done through a heat transfer system. Such a system has many components including a pump, process adjacent piping, valves, gaskets and a suitable heat transfer fluid (HTF). HTF systems, depending on design and volume, may introduce several types of industrial hazards to a site. These hazards could be human-health based, such as thermal or inhalation exposures, or environmentally based, including accidental releases or unresolved fugitive emissions. However, any risk that an HTF system introduces can be mitigated with the correct system design, maintenance and operator training. As such, working with experts to design the system and using the correct HTF for your application is a critical step in ensuring operator, environmental and public safety.

As an HTF industry leader, Eastman has opted to proactively educate the market on safe use of HTFs with hazardous properties. This paper will provide users with a resource that illustrates how to properly handle and maintain heat exchangers that contain HTFs with hazardous properties. Safe handling will be demonstrated through discussion on international and regional classification systems and their requirements, elucidation of hazard and risk, and how these requirements and issues relate back to proper system design and operator training.

International hazard classification systems

To frame our understanding, it is necessary to briefly review the hazard classification systems applied in different regions. The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is the internationally accepted standard introduced by the United Nations. Regarding classification and labelling, GHS is majorly adapted or represented in every chemical legislation globally. This mandate to develop and establish a classification system was ratified by the United Nations Conference on Environment and Development (UNCED) in 1992. In chapter 19, from the agenda of UNCED, the following was concluded: "*A substantial use of chemicals is essential to meet the social and economic goals of the world community, and today's best practice demonstrates that they can be used widely* *in a cost-effective manner and with a high degree of safety."* [1] However, UNCED also concluded that there was a lack of information and resources for the risk assessment of chemicals. In response, governments have been expanding and accelerating programs for the assessment of chemicals, harmonization on classification and labelling, and information exchange on chemical risks.

The first edition of GHS was published in 2003 and updated about every two years. The 9th revision was published in September 2021. This revision was added to a list from the GHS subcommittee secretariat of the 85 countries that have implemented and adapted the GHS requirements [2]. This wide implementation illustrates how GHS has become a truly global system for classification and labeling. Most recently, the 10th revision has been published with some additions about classification procedure for desensitized explosives and the use of nonanimal testing methods for classification of health hazards.

The primary function of the GHS is to provide classification and labeling criteria for responsible parties. To do this, GHS differentiates between physical, human, and environmental hazards. There are several subcategories of these hazards including physical-chemical property descriptors like flash point and boiling point, as well as human health descriptors including reproductive toxicity, skin irritation and aspiration toxicity. These hazards and their descriptors are established via testing parameters standardized by GHS. In most regions, the onus for generating test data for new or existing products is placed on manufacturers. When data is generated, the behind-the-scenes process includes a manufacturer that has commissioned a laboratory that follows the outlined GHS standards to produce that data or has otherwise internally produced standard complaint results themselves. The responsible company must then classify and label that product according to the laboratory results and the requirements outlined in GHS. Each of the 85 countries and regions that have adopted the GHS guidelines have also adapted their own approaches to this system that are just as strict or stricter than the GHS system.

Regional hazard classification systems: example considerations

One example of a region's adoption and expansion of the GHS can be seen in the European Regulation on Classification, Labelling, and Packaging (CLP). The European regulatory framework adopts most of the GHS guidelines as is, but it does have some important distinctions.

1. GHS guidelines for some human and environmental health hazards have cutoffs of 0.3%, but the CLP lowers those concentrations to less than 0.1%.

2. Harmonization of classifications can be initiated by ECHA or EU (European Union) member states when data from studies provide a justification to do so. This can be a response from classifications and labels that are required to be submitted for substances on the EU market in the C&L inventory.

3. The EU has an adjoining poison control harmonization scheme where substances in classified mixtures are assigned unique formula identifiers (UFI) numbers that downstream users can reference when calling the poison control network (PCN) hotline with an exposure event. This system is protective of confidential business information (CBI) and protects downstream users when exposure occurs.

Another important regulation related to but independent of CLP is REACH (Registration, Evaluation, Authorization and Restriction of Chemicals). The European Chemicals Agency (ECHA) describes REACH as "*… a regulation … adopted to improve the protection of human health and the environment* *from the risks that can be posed by chemicals.*" [3] In practice, REACH's primary function is to register, evaluate, authorize and restrict or ban substances that are placed on the European market. REACH came into force in 2007 with preregistration phases and transitional periods which ended in 2018. Following the end of the transitional period, REACH was fully implemented and now applies to all member states of the European Union and three additional countries (Iceland, Liechtenstein and Norway), which constitute the European Economic Area. REACH provides valuable resources to individuals and corporations by summarizing data into REACH dossiers. These dossiers contain information from the identity of the substance to safe handling and toxicological properties. It is recommended that users familiarize themselves with the ECHA registered substance database to ensure they understand all the hazards associated with a substance.

Another important facet of regional regulatory framework implications is additional classifications that are not GHS based. REACH adds additional hazard characterization through listing systems such as the Persistent, Bioaccumulative and Toxic (PBT) and Substances of Very High Concern (SVHC) listings. These listings are described in detail by REACH legislation, but the key takeaway is to understand that the EU has additional tools that can heighten and accelerate the regulatory scrutiny of certain chemistries. This means that these chemistries may see accelerated paths toward regulatory measures on the European market.

In addition to the international regulations, additional requirements are laid out by national authorities. Some examples:

> **Germany** follows the requirements laid out in the Seveso III Directive, but it also employs its own water hazard classification under ordinance on facilities for handling substances that are hazardous to water. **Switzerland** has a special regulation to reduce emissions of volatile organic compounds (VOCs) while **France** introduced an extended producer responsibility which requires producers to contribute to the disposal of waste from their products. In the **USA**, the EPA has proposed rules for notifying about the use of certain chemicals in significant new uses (SNUR) under the Toxic Substances Control Act.

These regulations have important implications for operators of HTF systems. Lowered concentration limits, classification harmonization procedures and the different listings can introduce administrative and financial burdens on industrial sites. It is important for downstream users to stay up to date with these listings and be familiar with the regulatory inventory databases such as the ECHA database [4].

Hazard discussion

The use of HTF fluids with hazardous properties may imply certain risks for employees and the environment depending on the characteristics of the HTF. Besides the inherent risk derived from high temperatures and elevated pressures of the HTF system, the physical-chemical properties of some HTF products that allow sufficient thermal stability at high temperatures also result in additional hazards and, depending on the region, regulatory obligations for a site.

One hazard applicable to all HTFs used at high temperatures is the potential exposure of operators to high temperature fluids or surfaces. A thermal exposure at process temperature may result in serious burns. Thankfully, there are ways to prevent thermal exposures such as using adequate personal protection equipment, mechanical barriers, and warning signs to prevent accidental contact to hot surfaces.

Other potential hazards found in using high-temperature HTFs may include aspiration, acute toxicity, reproductive toxicity and skin irritation or sensitization. In the following, we will use the definitions of the GHS. [5] They are also adopted in the European legislation for CLP. [6, 7]

- Aspiration hazard: hazard of acute effects caused by the entry of a liquid or solid chemical directly through the oral or nasal cavity, or indirectly from vomiting, into the trachea and lower respiratory system
- Acute toxicity: adverse health effects occurring after a single or short-term oral, dermal or inhalation exposure to a substance or a mixture
- Reproductive toxicity: adverse effects on sexual function and fertility in adult males and females, as well as developmental toxicity in the offspring, occurring after exposure to a substance or mixture
- Skin irritant: the production of reversible damage to the skin occurring after exposure to a substance or mixture
- Skin sensitizer: a chemical that will lead to an allergic response following skin contact
- Acute aquatic toxicity: the intrinsic property of a substance to be injurious to an organism in a short-term aquatic exposure
- Chronic aquatic toxicity: the intrinsic property of a substance to cause adverse effects to aquatic organisms during aquatic exposures which are determined in relation to the life cycle of the organism

Aspiration hazards are a result of the low viscosity of fluids. If a chemical is ingested, instructions are to induce vomiting. However, low-viscosity fluids have a chance of aspiration, or entering the lungs, when vomiting is induced. Coincidentally, the viscosity properties of Therminol™ and Marlotherm™ products are desirable within their suggested uses. These properties allow downstream users to operate their systems at a lower cost and with high efficiency due to low viscosity of the fluid. If operators are aware of what to do when an ingestion exposure occurs, there is little to no risk for this hazard.

The remaining human health and environmental hazards are a result of the physical-chemical properties necessary for HTFs to offer the thermal stability needed for process heat integrity. HTFs must be persistent in environments of high pressure, temperature, flow and, in some systems, with contaminants. As such, PBT listings, reproductive toxicity, and aquatic acute and chronic ratings tend to be prevalent in the highest temperature chemistries.

Finally, operators must consider the physical hazards that HTFs present. GHS describes 17 physical hazards, but HTFs should mainly consider the flash point, flammability and boiling point. A substance is considered flammable if it has a flash point of not more than 93°C. While fluids with higher flash points are not subject to classification, they may also be a potential safety hazard when operated above the flash point. This is usually the case for many HTF systems as most industrial processes require operating temperatures well above the flash point of HTFs. This is why it is important for operators to have designed a system that minimizes leaks of fluid or vapor. When fugitive emissions occur, it will result in significant issues for system operators. There is a risk that hot vapors or liquid in insulating material ignites with the right conditions (temperature, humidity and physical state of emission). If you have any concerns, consult with an expert to ensure system integrity.

Legally mandated information on all potential hazards for a substance will be published in the safety data sheet (SDS) of the product and summarized on the product label. In addition to the hazard identification, this document will also provide information about the supplier and emergency responses, first aid measures, accident prevention, measure for safe handling and storage, transport provisions and international- and country-specific national regulations. In REACH legislation, the SDS must include an annex that provides users with possible exposure scenarios. SDSs cover everything that a user of the material will need to know. Facilities should continuously review their hazardous material SDSs, handling procedures, local and national requirements, and the publicly available data to ensure they are providing the safest possible environment for operators.

Determining the hazard and risk

When facilities design heat transfer systems, they should incorporate considerations for hazard and risk relating to operators and the environment. A hazard is a scenario where an adverse event can occur, and the risk is the likelihood of that adverse event occurring. For example, not remediating fugitive emissions may result in a fire hazard around the emission area. It should be noted that fugitive emission volume tends to be low, it must encounter another flammable material, and the emission would need an appropriate ignition source. It should be noted that fugitive emission volume, and thus the risk of fire hazard, tends to be low. The fugitive emission must encounter another flammable material, and the emission would need an appropriate ignition source to ignite. Therefore, this type of risk is widely understood to be unacceptable for the operator, facility and environment, and it should be remediated accordingly. During that remediation, additional examples of hazard and risk are demonstrated. It is recommended that operators purge the HTF system with nitrogen and lower the system's temperature before opening to less than 100°C. Performing these steps removes the most significant hazard altogether by removing hot volatile organics as a potential exposure. If these steps are not tenable, operators can be provided with proper ventilation in the environment if the system is indoors, and with personal protective equipment and training to perform tasks quickly and effectively.

The key to minimizing both exposure and emissions is to operate the HTF in a strictly controlled closed system. When the heat transfer system is operated in this manner, the risk of fluid release and any potential exposures are minimized. Maintenance and routine events, including filling and draining, are major points of exposure for operators. Here are additional routine tasks that should have developed procedures and safety considerations:

- Maintaining or exchanging equipment on the process side of heat exchangers
- Cleaning the pump strainer and/or the side stream filter
- Replacing the sealing of a pump
- Exchanging a defective instrument or valve on the HTF loop
- Replacement of gaskets on flanges
- Cleaning or removal of fluid from equipment such as the expansion vessel that should be inspected by manual entry and HTF sampling for routine analysis

The best ways to minimize exposure risk is to ensure your system is properly designed; that the procedures for that system are standardized and captured in formal documentation; that appropriate training is provided for system operators; and use of personal protective equipment (PPE). These safety considerations should align with your facility's regional and national requirements. PPE is the last line of defense against exposures for operators. Facilities should consider all other aspects of the hierarchy of controls as they develop their system design. By the end, facilities should have a closed system that only presents hazards to operators when opened hot. As such, facilities can employ procedural, administrative and PPE controls to further minimize any risk of exposure. Suggested PPE for an HTF system includes gloves, long sleeves, goggles and chemical-resistant footwear. It is also recommended that operators don additional protection for the eyes and skin using chemically resistant aprons and face shields.

System design and maintenance

Applying appropriate constructive and design measures, in combination with organizational measures, can also lead to permanently technically tight plant(s). Apart from the human and technological factors, the organizational structure for safety measures also plays a key role when it comes to plant safety." [8]

When heat transfer systems are well designed and maintained, they can serve as cost-effective, low-exposure and low-maintenance system for industrial sites. Scheduling of maintenance events can vary from user to user, but it is recommended that systems be sampled every 12 months and that system inspections occur according to technical and regulatory requirements. System inspections may result in the need to perform system maintenance. Primary outcomes of system inspections, and the resulting maintenance activities, are as follows:

For maintenance scenarios, operators should always consider their own procedures first. Operators should also be cognizant of requirements laid out by their national and regional authorities when developing or adapting procedures.

- Filling and draining: Prior to unloading the contents of a bulk container, it should be properly positioned for safe access, centered in front of an unloading dock, and within spill containment areas. If bulk container heating is required during unloading — typically performed with pressurized steam — it is important not to exceed the maximum allowable pressure rating of the bulk container. The maximum allowable pressure of the bulk container can vary and should be referenced before unloading. HTF systems are normally filled from the bottom to the top. This technique is employed to prevent aeration of the fluid. While filling, top vents on the system should be opened for displacement of the vapors from the system to a predetermined and predictable location. During the filling process, it is recommended to have personnel inspect the piping network to confirm there are no leaks.
- Maintenance and repairs: Any maintenance and repair task must be carefully planned to reduce the risk of fluid release. Some typical maintenance activities, like pump seal repair, are performed in areas where fluid containment infrastructure is already implemented. Despite this, it is recommended that a review of potential leakages regarding location and volume be performed prior to each maintenance event.
- Sampling: When performing in-service fluid sampling, operators may also consider VOC-filtering respirators in addition to standard PPE. An even better management of system sampling is to use an in-line sampler which removes the potential of exposure from the operator.
- Spills: For all operations, it is important to clean up any spill immediately. Noncombustible absorbent material (either pads or bags filled with granular solids) should be readily available to soak up spilled HTF.
- Periodic inspections: Good examples of inspection checklists can be found in [8] and [9].

Industry standards and practices have been established and developed regarding design, construction and operation of a closed heat transfer fluid system. [8-19] They are published by industry associations, industry standard bodies, insurance companies and regulatory authorities. These standards can vary region to region, but there are some common principles to keep in mind when designing your system to minimize the risk of release and exposure:

- The heat transfer system should be located on an impermeable surface to avoid soil contamination. This area should be designed to allow containment of any leakage and to ease any cleanup efforts. To achieve this, it is recommended to slope the areas under equipment, and use dikes and other controlled drainage to divert leakage and runoff to a safe location. [9] Considering the equipment, all components selected should be designed to withstand the desired operating temperatures and pressures. This design must include a satisfactory safety margin which can be referenced by industry experts or in technical guidance documentation in your region. Reference and understanding of the required codes and regulations as well as equipment manufacturers' design data sheets are essential for proper fluid selection.
- Pipework and pumps are given extra attention in the standards due to their higher likelihood of fluid or vapor release. Pipework flanges should be minimized and welded as much as technically and economically feasible. For easier inspection and maintenance, flanges should be located where they can be regularly inspected. In higher temperature heat transfer systems (> 250°C), flange connections made of stainless steel, spiral-wound gaskets with a flexible graphite insert have been proven to be reliable. Where these materials aren't available or economically feasible, pure graphite gaskets have proven to be a reliable alternative. Proper installation is critical as gaskets are only used once. Threaded connections should be eliminated from use in an HTF system as they are difficult to seal. Finally, it is important to do a proper stress analysis of the pipework and provide sufficient room for thermal expansion and contraction by deploying stress relief components throughout the system. Stress relief components can include hangers, expansion joints and expansion loops. Three different types of pumps are utilized in HTF systems — centrifugal, canned motor and magnetic driven. All are valid choices for a heat transfer system. However, it is worth noting that choosing a centrifugal pump will require that the pump come equipped with a double mechanical seal and/or a liquid barrier to minimize any potential of leakage. To ensure a long life for the pump with minimal emissions, the alignment of the pump and motor should be done while the pump is hot. Special attention should be given to minimizing the risk of thermal burns while doing this alignment. It is important to consider exposure potential and regional and national requirements on protection when performing this maintenance step. Pump leaks from the shaft seal must be safely diverted and collected. [13]

Another important factor to minimize risk in operating an HTF system is to employ proper procedures and adequate training. The National Fire Protection Agency (NFPA) has stated, "Most cases of failures can be traced to human error. The most significant failures include inadequate training of operators, lack of proper maintenance, and improper application of equipment." [10] Therefore, all employees working with HTFs must be trained in established handling procedures and specific instructions on how to operate the system. The importance of this is highlighted by the fact that more than 50% of claims related to incidents with thermal fluid systems are neither equipment nor design related. [14] A thorough inspection and detailed training plan should be developed to ensure high plant reliability and safety is in place to minimize risk of chemical exposure.

Any risk stemming from the hazardous properties of HTFs can be managed. The risk associated with the different hazards of HTFs are controlled by minimizing the release and exposure of chemicals through system design and proper training. The biggest health risk associated with a heat transfer system is the risk of thermal burns. This risk can be effectively reduced by correct design and handling. Heat transfer systems of all process temperatures and fluids can be operated in a safe manner for employees and the environment.

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SFE-HTF-18046 11/23