

# PHOSPHOROUS PENTASULFIDE LISTING BACKGROUND DOCUMENT FOR THE INORGANIC CHEMICAL LISTING DETERMINATION

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U.S. ENVIRONMENTAL PROTECTION AGENCY ARIEL RIOS BUILDING 1200 PENNSYLVANIA AVENUE, N.W. WASHINGTON, D.C. 20460

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#### 1. SECTOR OVERVIEW

# 1.1 SECTOR DEFINITION, FACILITY NAMES AND LOCATIONS

Phosphorous Pentasulfide is currently being produced in the United States by three manufacturers. These manufacturers are FMC in Lawrence, KS; Rhodia in Morrisville, PA; and Solutia (formerly Monsanto Chemicals) in Sauget, IL.<sup>1</sup> **Table 1.1** presents the name and location of the manufacturers. **Figure 1.1** shows the geographical locations of the facilities presented in Table 1.1.

Facility Name	Facility Location
1. FMC CorpLawrence Plant	440 North 9 <sup>th</sup> Street Lawrence, KS 66044
2. Rhodia Inc Morrisville Plant	2300 South Pennsylvania Avenue Morrisville, PA 19067
3. Solutia Inc William G. Krummrich Plant	500 Monsanto Avenue Sauget, IL 62206

Table 1.1	Phosphorous	Pentasulfide	Producers
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Solutia discontinued phosphorus pentasulfide production at a 25,000-ton-per-year plant in Anniston, AL, during 1987, but continues to produce at the Sauget, IL facility. The Sauget facility and FMC's pentasulfide plant in Lawrence, KS, are part of the Astaris joint venture involving the phosphorus and phosphate assets of FMC Corporation and Monsanto/Solutia. Occidental Chemical withdrew from the pentasulfide market after closing a 15,000-ton facility in Columbus, MO, in 1985. Zeneca Inc. discontinued its Mt. Pleasant, TN phosphorus pentasulfide operation, rated at 20,000 tons per year, in mid-1998.<sup>2</sup>

# 1.2 PRODUCTS, PRODUCT USAGE AND MARKET

The chemical formula of phosphorus pentasulfide is  $P_2S_5$ . The compound is generally a grey-yellow powder and has a molecular weight of 222.27 gram (g)/mol. Phosphorous pentasulfide has a melting point of 286° Celsius (C) and a boiling point of 514 C.

<sup>2</sup> Id.

<sup>&</sup>lt;sup>1</sup> ChemExpo Home Page, www.chemexpo.com/news/PROFILE990920.cfm





1 See Table 1.1 for facility name and location.

The current breakdown of phosphorous pentasulfide feedstock usage is 65% for lubricating oil and grease additives (mainly zinc dialkyldithiophosphates ZDDP), 33% for organophosphorous insecticides (such as acephate, chlorpyrifos, and terbuphos), and 2% for miscellaneous uses, such as mineral ore flotation.<sup>3</sup>

The historical market for phosphorous pentasulfide has shown a negative growth of approximately minus 1.5 percent per year in the period spanning the years 1989-1998, thus accounting for the withdrawal of several manufacturers from this product. From the present time until the year 2003 the market is expected to continue to decrease at anywhere from 0 to minus 1.5 percent per year. Market demand for this product was approximately 55,000 tons in 1998.<sup>4</sup>

#### **1.3 PRODUCTION CAPACITY**

As of 1998, the maximum production capacity in the United States was approximately 85,000 short tons per year. This production capacity is split among the three current manufacturers as follows in **Table 1.2**.<sup>5</sup>

Facility	Location	Capacity (short tons/yr*)
FMC CorpLawrence Plant	440 North 9 <sup>th</sup> Street Lawrence, KS 66044	20,000
Rhodia Inc Morrisville Plant	2300 South Pennsylvania Avenue Morrisville, PA 19067	20,000
Solutia Inc William G. Krummrich Plant	500 Monsanto Avenue Sauget, IL 62206	45,000

#### Table 1.2 Phosphorous Pentasulfide Production Capacity

\*one short ton equals 2,000 pounds

# 1.4 PRODUCTION, PRODUCT AND PROCESS TRENDS

A continued reduction in the consumption of phosphorus pentasulfide for pesticide uses and heavy pressure on producers to lower phosphate levels in lubricating oils are the main reasons for the phosphorous pentasulfide's market decline. Phosphorous pentasulfide consumption, which ranged from

<sup>3</sup> Id.

<sup>4</sup> <u>Id</u>.

<sup>5</sup> <u>Id.</u>

60,000 to 70,000 tons per year during the 1990s, is unlikely to grow and may shrink even further.<sup>6</sup> The reduction of the phosphorus content of lube oil additives has meant cutbacks in phosphorus pentasulfide manufacturing. Major additive producers have had to close excess capacity, and overall US demand for lubricants is expected to remain static or grow only slightly. Demand for ZDDP, the most widely used phosphorus-based oil additive, is flat. During the past decade, phosphorous pentasulfide use has also declined substantially in the pesticide market as the production of parathions and malathion were discontinued.

Industrial markets for phosphorous pentasulfide, although small compared to automotive uses, have enabled additive producers to expand. The manufacture of phosphorous pentasulfide-based lube oil and grease additive formulations remains flat overall, though the market is still estimated to be larger than 50,000 tons per year.<sup>7</sup>

Historically (1981-1996), phosphorus pentasulfide sales have followed a declining trend of minus 1.5 percent per year. This trend is projected through the year 2003.

#### 2. DESCRIPTION OF MANUFACTURING PROCESS

#### 2.1 PRODUCTION PROCESS DESCRIPTION

The following is a general description of the production process and does not account for specific variations reported by manufactures of phosphorous pentasulfide. The production of phosphorous pentasulfide begins by feeding liquid phosphorous and liquid sulfur into a cast iron reactor. The reactor temperature starts at 200° Celsius and quickly rises due to the exothermic reaction taking place. The reactor is continually filled with nitrogen gas to prevent oxidation of sulfur. The reactor batches are forced by nitrogen gas into an electrically heated vacuum still where the liquid product is cleaned, leaving a residue in the still consisting of glassy phosphates, carbon, and iron sulfur compounds. The residue is sent to an off-site facility for incineration. The reactor is vented to a scrubber designed to remove both sulfur dioxide and residual hydrogen sulfide. These contaminants are scrubbed and the wastewater from the scrubber is sent to a WWTP for neutralization prior to discharge. The scrubber vent is then nearly clean and is vented to the atmosphere. Product is loaded into the shipping containers known as tote bins. Phosphorous pentasulfide residue is washed from returned bins at the tote wash station.

#### 2.2 PRODUCTION TRENDS, CHANGES AND IMPROVEMENTS

No current or upcoming production changes from current practices are anticipated.

<sup>6</sup> <u>Id</u>.

<sup>7</sup> <u>Id</u>.

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# 2.3 PROCESS FLOW DIAGRAM



#### 3. WASTE GENERATION AND MANAGEMENT

**Appendix A** presents a complete summary of the wastestreams generated at each of the facilities in the phosphorous pentasulfide sector, volume of the wastestreams generated in MT/yr, and the associated final management step. **Section 3.1** discusses waste reported by the facility, in the RCRA §3007 questionnaire, that are outside the scope of the Consent Decree. **Section 3.2** presents a discussion of each wastestream and identifies where in the process the waste is generated, and the subsequent management steps employed at each facility emphasize on the final management steps for the wastestream. It also presents a characterization of the wastestream, the generated volume, and a results of initial risk screening analysis.

# 3.1 WASTES OUTSIDE THE SCOPE OF THE CONSENT DECREE

EPA does not consider some kinds of debris and plant component materials to fall within the scope of the consent decree. The Solutia Inc.-William G. Krummrich Plant (Sauget, IL) reported the generation of 0.185 MT phosphorous debris (i.e. contaminated insulation) in 1998. This wastestream is outside the scope of the consent decree. Furthermore, this waste is stored in containers and disposed of at off-site incineration facilities.

# 3.2 SUMMARY OF WASTE GENERATION PROCESSES

According to the EPA, RCRA §3007 Survey, the facilities that produced phosphorous pentasulfide in 1998 reported the generation of similar wastestreams. Because processes are basically the same, there are only small variations of wastestreams between facilities.

Together, the different manufacturing process units produced ten different types of wastestreams. The units (waste source) of manufacturing process and corresponding wastestreams are as follows:

Reactor:

C Still Residue / Reactor Waste

Scrubber:

- C Scrubber Water
- C Caustic Scrubber Water

Cooling and Solidification:

# C Contaminated Absorbents

- C Waste Therminol
- C Phosphorous Pentasulfide Scrap Waste

Maintenance:

- C Phosphorous Impurities
- C Scrap Sulfur
- C Phosphorous Debris
- C Tote Bin Wash Water

Table 3.1 provides a summary of the identified wastestreams generated by facilities.

# Table 3.1 Wastes Generated from the Production of Phosphorous Pentasulfide

Facility	Still Residue/ Reactor Waste	Phosphorous Pentasulfide Scrap Waste	Process Scrubber Water	Caustic Scrubber Water	Phosphorous Impurities	Tote Bin Wash Water	Scrap Sulfur	Contaminate d Absorbents	Phophorous Debris	Waste Therminol
FMC- Lawrence Inc., Lawrence, KS		x		X	X	x				
Rhodia, Inc. Morrisville, PA	х	x		x		х				
Solutia Inc William G. Krummrich Plant, Sauget, IL	х	x*	x				X	x	x	X

\* Due to process modifications this wastestream has not been generated in the last couple of years.

#### 3.2.1 Still Residue / Reactor Waste

#### Waste Generation

This waste is generated in the reactor when phosphorous is added to sulfur. It consists of the high boiling fractions of phosphorous compounds found as impurities in phosphorous or formed during the reaction. The boiling process leaves behind a residue in the reactor consisting of glassy phosphates, carbon, and iron sulfide compounds. The clean out is conducted when the heat transfer of the reaction has diminished to a point that production is hampered. Two facilities reported generation of this wastestream.

#### Waste Management

This waste is removed from the reactor typically once a year. This waste is sent to an off-site Subtitle C incineration facilities. **Table 3.2** presents the generated volume and the final management step used by the facilities for this wastestream.

#### Table 3.2 Waste Management Summary for Still Residue /Reactor Waste

Final Management	# of Wastestreams with Reported Volumes	# of Wastestreams with Unreported Volumes	Total Volume, MT/yr*
Off-site Hazardous Waste Incineration	2	0	4.6

\* one metric ton (MT) equal 2,204.6 pounds.

#### Waste Characterization

This waste is assigned waste codes D003 (reactive) and D007 (chromium). It contains trace amount of arsenic.

#### Results of Initial Risk Screening Analysis

- 1. The composition of the waste exhibited one or more hazardous waste characteristics.
- 2. The waste is currently managed as hazardous from the point of generation through disposal because it is characteristically hazardous. This includes meeting applicable LDR standards.

# 3.2.2 Phosphorous Pentasulfide Scrap Waste

#### Waste Generation

All three facilities reported generation of this wastestream. The phosphorous pentasulfide scrap waste is occasionally generated during certain maintenance operations and clean-up activities. This waste can also consist of commercial off-spec material and fugitive dust from packaging operations. Due to process modification this waste has not been generated in couple of years at Solutia, IL facility.

#### Waste Management

This waste is stored in drums and sent off-site for incineration. **Table 3.3** presents the generated volume and the final management step used by the facilities for this wastestream.

Table 3.3	Waste Management	<b>Summary for</b>	Pentasulfide	Scrap Waste
		,		

Final Management	# of Wastestreams with Reported Volumes	# of Wastestreams with Unreported Volumes	Total Volume, MT/yr
Off-site Hazardous Waste Incineration	2	1*	67.75

\*Solutia, IL did not generate this waste in 1998.

#### Waste Characterization

The waste is assigned waste codes D001 (ignitable), D003 (reactivity) and U189 (phosphorous sulfide).

# Results of Initial Risk Screening Analysis

- 1. The composition of the waste exhibited one or more hazardous waste characteristics.
- 2. The waste is currently managed as hazardous from the point of generation through disposal because it is characteristically hazardous and listed as U189. This includes meeting applicable LDR standards.

# 3.2.3 Process Scrubber Water

#### Waste Generation

This wastestream is generated when water is passed through the scrubber system designed to remove both sulfur dioxide and residual hydrogen sulfide. One facility generated this wastestream.

#### Waste Management

This wastewater goes to the on-site wastewater pretreatment system and then is discharged to a POTW. **Table 3.4** presents the generated volume and the final management step used by the facility for this wastestream.

Table 3.4	Waste Management	Summary for	Process Scrubber	Water
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Final Management	# of Wastestreams with Reported Volumes	# of Wastestreams with Unreported Volumes	Total Volume, MT/yr
POTW discharge	1	0	77,377

#### Waste Characterization

This waste was found to be non-hazardous. The Solutia Inc.- William G. Krummrich Plant, Sauget, IL reported that this wastewater contains phosphoric acid in concentrations of one percent.

#### Results of Initial Risk Screening Analysis

- 1. The wastewater is managed in enclosed systems. Therefore, no exposure pathway exists.
- 2. Discharges to POTWs are exempt from RCRA regulation and regulated extensively under the Clean Water Act.
- 3. The primary constituents of concern, phosphoric acid and hydrogen sulfide are readily controlled via neutralization.

# 3.2.4 Caustic Scrubber Water

#### Waste Generation

The reactor, packaging and tote bin wash system vent to scrubbers to remove both sulfur dioxide and residual hydrogen sulfide generating this wastestream. Two facilities reported the generation of this wastestream.

#### Waste Management

For one facility the wastestream goes to the waste water pretreatment system and then to a POTW. For the second facility, the wastestrem is collected in a tank and discharged via NPDES. **Table 3.5** presents the generated volume and the final management step used by the facilities for this wastestream.

Table 3.5	Waste Management	<b>Summary for</b>	<b>Caustic Scrubber</b>	Water

Final Management	# of Wastestreams with Reported Volumes	# of Wastestreams with Unreported Volumes	Total Volume, MT/yr
POTW or NPDES discharge	2	0	2,177

Waste Characterization

The facilities reported this wastestream as a non-hazardous.

# Results of Initial Risk Screening Analysis

- 1. The wastewater is managed in enclosed systems. Therefore, no exposure pathway exists.
- 2. The tanks employed prevent releases to groundwater in all but the most catastrophic scenarios.
- 3. Discharges to surface water via NPDES or to POTW are exempt from RCRA regulation. Point source discharges are regulated extensively under the Clean Water Act.
- 4. The primary constituents of concern, phosphoric acid and hydrogen sulfide are readily controlled via neutralization.

#### 3.2.5 Phosphorous Impurities

#### Waste Generation

FMC-Lawrence Inc., Lawrence, KS reported the generating this wastestream during purification of elemental phosphorous prior to feeding into the reactor.

#### Waste Management

Phosphorous impurities are managed in tanks and then piped to the on-site acid production furnace as raw material. **Table 3.6** presents the generated volume and the final management step used by the facility for this wastestream.

#### Table 3.6 Waste Management Summary for Phosphorous Impurities

Final Management	# of Wastestreams with Reported Volumes	# of Wastestreams with Unreported Volumes	Total Volume, MT/yr
Recycled	1	0	442.0

#### Waste Characterization

No characterization data is available.

#### Results of Initial Risk Screening Analysis

This waste was not sampled and did not warrant a risk assessment because there is no potential for release to the environment prior to entering the phosphoric acid production process. Wastes from the phosphoric acid process are addressed in the phosphoric acid sector in this rulemaking and in a separate background document.

#### 3.2.6 Tote Bin Wash Water

#### Waste Generation

Tote bin wastewater is generated when tote bins are washed with water and caustic. Phosphorous pentasulfide residue is washed from returned bins at the Tote Bin Wash Station. Two facilities reported the generation of this wastestream.

#### Waste Management

The tote bin wash water is pumped to an on-site hazardous waste tank and sent off-site for neutralization and disposal. **Table 3.7** presents the generated volume and the final management step used by the facilities for this wastestream.

Final Management # of Wastestreams with Reported Volumes		# of Wastestreams with Unreported Volumes	Total Volume, MT/yr
POTW or NPDES discharge	1	1*	188.0

# Table 3.7 Waste Management Summary for Tote Bin Wash Water

\* Rhodia Inc., PA did not report a volume for this waste in 1998.

#### Waste Characterization

This wastestream is classified by FMC-Lawrence Inc. (Lawrence, KS) as hazardous due to elevated levels of sulfides and caries code D003 (reactivity).

#### Results of Initial Risk Screening Analysis

This waste was not sampled and did not warrant a risk assessment for the following reasons:

- 1. The wastewater is managed in enclosed systems. Therefore, no exposure pathway exists.
- 2. The tanks employed prevent releases to groundwater in all but the most catastrophic scenarios.
- 3. Discharges to surface water via NPDES or to POTW are exempt from RCRA regulation. Point source discharges are regulated extensively under the Clean Water Act.
- 4 The primary constituents of concern, phosphoric acid and hydrogen sulfide are readily controlled via neutralization.

# 3.2.7 Scrap Sulfur

#### Waste Generation

The Solutia Inc.-William G. Krummrich Plant (Sauget, IL) reported the generation of scrap sulfur. Scrap sulfur is occasionally generated when making or breaking hose couplings where sulfur comes into reaction.

# Waste Management

The wastes are stored in containers and sent off-site for incineration at Subtitle C facility. **Table 3.8** presents the generated volume and the final management step used by the facility for these wastestream.

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Final Management	# of Wastestreams with Reported Volumes	# of Wastestreams with Unreported Volumes	Total Volume, MT/yr
Off-site Hazardous Waste Incineration	1	0	0.12

#### Table 3.8 Waste Management Summary for Scrap Sulfur

#### Waste Characterization

The facility reported this wastestream as a non-hazardous.

#### Results of Initial Risk Screening Analysis

This waste was not sampled and did not warrant a risk assessment because the waste is currently managed as hazardous from the point of generation through disposal.

#### 3.2.8 Contaminated Absorbents

#### Waste Generation

The Solutia Inc.-William G. Krummrich Plant (Sauget, IL) reported the generation of absorbents contaminated with phosphorous pentasulfide and therminol. This waste is generated during the solidification and milling process.

#### Waste Management

The waste is stored in containers and sent off-site for incineration at Subtitle C facility. **Table 3.9** presents the generated volume and the final management step used by the facility for this wastestream.

Table 3.9	Waste Managemen	t Summary for	Contaminated	Absorbents
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Final Management	# of Wastestreams with Reported Volumes	# of Wastestreams with Unreported Volumes	Total Volume ( MT in 1996)
Off-site Hazardous Waste Incineration	1	0	$1.2^{*}$

\*Reported quantity for 1996; none reported for 1998.

#### Waste Characterization

# Results of Initial Risk Screening Analysis

This waste was not sampled and did not warrant a risk assessment for the following reasons:

- 1. The waste exhibits a hazardous waste characteristic.
- 2. The waste is currently managed as hazardous from the point of generation through disposal because it is characteristically hazardous. This includes meeting applicable LDR standards.

# 3.2.9 Waste Therminol

# Waste Generation

The Solutia Inc.-William G. Krummrich Plant (Sauget, IL) reported the generation of waste therminol(benzylated ethyl benzene). Waste therminol is a spent heat transfer product used for vessels and piped to prevent freezeup of the liquid phosphorous pentasulfide.

# Waste Management

The wastes are stored in containers and sent off-site for incineration at Subtitle C facility. **Table 3.11** presents the generated volume and the final management step used by the facility for these wastestream.

<b>Table 3.10</b>	Waste Management	Summary f	for Waste	Therminol
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Final Management	# of Wastestreams with Reported Volumes	# of Wastestreams with Unreported Volumes	Total Volume, MT/yr
Off-site Hazardous Waste Incineration	1	0	1.4

Waste Characterization

This waste is assigned waste code D018 (benzene).

# Results of Initial Risk Screening Analysis

- 1. The waste exhibits a hazardous waste characteristic.
- 2. The waste is currently managed as hazardous from the point of generation through disposal because it is characteristically hazardous. This includes meeting applicable LDR standards.

# APPENDIX A

Summary of Waste Generation and Management

Wastestream	Facility	Waste Volume (MT/vr)	Hazardous Waste #	Final Waste Management Step
Still	Rhodi <b>a</b>	2.7	D003, D007	Off-site Hazardous Waste
Waste	Solutia	1.9	D003	Incineration
Phosphorous Pentasulfide Scrap	Rhodia	6.55	D001,D003, U189	Off-site Hazardous Waste Incineration
Waste	Solutia	not generated since early 90's	D003, U189	
	FMC	61.2	not available	
Scrubber Water	Solutia	77,377	none	POTW discharge
Caustic Scrubber	Rhodia	1,550	none	NPDES discharge
Water	FMC	627.0	none	
Phosphorous Impurities	FMC	442.0	not available	Recycled
Tote Bin Wash	FMC	188.0	D003	NPDES discharge
Water	Rhodia	not reported	not available	POTW discharge
Scrap Sulfur	Solutia	0.12	none	Off-site Hazardous Waste
Contaminated Absorbents		1.2 (1996)	D003	
Phosphorous Debris		0.185	D001, D008	
Waste Therminol		1.4	D018	