Product Information Bulletin

EXACT-S® DMS

dimethyl sulfide

The sensible presulfiding agent for petroleum catalysts

Gaylord® Chemical Corporation

Introduction

Most catalysts used in hydrocracking (HDC), hydrodenitrification (HDN), hydrodesulfurization (HDS) and catalytic reforming processes are supplied to the refining industry in their oxide form. These catalysts must be converted to their active sulfide form inside the process unit. The usual practice is to add a sulfur spike during the start-up of the unit to prevent reduction of the catalysts to their base metals. This process is commonly known as presulfiding. Many organic sulfur compounds have been used over the years for the sulfur spike. These include butyl mercaptan (BM), ethyl mercaptan (EM), methyl mercaptan (MM), dimethyl sulfide (DMS), dimethyl sulfoxide (DMSO), dimethyl disulfide (DMDS) and tertiary nonyl polysulfide (TNPS).

Organic sulfur presulfiding agents can be divided into two classes. Compounds in the first class are less expensive, but they are **odorous**. They include BM, EM, MM, DMS and DMDS. Presulfiding agents in the second class are more expensive, and they are virtually **odorless**. These include DMSO and TNPS and other high boiling polysulfides.

Petroleum catalysts convert organic sulfur compounds to hydrogen sulfide. The hydrogen sulfide reacts with the metal oxide catalysts to form metal sulfide and water.

Typical presulfiding process with EXACT-S® DMS

EXACT-S DMS can be used to presulfide catalysts simply and successfully with conventional presulfiding equipment. Layers of catalysts are arranged inside the reactor where presulfiding will take place. Air (containing oxygen) is displaced from the atmosphere inside the reactor with an inert gas or hydrogen. Temperature in the reactor is increased to 200 - 250° F. After drying the metallic catalysts and stripping the inert gas (if used) hydrogen is injected under pressure. The start-up oil is introduced and the temperature in the reactor is raised to 350° F. The presulfiding agent should be injected at 350 - 400° F.

Approximately two-thirds of the catalysts' surface area is presulfided between 400 - 500° F. The remaining one-third of the catalysts' surface is presulfided between 500 - 600° F. The propensity for presulfiding agents to be adsorbed by the catalysts is a phenomenon that protects the catalysts from being reduced to base metal by heat. Our data show that organic sulfur should be present with the catalysts prior to increasing the temperature to 400° F. It is more critical to have organic sulfur present below 400° F than it is to have hydrogen sulfide present.

When the temperature of the catalysts' bed is increased, and then maintained at 450 - 500° F, **EXACT-S DMS** decomposes under heat and catalytic action. It should be recognized that the decomposition is catalytic and thermal rather than just thermal. **Hydrogen sulfide reacts with the metallic oxide catalysts to form metal sulfides and water.**

Eight to 10 hours are usually required to presulfide a typical batch (200,000 pounds) of catalysts.

How to choose your presulfiding agent

Many organic sulfur compounds are available for pretreating catalysts. The choice of a presulfiding agent should be guided by three factors:

- **Operational safety, toxicity and odor**
- **Maximum presulfiding capability**
- **Cost effectiveness**

Operational Safety

EXACT-S DMS is one of the least toxic organic chemicals. It is easier and safer for plant personnel to handle than many other sulfur compounds. By using only the most advanced manufacturing procedures and state-of-the-art high pressure shipping equipment, Gaylord Chemical carries through on its intention of not releasing DMS into the environment.

Toxicity

No toxicity problems have ever been encountered with **EXACT-S DMS** since it became available in the late 1960's. Risks to workers are minimal. Its measured LC_{50} concentrations show it has much lower acute toxic levels than DMDS, EM, NBM and H_2S.

Inhalation Toxicity of Presulfiding Agents in Common Use (LC_{50} for Rats)

EXACT-S DMS	40,250 ppm	DMDS	805 ppm
ethyl mercaptan	4,420 ppm	methyl mercaptan	675 ppm
butyl mercaptan	4,020 ppm	hydrogen sulfide	444 ppm

Odor

Most organic sulfur compounds have an odor. All of the less expensive presulfiding agents (BM, EM, MM, DMDS and DMS) have significant odors. The odor of DMDS is particularly obnoxious and persistent. **EXACT-S® DMS**'s odor is, however, considered to be less obnoxious and less persistent than the other compounds. The equipment and technology that Gaylord Chemical provides with each presulfiding job helps insure a leak-free and odor-free presulfiding process. If a leak or spill occurs, **EXACT-S DMS** is easily converted to dimethyl sulfoxide with sodium hypochlorite (liquid bleach).

Maximum Presulfiding Capability

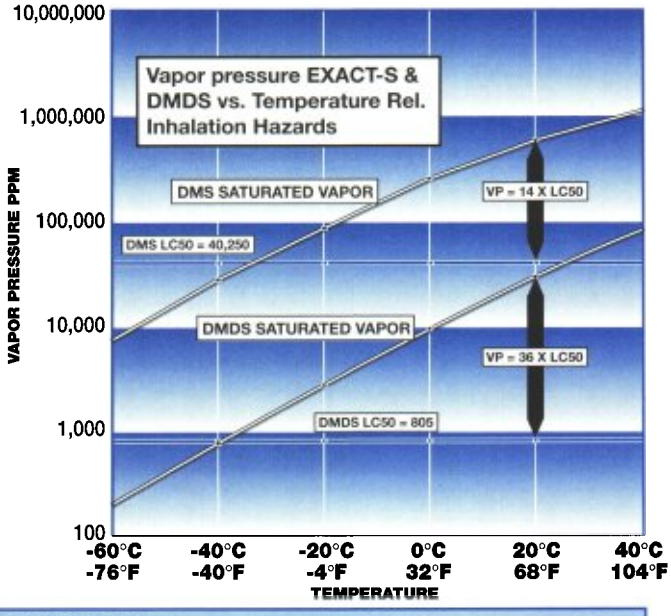
EXACT-S DMS is free of contaminates such as nitrogen, metals and nonvolatiles, which are generally harmful to catalysts. Because of the purity of **EXACT-S DMS**, it does not vary during presulfiding. The entire presulfiding process can be predictably controlled.

The low start-of-run temperature achieved by **EXACT-S DMS** makes possible a longer catalyst cycle life. It has been demonstrated many times that catalysts presulfided with **EXACT-S DMS** have maximum catalytic activity and long life.

Physical Properties of EXACT-S® DMS

	British Units	Metric Units
Molecular weight	62.134	62.134
Percent sulfur	51.5%	51.5%
Boiling point	99.0° F	37.34° C
Freezing point	-145° F	-98.27° C
Solubility in water (77°F, 25°C)	2% max.	2% max.
Vapor pressure (77°F, 25°C)	9.38 psi	485 mm Hg
Density (68°F, 20°C)	7.07 lb/gal	0.847 g/cc
Viscosity (68°F, 20°C)		0.289 cps
Critical temperature	444° F	229° C
Critical pressure	56.14 atm	42,664 mm Hg
Heat of vaporization ΔH_v (77°F)	191 Btu/lb	106 cal/g
(boiling point)	187 Btu/lb	104 cal/g
Heat of formation ΔH_f (77°F, 25°C)	-453 Btu/lb	-252 cal/g
Heat of combustion ΔH_c(77°F, 25°C)	-15,100 Btu/lb	-8387 cal/g
Dielectric constant (68°F, 20°C)	6.2	6.2
Flash point, closed cup	-36° F	-38° C
Autoignition temperature	403° F	206° C
Shipping specification is 99.0 min. by gas chromatography		

SATURATED VAPOR CONCENTRATIONS & LC_{50} vs TEMPERATURE



Cost Effectiveness

To determine the cost effectiveness of a presulfiding agent for a specific refinery, the following factors should be considered:

- **refinery's operational presulfiding requirements and objectives**
- **refinery's environmental considerations and safety measures**
- **cost per pound of sulfur in the presulfiding agent**
- **physical properties of the presulfiding agent including toxicity and odor**
- **supplier's history of dependability as a product source and on-time delivery**
- **technical service provided by supplier.**

There are significant differences in cost and availability of common organic sulfur compounds. The following table summarizes the relative cost per pound of sulfur in these compounds.

Relative Cost Per Pound of Sulfur in Common Presulfiding Agents

	Relative Cost	Availability
EXACT-S DMS	$1.00	readily available
methyl mercaptan	$1.00	readily available
butyl mercaptan	$1.05	very seldom available
ethyl mercaptan	$1.07	very seldom available
DMDS	$1.42	usually available

Summary

EXACT-S® DMS simplifies presulfiding and minimizes costs. Pure organic sulfur costs less per pound in **EXACT-S DMS** than in any other commonly used presulfiding agent. Its low toxicity translates into lower handling costs and reduced environmental risks. Gaylord Chemical has an impressive record as a dependable source of supply. Our refinery customers can establish a cost efficient routine that will not be plagued with out-of-stock situations, late deliveries, and off-specification product. An ample supply of consistently high quality product delivered when and where it is needed is extremely important.

Gaylord Chemical provides technical service to customers on products, equipment, safety and environmental matters. Our high quality delivery equipment gives customers the latest and most efficient presulfiding delivery service available. From logistics to off-loading, our customers expect ... and receive exemplary service. It's Gaylord Chemical's way of providing maximum value to our presulfiding customers.

Comparison of Presulfiding Agents in Common Use

Agent	Sulfer Content %	Boiling Point	Flash Point	Autoignition Temperature
Exact-S DMS				
dimethyl sulfide	51.5	99°F	<32°F	>403°F
ethyl mercaptan	51.5	95°F	<32°F	>575°F
methyl mercaptan	67	46°F	<32°F	–
dimethyl disulfide	68	228°F	61° F	>575°F
butyl mercaptan	35.5	205°F	19°F	–

Basic information about petroleum catalysts

Properly presulfided catalysts have three properties — activity, selectivity, and stability. Catalysts are presulfided to achieve these basic properties.

Activity. Presulfiding makes catalysts more controllable. **EXACT-S DMS** is used to enhance activity and to control hyperactivity.

- *In some presulfiding operations such as hydrodesulfurization, the active form of the catalyst is a metal sulfide. With an* **EXACT-S DMS** *pretreatment of catalysts insitu before start-up and after regeneration, metal oxides in the catalysts will be converted to metal sulfides.*

- *In many hydrocracking operations, fresh and regenerated catalysts are initially hyperactive. This can result in excessive demethylation, high heat release, heavy coking and reduced catalysts' life. This hyperactivity can be controlled by presulfiding with* **EXACT-S DMS**.

Selectivity. *Catalysts are presulfided to make them more selective so they can better perform their desired reactions and suppress their undesirable reactions. A catalyst's selectivity is measured by its ability to yield desired products from the designed process.*

Stability. *A catalyst's stability is related to its activity and selectivity. If a catalyst loses activity and selectivity quickly, it has poor stability. A stable catalyst with a long life cycle is the result of efficient presulfiding.*

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