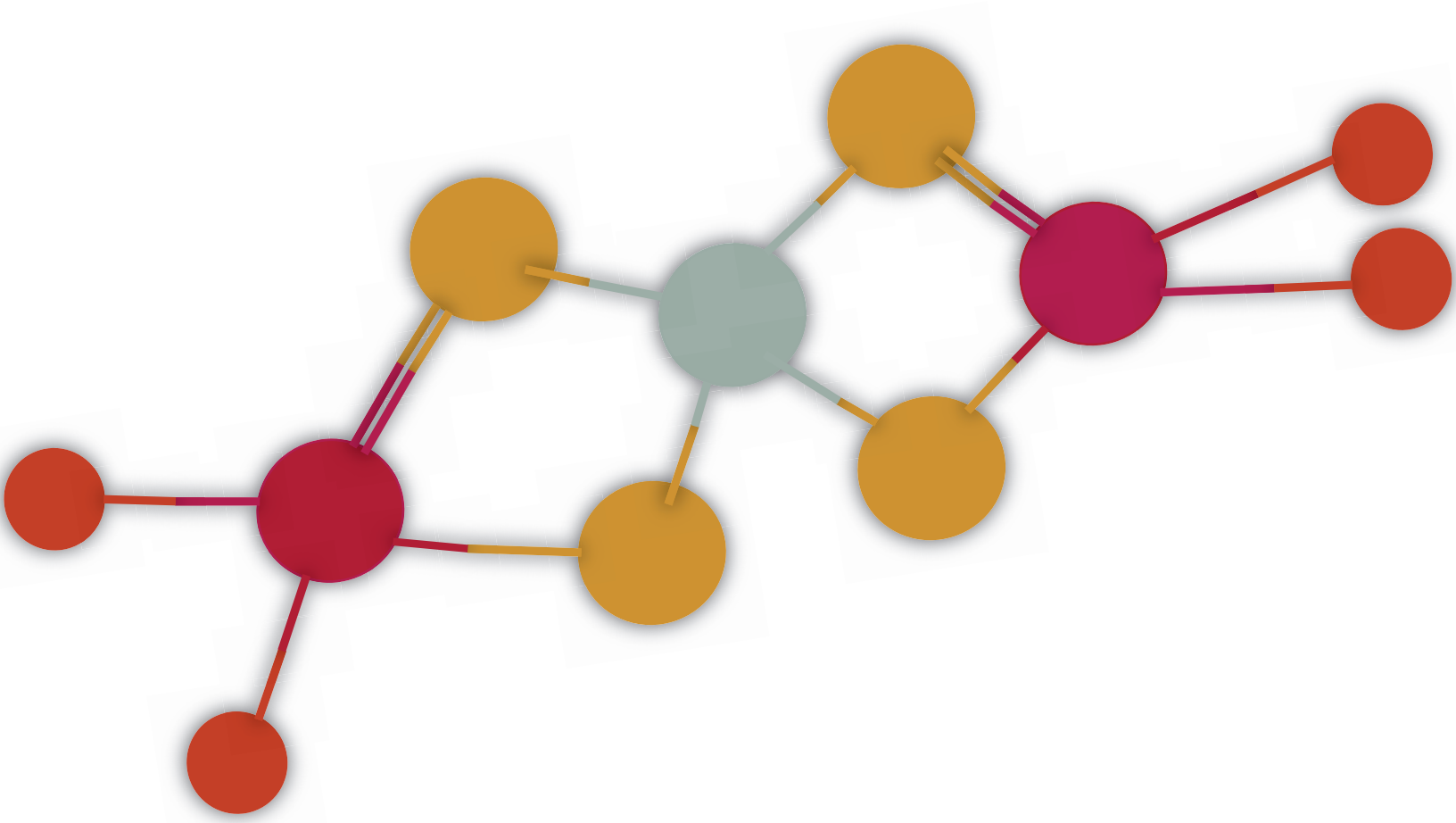
# Safe Handling Guidelines for ZDDP* Components and Blends

*September 2015*



*** Zinc Dialkyl Dithio Phosphate**



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### Authors

This document, Safe Handling Guidelines for ZDDP Components and Blends, was jointly prepared by the members[1] of the American Chemistry Council's Petroleum Additives Safety Task Group.

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# 1 INTRODUCTION

Zinc Dialkyl Dithio Phosphate (ZDDP, also referred to as ZDTP, ZDP and ZnDTP) is a well-known and widely used anti-wear chemical component in automotive lubricating oil additives. It is manufactured as a pure component but is usually transported and sold in blends with other components in concentrations up to 30%.

Pure ZDDP (neat) and packages containing ZDDP (blends) are sensitive to temperature and can decompose if overheated, leading to the formation of toxic and flammable gases that include hydrogen sulfide (hereafter referred to as $H_2S$), mercaptans and olefins. The gases also generate a very strong and unpleasant odor that can travel long distances and can be detected at very low concentrations.

This document contains suggested safe handling guidelines for customers and contractors when handling or blending with ZDDP to help prevent a decomposition incident. It also provides information on steps to be taken should a decomposition event occur. The document should be used in conjunction with the relevant, product specific Safety Data Sheet (SDS) for the particular product being handled. SDS and other supplementary information for all ZDDP containing products are available from your local contact / supplier. For purposes of this document, the term ZDDP will be used to represent both pure ZDDP and ZDDP blends, unless otherwise specifically stated.

Information contained herein is provided as general guidance only; responsibility for the appropriate management of ZDDP and ZDDP containing materials and for preventing and managing any product decomposition resulting from any activity specific to their facilities or handling practices rests entirely with the user. This document is not a substitute for safety and handling training for personnel working with ZDDP.

# 2 ZDDP THERMAL STABILITY AND DECOMPOSITION CHEMISTRY

## 2.1 THERMAL STABILITY

ZDDPs are stable when stored and handled as recommended by the SDS. ZDDPs are sensitive to temperature and will decompose if overheated or stored at elevated temperatures for extended periods of time. Some of the factors that can affect ZDDP stability are listed below.

### 2.1.1 ZDDP type

The thermal stability of ZDDPs can be impacted by the type of alcohol(s) that was used to manufacture the ZDDP as well as the residual basicity of the ZDDP salt.

### 2.1.2 Water content

The presence of water may lead to a hydrolytic decomposition if the ZDDP is held above the recommended temperature for an extended period of time.

### 2.1.3 Bulk temperature

Average temperature of the fluid.

### 2.1.4 Skin temperature

The skin temperature is the temperature of contact between the product and the hot surface transmitting heat. The skin temperature is obviously higher than that of the bulk temperature of the liquid. Both temperatures are important, particularly when the product is heated under static conditions (as happens when re-heating the product in a transport container).

### 2.1.5 Storage and handling temperatures

Storage and handling temperatures can impact the stability of ZDDPs, which decompose if stored at elevated temperatures for extended periods of time. Consult supplier SDS for storage and handling temperatures for the specific product. Table 1 provides some general guidance on the suggested maximum storage and handling temperatures for ZDDP.

Table 1 – General Guidance for Maximum ZDDP Storage and Handling Temperatures

| Description | Products Containing ZDDPs | Neat ZDDP Component |
|---|---|---|
| Maximum heating media temperature* | 100-120˚C | 100˚C |
| Maximum short-term storage and handling temperature (less than 1 week)* | 60-70˚C | 60-70˚C |
| Maximum long-term storage and handling temperature (more than 1 week)* | 40-45˚C | 40-45˚C |

**This is general guidance. Always consult supplier SDS for storage and handling temperatures for the specific product.*

When ZDDP is blended with other components, its stability is significantly affected by the nature and composition of the mixture. However, even when sensitivity to the temperature is reduced by dilution and the presence of other basic components, the thermal instability remains and there is a temperature at which the ZDDP contained in the blend will decompose.

## 2.2 ZDDP DECOMPOSITION CHEMISTRY

The thermal decomposition of a ZDDP can ultimately lead to the generation of significant quantities of gases including toxic $H_2S$, odorous low molecular weight mercaptans and flammable light olefins, leaving behind a highly odorous, tarry residue. The National Institute of Occupational Health and Safety's (NIOSH) industrial hygiene information for $H_2S$ is shown in Table 2. The table does not include industrial hygiene information for mercaptans or olefins because the types of mercaptans and olefins that can be released are product dependent. Consult the ZDDP product supplier and supplier SDS for more information on potential decomposition products.

Table 2 – $H_2S$ Industrial Hygiene Information

| Compound | NIOSH IDLH* (ppm) | NIOSH REL C (10 min)(ppm) | Flash Point (˚C) | Lower Explosive Limit (%) | Upper Explosive Limit (%) | Comments |
|---|---|---|---|---|---|---|
| $H_2S$ | 100 | 10 | NA | 4 | 44 | Rotten egg smell. Ability to detect $H_2S$ above 100 ppm is rapidly lost due to olfactory fatigue |

**National Institute of Occupational Health and Safety, Immediately Dangerous to Life and Health*

# 3 ZDDP DECOMPOSITION PERSONAL PROTECTIVE EQUIPMENT

Due to the potential for $H_2S$ generation, NIOSH recommends that personnel wear a self-contained breathing apparatus (SCBA) or supplied air respirator. Consider wearing a personal $H_2S$ monitor when entering an area with a suspected decomposition. Select any additional personal protective equipment (PPE) based on the potential chemical exposure. Consult the ZDDP product supplier and supplier SDS for more information on appropriate PPE.

# 4 ZDDP DECOMPOSITION DETECTION

## 4.1 DECOMPOSITION DETECTION

An unpleasant odor caused by the decomposition products ($H_2S$ and mercaptans) may be one of the first signs of decomposition. Personnel entering an area with a suspected ZDDP decomposition should refer to Section 3 for guidance on appropriate PPE. Other considerations during a ZDDP decomposition are below.

### 4.1.1 $H_2S$ Detection

Prior to detection, make $H_2S$ monitors available in areas with suspected decomposition.

Lead acetate paper can be used to detect the presence of $H_2S$ in ZDDP samples. To use lead acetate paper, wet the paper with water and hold in the vapor space of the sample. The amount of $H_2S$ being generated is typically determined qualitatively by the darkness of the test strip. Figure 1 shows the lead acetate paper darkening slightly with low $H_2S$ levels, while dark brown / black test paper indicates high levels of $H_2S$ are present. Colorimetric gas detector tubes can also be used to measure $H_2S$ levels.


Figure 1: Impact of increasing $H_2S$ concentrations on lead acetate paper

# 5 GENERAL ZDDP STORAGE AND HANDLING GUIDELINES

## 5.1 GENERAL CONSIDERATIONS

### 5.1.1 Bonding and grounding

Consider utilizing bonding and grounding when handling ZDDPs, due to their potential for static accumulation.

### 5.1.2 Inert container headspace

**Since ZDDP decomposition products can form explosive mixtures with air, inert the headspace of ZDDP containers during a decomposition.**

### 5.1.3 Precautions when opening a ZDDP vessel or container

Exercise care if it is necessary to open any ZDDP vessel, container, or line as the vapor space might contain toxic / flammable vapors due to decomposition. Refer to Section 3 for guidance on appropriate PPE.

## 5.2 STORAGE AND HANDLING TEMPERATURE GUIDELINES

In general, the higher the ZDDP temperature is maintained, the shorter the time that the ZDDP can be held at that temperature before decomposition occurs. Thus, recommended storage temperatures are lower than the recommended temperatures used during loading and unloading operations. This document provides general guidance on storage and handling temperatures for ZDDPs in Section 2.1.5, and always consult supplier SDS for storage and handling temperatures for the specific product.

## 5.3 GUIDELINES FOR HEATING ZDDPS

Facilities are typically designed to handle ZDDPs without heating. If it is necessary to heat ZDDPs, monitor the ZDDP temperature to ensure it does not go above the temperatures set forth in the SDS. Ensure that all temperature sensors which measure the bulk ZDDP temperature are fully immersed in the ZDDP liquid to prevent overheating, this is particularly important when heating small amounts of ZDDP that remain at the bottom of containers. If possible, use an agitator or recirculating pump to agitate the ZDDP during heating to try to avoid the presence of localized hotspots in the bulk ZDDP. Avoid using any heating media which could lead to high skin temperatures. Refer to the supplier SDS for storage and handling temperatures. See Section 2.1.5 for general temperature guidance for heating ZDDPs.

### 5.3.1 Heating with electric, warm oil or water systems

If heating is necessary, conduct an engineering review to ensure that the product will not be overheated, as overheating can result in the evolution of $H_2S$, mercaptans, and olefins due to ZDDP decomposition. Electric, warm oil and water heating systems may be less likely than steam to initiate a ZDDP decomposition because of the capability to control temperature more rigorously.

### 5.3.2 Heating with steam

Conduct an engineering review when heating with steam which may be more likely to initiate a ZDDP decomposition than the methods listed in Section 5.3.1. Check the bulk ZDDP temperature during heating and consider utilizing over-temperature alarms and controls to avoid overheating the ZDDP.

# 6 ZDDP SHIPPING CONTAINER UNLOADING SITE DESIGN GUIDELINES

## 6.1 GENERAL GUIDELINES

In general, ZDDP shipping containers and transfer lines are kept free of water, since exposure to water may generate acidic species that can catalyze a decomposition.

## 6.2 ZDDP UNLOADING SITE DESIGN

ZDDPs are shipped in rail cars, isotainers, drums or tank trucks. Design guidelines for each may be similar. An example of a configuration for a ZDDP unloading site is shown in the figure below, but follow local design standards. This configuration is only an example and does not apply to drums. Consult the ZDDP supplier for further design guidance.

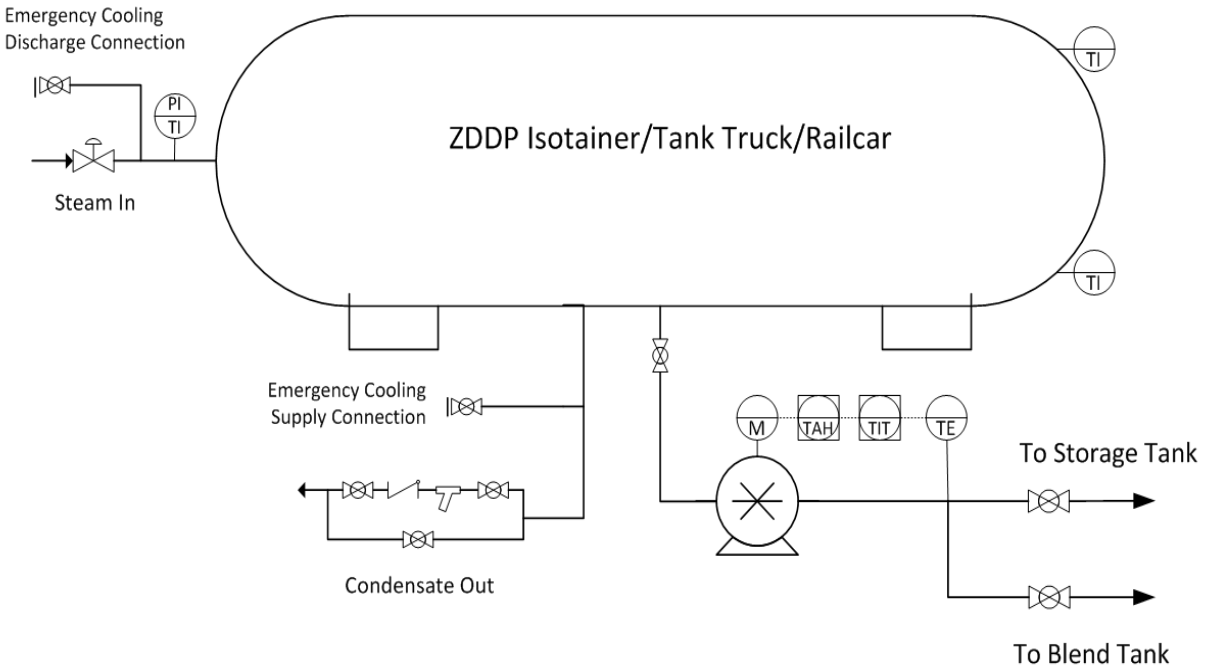


Figure 2: Example of an unloading site configuration for ZDDP isotainers, tank trucks and railcars

In the event of decomposition, cool the material to less than the maximum recommended storage temperature as quickly as possible. Refer to the supplier SDS for storage and handling temperatures. See Section 2.1.5 for general ZDDP storage temperature guidance. For example, this can be achieved by cooling the material using the emergency cooling connections or recirculating the material through an external heat exchanger.

## 6.3 ZDDP UNLOADING SITE INSTRUMENTATION

### 6.3.1 Redundant temperature elements

Given that there is no agitation in isotainers, tank trucks or rail cars, consider installing redundant temperature elements. Indicators are typically installed at the bottom of the vessel and at the top of the vessel (below the liquid surface) respectively. This helps ensure that the bulk fluid does not exceed the maximum recommended short term handling temperature listed in the SDS. If possible, recirculate the ZDDP using a pump to avoid the creation of hotspots. During recirculation, secure all lines, fittings, and temporary hoses to prevent a spill.

### 6.3.2 Heating media temperature monitoring

Install a temperature transmitter and associated interlock on the heating media inlet to monitor the temperature and check that it does not exceed the maximum recommended short term temperature. Refer to the supplier SDS for storage and handling temperatures or Section 2.1.5 for general ZDDP temperature guidance.

### 6.3.3 Pump temperature monitoring

To monitor pump temperature, consider placing one or more temperature indicators directly downstream of the recirculation pump, prior to any valves. Interlock temperature indicators with a high temperature alarm, which is designed to stop the pump motor in the event of overheating. Place the temperature probe in close proximity to the pump and prior to any valves.

# 7 ZDDP STORAGE TANK DESIGN GUIDELINES

## 7.1 GENERAL GUIDELINES

In general, ZDDP shipping containers and transfer lines are kept free of water, since exposure to water may generate acidic species that can catalyze a decomposition.

Use a storage tank designed to handle the gas evolution from ZDDP decomposition. Consult your supplier for information on vessels suitably designed to address appropriate emergency scenarios.

## 7.2 ZDDP STORAGE TANK PROCEDURES

A diagram of a possible storage tank configuration for ZDDPs and ZDDP containing materials is shown in Figure 3. This configuration is only an example of a possible configuration, follow local design standards.

In the event of decomposition, cool the material to less than the maximum recommended storage temperature as quickly as possible. Refer to the supplier SDS for storage and handling temperatures. See Section 2.1.5 for general ZDDP storage temperature guidance. For example, this can be achieved by cooling the material using the emergency cooling connections or recirculating the material through an external heat exchanger.

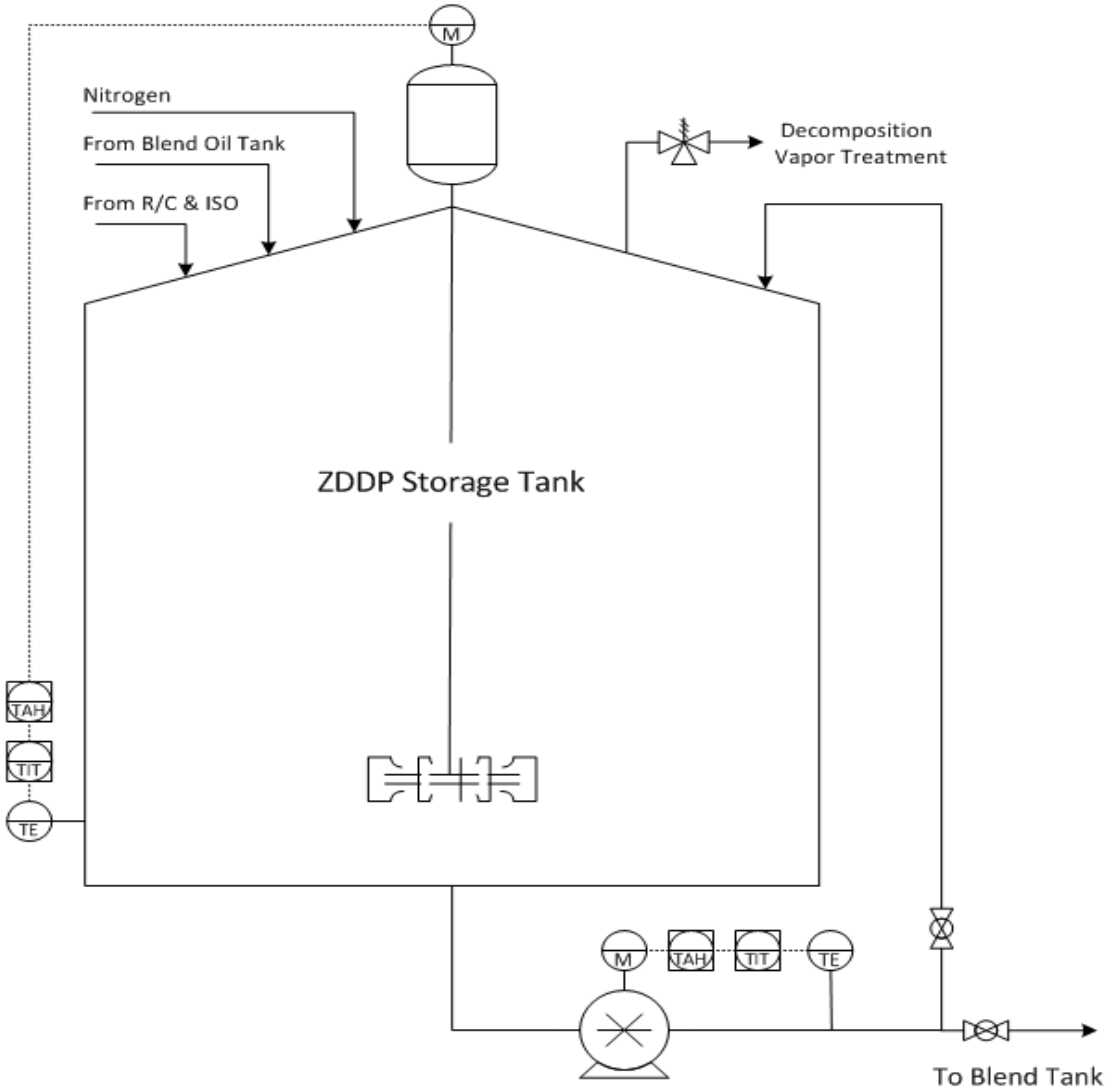


Figure 3: Example of ZDDP storage tank equipment configuration

## 7.3 ZDDP STORAGE TANK INSTRUMENTATION

### 7.3.1 Redundant temperature readings and alarms

Include redundant temperature sensor read-outs and alarms as part of ZDDP storage tank instrumentation. Locate at least one temperature sensor low in the storage tank to monitor the temperature of the material when the tank contents are low. Place an additional temperature indicator directly downstream of the recirculation pump, prior to any valves.

Use temperature indicators with a high temperature audible alarms that are interlocked to stop all mechanical equipment associated with the storage tank in the event of overheating. Consider interlocking the recirculation pump and / or agitator with a high temperature alarm with the ability to be overwritten in the event cooling is needed. Over long periods of time, significant mechanical shear may result in localized temperature hotspots which can initiate a decomposition. If the high temperature alarm is activated, initiate emergency cooling. Refer to the supplier SDS for storage and handling temperatures. See Section 2.1.5 for general ZDDP temperature guidance.

# 8 EMERGENCY RESPONSE PROCEDURES

## 8.1 EMERGENCY RESPONSE PROCEDURE OVERVIEW

## 8.2 DECOMPOSITION

If the presence of a strong and offensive odor - similar to rotten eggs – is detected around the container, then the ZDDP may be decomposing. Activate your emergency response plan. The following are considerations to be undertaken when responding to decomposition of ZDDP:

**Decomposition Considerations Include:**

- Activate Emergency Response plan
- Disconnect heating systems
- Apply cooling (if possible)
- Remove ignition sources
- Check tank pressure and monitor area for the presence of $H_2S$
- Move portable containers to isolated area (if possible)
- Route decomposition material to vent for treatment (if possible)
- Consult local emergency response organization and supplier

The above considerations are not meant to be exhaustive and other steps may be appropriate. Please contact supplier for further information on what to consider when responding to decomposition of ZDDP.

### 8.2.1 Activate emergency response plan

The vapor from ZDDP decomposition will have a strong offensive odor of $H_2S$ and mercaptans that is similar to the smell of rotten eggs. It can travel long distances and can be detected at very low concentrations (parts per billion). Even at very low levels of concentration, there can be temporary effects associated with the odor (headache, nausea and vomiting). Consider controlling access to the area downwind and notify the community downwind if it appears they will be affected. Follow guidance provided in supplier SDS regarding appropriate medical response.

### 8.2.2 Disconnect heating systems

Immediately disconnect any heating systems, instead of simply closing valves or switching off the electrical system. Verify positive isolation.

### 8.2.3 Apply Cooling

If possible, cool down the product. The vessel can be cooled by physically cooling using a heat exchanger or vessel jacket or if possible, by adding a cool neutral blend oil to act as a heat sink. If possible, turn on agitator or pump after cooling is applied.

### 8.2.4 Remove ignition sources

Remove possible sources of ignition.

### 8.2.5 Check tank pressure and presence of $H_2S$

Taking the necessary precautions, check the pressure inside the tank or vessel and sample the tank to check for the presence of $H_2S$ (See Section 4.1.1). This operation is necessary to determine whether or not decomposition has occurred. As $H_2S$ is a toxic gas, when entering an area with a suspected decomposition NIOSH recommends wearing SCBA or a supplied air respirator. Also, consider wearing a personal $H_2S$ monitor when entering an area with a suspected decomposition. Select any additional PPE based on the potential chemical exposure. Consult the ZDDP product supplier and supplier SDS for more information on appropriate PPE.

### 8.2.6 Control venting to atmosphere

If possible, collect and treat any release to the atmosphere. Vapors from ZDDP decomposition can be treated by passing the vents through a caustic abatement system or vapor incinerator. Contact supplier for specific information.

### 8.2.7 Consult with local emergency response organization and supplier

Consult with the local emergency response organization and supplier to summarize the steps taken and verify next steps.

## 8.3 ZDDP OVERHEATING

In the event that excessive temperature of ZDDP is detected or suspected, consider the following items. Note that high skin temperature or high bulk liquid temperature can reduce the stability of the ZDDP, so detect and address high temperatures as quickly as possible.

**ZDDP Overheating Considerations:**

- Disconnect heating system
- Cool ZDDP material
- Remove ignition sources
- Check tank pressure and for presence of $H_2S$
- Consult with local emergency response agency and supplier

The above considerations are not meant to be exhaustive and other steps may also be appropriate.

### 8.3.1 Disconnect heating systems

Immediately disconnect any heating systems, instead of simply closing valves or switching off the electrical system. Verify positive isolation.

### 8.3.2 Apply cooling

If possible, cool down the product. The vessel can be cooled by physically cooling using a heat exchanger or vessel jacket or if possible, by adding a cool neutral blend oil to act as a heat sink. If possible, turn on agitator or pump after cooling is applied.

### 8.3.3 Remove all ignition sources

Remove possible sources of ignition.

### 8.3.4 Check tank pressure and presence of $H_2S$

Taking the necessary precautions, check the pressure inside the tank or vessel and sample the tank to check for the presence of $H_2S$ as per Section 4.1.1. This operation is necessary to determine whether or not decomposition has occurred. As $H_2S$ is a toxic gas, when entering an area with a suspected decomposition NIOSH recommends wearing SCBA or a supplied air respirator. Also, consider wearing a personal $H_2S$ monitor when entering an area with a suspected decomposition. Select any additional PPE based on the potential chemical exposure. Consult the ZDDP product supplier and supplier SDS for more information on appropriate PPE.

If:

- **$H_2S$ detected in headspace:**
  If $H_2S$ is detected in the headspace, treat as a decomposition. Then, please see Step 8.2.6, Control venting to the atmosphere.

- **$H_2S$ not detected in headspace:**

  If $H_2S$ is not detected, continue normal processing. Continue monitoring the headspace of the overheated material for $H_2S$ until ZDDP processing is **complete**.

### 8.3.5 Consult with local emergency response organization and supplier

Consult with the local emergency response agency and supplier to summarize the steps taken and verify next steps.

## 9 SUMMARY OF SAFE HANDLING GUIDELINES

- Personnel involved in the handling of pure ZDDP or products containing ZDDP are fully trained on proper ZDDP handling.
- **Avoid** heating ZDDPs whenever possible. If heating is necessary, then refer to the supplier SDS for storage and handling temperatures for the specific ZDDP. In addition, consider the following:
  - Use heating systems with self-limiting maximum temperature controls when re-heating ZDDP solutions in static conditions.
  - Use redundant temperature readings and alarms.
  - Check the temperature of the bulk liquid regularly during re-heating.
- Consider hazards of opening vents or manholes if product has been re-heated as $H_2S$ might be present in the vapor space of the tank. NIOSH recommends wearing SCBA or a supplied air respirator. Also, consider wearing a personal $H_2S$ monitor when entering an area with a suspected decomposition.
- Establish emergency procedures to address the potential for ZDDP overheating and decomposition.

For more detailed information on the material presented in this general guidance document, please contact your supplier.

## 10 EXAMPLE OF EMERGENCY CONTACT DETAILS

The following example of an emergency contact list may be used as a guide in developing your own emergency contact list. Also, consider referring to your site plan for any additional contacts, which may include local, state or national authorities, but are not limited to the following example of a contact list.

Company / Site Emergency Response Personnel

Supplier contact

Local emergency services

Regional contact

Notes