

Interoffice Memorandum

TO (Name and Location) D. G. Bremer	DATE April 12, 1977
FROM (Name and Location) J. L. White	REFERENCE NO. JLW-14-77

SUBJECT: Loading of the Prehydrogenation Catalyst

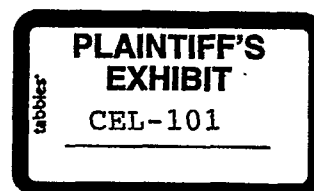
In Frank Girolamo's letter, FJG-307-76 (attached), the Bay City Plant was cautioned about the possibility of getting platinosis from working with the prehydrogenation catalyst. Employees working with Engelhard experienced symptoms of platinosis from being exposed to the prehydrogenation catalyst. Engelhard recommended that persons loading the catalyst wear dust protectors over their mouth and nose and wear protective clothing. The symptoms of platinosis are wheezing, coughing, running of the nose, tightness in the chest, shortness of breath, a bluish discoloration of the skin and mucous membranes, and skin irritation. Personal air samples were taken to determine the dust concentration while the catalyst was being loaded into the catalyst baskets.

The catalyst loading procedure is described in Bill Seeliger's letter, WJS-13-77. There are six baskets; three baskets have six 10" sections of packing. These three baskets were loaded dry to insure proper catalyst distribution throughout the packing. After the catalyst was evenly distributed through the packing, the baskets were then submerged in demineralized water and the remaining catalyst was loaded while the basket was submerged. The other three baskets were loaded while submerged in demineralized water.

The catalyst is shipped in plastic bags placed in drums. When loading the catalyst between the packings, one operator fills a bucket with the catalyst. By means of a rope, another operator hauls the bucket of catalyst to the top of the basket, another operator lowers the bucket into the basket, and the fourth operator evenly distributes the catalyst with his hand. The person filling the bucket is exposed to black puffs of dust when she dips into the catalyst and empties her cup into the bucket. There was a slight breeze to give her some natural ventilation. The two people lifting and lowering the buckets received little dust exposure or skin contact. The person in the basket had no natural ventilation except for the updraft which blew more catalyst into his breathing zone and on his clothing and skin. The total operation took about three hours. There were four people doing the dry loading. The people loading the catalyst wore dust masks for protection, but no one wore any protective clothing. It is estimated that the prehydrogenation catalyst will last over six months before a new charge will be required.

OSHA has set PEL's for inert dust at (1) 5 mg/m³ respirable dust and (2) 15 mg/m³ total dust. There is a PEL for soluble salts of platinum of .002 mg/m³, but Bay City's catalyst is platinum metal on carbon. There is no standard for exposure to platinum metal which is not known to cause any ill effects.

UNITERMS: OSHA
Catalyst
CHOX

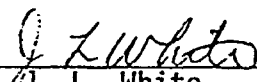


004905

The catalyst dust was collected with a MSA Gravimetric Pump, with a cyclone assembly and 0.5 micron filter paper. The result from the catalyst loaded wet was 0.0018 mg/m³ for total dust. The result from the catalyst loaded dry was 1.16 mg/m³ for total dust, 0.011 mg/m³ for respirable dust, and 0.0001 mg/m³ platinum dust. This sample was taken on the man in the basket who got the greatest exposure.

I watched both the dry and wet loading of the catalyst. The wet loading showed very small quantities of dust. The dry loading met OSHA standards; however, people coming in direct contact with the catalyst were covered with the dust. Their clothing was shades darker from dust, and the man in the basket had to change his dust mask four times. The man in the basket has no natural ventilation except for the updraft which blows more catalyst into his face. I talked with him several days later and again a week later. He developed no skin rash or any other symptoms of platinosis from working with the catalyst. No other employee has reported any discomforts suffered because of the catalyst dust.

According to the PEL's established in the Federal Register for inert dust, there was not enough catalyst dust present to be harmful. I feel, however, that employees working with the platinum catalyst should continue to use dust masks. I would also recommend that employees working in the dustier jobs be supplied coveralls and be required to shower before leaving the plant. This precaution will protect them and others from being exposed to the dust away from the job.


J. L. White

JLW/jg
Attachment

cc: D. H. Miller
K. A. Dunn
W. F. Soward
J. N. Gann
C. J. Duey
W. J. Seeliger
J. M. Ramey, NYO
C. D. Barrett, CCCTC
W. T. McNair, CCCTC
Central Files, CCCTC (2)

Tech. Obj. X.

File: 71-1

004906

Tickets 3/7/77 what about this & HNE int? I assume
Interoffice Memorandum

GEN 55 (REV. 6/77)

file 71-3

TO (Name and Location)	<i>Safety Comm mty agenda</i>	DATE
Bay City		Dec. 20, 1976
FROM (Name and Location)	<i>and copies to each mty agenda</i>	REFERENCE NO.
F. J. Girolamo - HPO		FJG/307/76

50 in case you want for your files - stamp discard.
Subject: Platinum Catalyst Safety Precautions *OK* *Ret 11/16*

Engelhard has advised me that some of their employees involved in loading and sampling our platinum on carbon COP acids prehydrogenation catalyst have experienced ~~platinosis problems~~. They have had to remove some persons from this work area for a period of time to allow them to get over the effects of this illness. It is my understanding that this is not uncommon when working with platinum group metal catalysts, especially on carbon support. There is a very small amount of dust produced at the point where the catalyst loads into the drums. This is where the material is sampled. ~~The symptoms of platinosis are breathing difficulty and skin irritation.~~ These are reportedly reversed when the person is removed to fresh air.

Engelhard is making us aware of this so that we can take precautions to protect our personnel who will be close to the catalyst during loading into the reactor. They recommend that these persons wear dust protectors over their mouth and nose and wear protective clothing. I think you should become familiar with this condition before we receive the catalyst and be prepared to handle it in the appropriate manner.

Engelhard has offered to have one of their people talk to us about this. Please contact me if more detailed information is desired and I will get you in touch with Engelhard.

F. J. Girolamo
Frank J. Girolamo

FJG/es

cc: K. A. Dunn - Bay City
W. F. Soward - Bay City
J. S. Alder - Bay City
L. E. Hackfeld - Bay City
J. C. Bird - HPO
S. H. Warren - HPO
J. M. Ramey - NYO
B. L. Pritchard - NYO

004907

Interoffice Memorandum

TO (Name and Location)	J. M. Ramey, NYO	DATE	April 12, 1977
FROM (Name and Location)	J. L. White, BCP	REFERENCE NO.	JLW-15-77

SUBJECT: Monthly Report of Bay City Employee Monitoring

I have attached a summary of the monitoring done at the Bay City Plant for the month of March. The CHOX prehydrogenation catalyst was loaded the first of March. The catalyst is loaded into six baskets. Three baskets were loaded while submerged in demineralized water and the remaining baskets were loaded without water. Both loading procedures were below the action level for inert or nuisance dust and below the action level for soluble platinum. The Bay City Plant catalyst should be platinum metal on carbon instead of the soluble salt. A report is being prepared.

A method for collecting and analyzing for nitrogen dioxide was given to us by David Barrett. The area samples collected were below the PEL for NO₂. Additional samples will be taken.

The Nylon Salt Unit had a shutdown March 20th and methanol samples were taken. Both the inside and outside operators were monitored. Also, the Century Organic Analyzer was used for spot sampling. The inside operator had an exposure of 25 mg/m³ and the outside operator had exposure of 379 mg/m³. The Century Organic Analyzer registered spot samples exceeding 10,000 ppm.

There have been two samples of benzene taken in the lab that exceeded the recommended PEL. The problem has been corrected by enclosing the pyridine, methanol and benzene solvent. A Drager Tube sample was taken as the employee used the new system. No exposure was registered.


J. L. White

JLW/jg
Attachments (3)

cc: D. H. Miller
J. N. Gann
C. J. Duey
D. G. Bremer
J. M. Jackson, Bishop
M. P. Neff, Bishop
J. W. Coe, CLP
R. E. Green, CLP
J. E. Sanborn, Bayport
M. R. Stenzel, Pampa
H. A. Thomas, Pampa
C. D. Barrett, CCCTC
B. J. Bland, CCCTC
J. P. Hawthorne, CCCTC
E. S. Ramey, CCCTC
W. T. McNair, CCCTC
Central Files, CCCTC (2)

004908

INDUSTRIAL HEALTH MONTHLY MONITORING SUMMARY

Sequence No. (Where Applicable)	Date	Unit	Employee Name (Social Security Number)	Job Description	Contaminant Monitored	Monitoring Method	8-Hour TWA Exposure Mg/M3	Acceptable TWA(1) Mg/M3	Ceiling Level Mg/M3 (Duration in Minutes)(1)	Highest Concentration Mg/M3 Detected	Comments
	3-2-77	Nylon Salt	Larry Woffard 452-98-0473	Outside Operator	Methanol	Alumina Tubes Modified NIOSH Method S59	319	260	1040	314	
	3-7-77	Main- tenance	Ruben Garcia 466-42-7931	To load the pre- hydro- genation catalyst	Total Dust	Gravimetric Dust	.0018	15			
	3-8-77	Adipic Acid	Area	Near the table filters	Nitrogen Dioxide	NIOSH Method P&CAM 108			9.0	6.4	
	3-9-77	Main- tenance	Tommy Benavides 461-52-6369	To load the pre- hydro- genation catalyst	1. Total Dust 2. Res- pirable Dust 3. Platinum	Gravimetric Dust	1.16 .011 .0001	15 5 -			Soluble pt. has a PEL of .002 mg/m ³
004909	3-10-77	Main- tenance	Wayne Miles 425-78-0922	To bolt the centri- fuges in Nylon Salt	Methanol	Alumina Tubes Modified NIOSH Method S59	17.4	260			Sample was taken for 3 hours

INDUSTRIAL HEALTH MONTHLY MONITORING SUMMARY

Sequence No. (Where Applicable)	Date	Unit	Employee Name (Social Security Number)	Job Description	Contaminant Monitored	Monitoring Method	8-Hour TWA Exposure Mg/M ³	Acceptable TWA (1) Mg/M ³	Ceiling Level Mg/M ³ (Duration in Minutes)	Highest Concentration Detected Mg/M ³	Comments
	3-10-77	Nylon Salt	Kenneth Tyler 450-06-7995	Outside Operator	Methanol	Alumina Tubes Modified NIOSH Method S59	104	260	1040	757	
	3-15-77	Vinyl Acetate	Robert O'Neal 466-72-6023	Outside Operator	Vinyl Acetate	Charcoal Tubes GC	14	Not Established			The ACGIH has recommended a PEL of 30 mg/m ³
	3-16-77	Adipic Acid	Area	Downwind of the table filters	Nitrogen Dioxide	NIOSH Method P&CAM 108			9.0	4.2	
	3-17-77	Nylon Salt	Ted Perkins 451-92-2751	Outside Operator	Methanol	Alumina Tubes Modified NIOSH Method S59	161	260	1040	3012	
	3-20-77	Nylon Salt	Larry Hoffard 452-98-0473	Outside Operator	Methanol	Alumina Tubes Modified NIOSH Method S59	379	260			

004910

INDUSTRIAL HEALTH MONTHLY MONITORING SUMMARY

Sequence No. (Where Applicable)	Date	Unit	Employee Name (Social Security Number)	Job Description	Contaminant Monitored	Monitoring Method	8-Hour TWA Exposure Mg/M ³	Acceptable TWA(1) Mg/M ³	Ceiling Level Mg/M ³ (Duration in Minutes)	Highest Concentration Detected Mg/M ³	Comments
	3-20-77	Nylon Salt	Mary Crawford 450-70-1203	Inside Operator	Methanol	Alumina Tubes Modified NIOSH Method S59	25	260			
	3-22-77	Lab- oratory	Area	Near the K. Fisher methanol, pyridine, benzene solvent	Benzene	Drager Tubes			3.26	4 5 9 2	
	3-24-77	Lab- oratory	Carl Rhymes 452-60-7261	Finished Product Analysis	Benzene	Charcoal Tubes GC	7.2	3.26			Found 24.5 mg/m ³ for 140 min.; this was averaged for 8-hr. TWA
	3-31-77	Lab- oratory	Area	K. Fisher methanol, pyridine, benzene solvent	Benzene	Drager Tubes			3.26	None Detected	

004911

Interoffice Memorandum

TO (Name and Location) D. W. Steele	DATE July 18, 1977
FROM (Name and Location) C. J. Duey	REFERENCE NO. CJD-218-77

SUBJECT: Safe Handling of Oxalic Acid

I understand that the Lube Acids process will use oxalic acid to precipitate manganese and copper from the SO reactor product. The oxalic acid will be purchased in bags. It will be added to a mix vessel for solutioning before use. It is important that we plan now for the safe handling of oxalic acid to prevent creating an employee health problem.

Oxalic acid can cause severe burns of the skin, eye, or mucous membranes either as a dust or in solution.¹ Exposure of teeth to oxalic acid dust could cause dental erosion. OSHA has set a PEL for oxalic acid dust of 1 mg/m³ of air for an 8 hour TWA exposure. ACGIH has recommended a 15 minute STEL (short term exposure limit) of 2 mg/m³.

There will be potential for brief employee exposure to oxalic acid dust when the employee dumps the bags into the mix vessel. The amount of exposure would depend a great deal on how much fine powder is present in commercial oxalic acid. (Laboratory reagent oxalic acid is not very dusty). The following suggestions are made for the safe handling of oxalic acid:

1. The employee dumping the oxalic acid should wear a full face mask to protect the eyes, teeth, and lungs from dust exposure.
2. Gloves and possibly other protective clothing should be worn to prevent skin contact. A safety shower and/or eye wash facility should be located nearby.
3. Local exhaust ventilation may be necessary if the commercial material is very dusty.

C. J. Duey
C. J. Duey

CJD/jg

cc: D. H. Miller
J. N. Gann
D. G. Bremer
C. D. Barrett, CCCTC
W. T. McNair, CCCTC
Central Files, CCCTC (2)

File: 71-1
Tech. Obj. X.

¹Patty, Frank A., "Industrial Hygiene and Toxicology," Volume II, Interscience Publishers, New York, 1963.

UNITERMS: Lube Acid, Oxalic Acid, OSHA, Safety

004912

Page 1 INDUSTRIAL HEALTH MONTHLY MONITORING SUMMARY

Sequence No. (Where Applicable)	Date	Unit	Employee (Name, Social Security Number)	Job Description	Contaminant Monitored	Monitoring Method	8-Hour TMA Exposure (Mg/M ³)	Acceptable TMA (Mg/M ³)	Celling Level (Mg/M ³) (Duration in Minutes)	Highest Concentration Detected (Mg/M ³)	Comments
	5-3-77	Area 1	--	Analyzer Room	Acetic Acid	Drager Tubes		25		13	
	5-5-77	Nylon Salt	David Orsak 457-21-3145	Outside Operator	Methanol	SKC Jumbo Alumina Tubes GC Analysis	11	260			
	5-12-77	Nylon Salt	Roger Schneider	Outside Operator	Methanol	"	126	260			Operator wore a respirator
	5-16-77	Area 1	Roxy Robinson 465-66-1262	Outside Operator	Vinyl Acetate	SKC Charcoal Tubes GC Analysis	None Detected				The ACGIH has established a PEL of 30 mg/m ³
	5-16-77	Laboratory	Pete Rodriguez 463-68-5661	Analyst	Benzene	"	None Detected	3.2			Less than 1 mg/m ³

004914

Page 2 INDUSTRIAL HEALTH MONTHLY MONITORING SUMMARY

Sequence No. (Where Applicable)	Date	Unit	Employee Name (Social Security Number)	Job Description	Contaminant Monitored	Monitoring Method	8-Hour TMA Exposure Hq/H3	Acceptable TMA (1) Hq/H3	Ceiling Level (Hq/H3) (Duration in Minutes)	Highest Concentration Detected Hq/H3	Comments
	5-16-77	Laboratory	Jill Luppas 478-72-0753	Chemist	Benzene	SKC Charcoal Tubes GC Analysis	Less than 1 mg/m ³	3.2			
	5-16-77	Laboratory	Carl Rhymes 452-60-7261	Analyst	Benzene	"	Less than 1.5 mg/m ³	3.2			
	5-20-77	Nylon Salt	David Orsak 457-21-3945	Outside Operator	Methanol	SKC Jumbo Alumina Tubes GC Analysis	130	260			Operator wore a respirator
	5-23-77	Nylon Salt	Jerry Waters 456-88-6945	Outside Operator	Benzene	SKC Charcoal Tubes GC Analysis	Less than .1 mg/m ³	3.2			
	5-23-77	Area 1	--	Area Sample	Acetic Acid	Drager Tubes	10 ppm		15		Sample was taken along the Area 1 sample taps

004915

Interoffice Memorandum

TO (Name and Location) J. M. Ramey, NYO	DATE July 20, 1977
FROM (Name and Location) J. L. White, BCP	REFERENCE NO. JLW-20-77

SUBJECT: Monthly Report of Bay City Employee Monitoring

Attached is a summary of the monitoring of various airborne substances throughout the Bay City Plant. This table contains information beginning May 1, 1977 and continuing to June 29, 1977.

Note that a mechanic was highly over exposed to methanol vapor on June 29th. A permit system for maintenance in the Nylon Salt Unit will be implemented to insure that this does not happen again.


J. L. White

JLW/jg
Attachments (6)

cc: D. H. Miller
J. N. Gann
C. J. Duey
D. G. Bremer
J. M. Jackson, Bishop
M. P. Neff, Bishop
J. W. Coe, CLP
R. E. Green, CLP
J. E. Sanborn, Bayport
M. R. Stenzel, Pampa
H. A. Thomas, Pampa
C. D. Barrett, CCCTC
B. J. Bland, CCCTC
J. P. Hawthorne, CCCTC
E. S. Ramey, CCCTC
W. T. McNair, CCCTC
Central Files, CCCTC (2)

File: 71-1

004913

INDUSTRIAL HEALTH MONTHLY MONITORING SUMMARY

Page 3

Sequence No. (Where Applicable)	Date	Unit	Employee Name (Social Security Number)	Job Description	Contaminant Monitored	Monitoring Method	8-Hour TMA Exposure Hq/H3	Acceptable TMA (1) Hq/H3	Ceiling Level Hq/H3 (Duration) (10 Minutes)	Highest Concentration Hq/H3 Detected	Comments
	5-23-77	Area 1	--	Area Sample	Carbon Monoxide	Drager Tubes		50		None Detected	Sample taken in the analyzer room
	5-23-77	Laboratory	Danny Fairchild 463-70-4695	Analyst	Vinyl Acetate	SKC Charcoal Tubes GC Analysis	Less than 6 mg/m ³	1			ACGIH has recommended a PEL of 30 mg/m ³
	5-26-77	CHOX	Jerry Waters 456-88-6945	Outside Operator	Nitrogen Dioxide	Widgit Impinger	.56	9			
	5-27-77	Nylon Salt	Mary Crawford 450-70-1203	Outside Operator	Methanol	SKC Jumbo Alumina Tubes GC Analysis	11	260			
	6-3-77	Nylon Salt	David Orsak 457-21-6945	Outside Operator	Methanol	"	788	260			Operator wore a respirator

004916

Page 4 INDUSTRIAL HEALTH MONTHLY MONITORING SUMMARY

Sequence No. (Where Applicable)	Date	Unit	Employee Name (Social Security Number)	Job Description	Contaminant Monitored	Monitoring Method	8-Hour TMA Exposure Mg/M3	Acceptable TMA Mg/M3	Celling Level Mg/M3 (Duration in Minutes)	Highest Concentration Detected Mg/M3	Comments
	6-3-77	Nylon Salt	Ben Kalner 454-58-5234	Table Filters Operator	Nitrogen Dioxide	Midget Impinger	7.5	9			
	6-8-77	CHOX	Joe Johnson 450-80-8530	Outside Operator	Benzene	SKC Charcoal Tubes GC Analysis	Less than .1 mg/m3	3			
	6-21-77	Adipic Acid	Hugo Breithaupt 460-74-3028	Table Filters Operator	Nitrogen Dioxide	Midget Impinger	6.5	9			
	6-22-77	Nylon Salt	--	Area Sample	Methanol	SKC Jumbo Alumina Tubes GC Analysis	279	260			Sample taken near the centrifuge floor fan
	6-22-77	Nylon Salt	--	Area Sample	Methanol	"	2369	260			Sample taken in the aisle of the centrifuge floor

004917

INDUSTRIAL HEALTH MONTHLY MONITORING SUMMARY

Page 5

Sequence No. (Where Applicable)	Date	Unit	Employee Name (Social Security Number)	Job Description	Contaminant Monitored	Monitoring Method	8-Hour TMA Exposure Mg/M3	Acceptable TMA Mg/M3	Coiling Level Mg/M3 (Duration in Minutes)	Highest Concentration Detected Mg/M3	Comments
	6-23-77	Nylon Salt	Roger Schneider 454-02-9196	Outside Operator	Methanol	SAC Jumbo Alumina Tubes GC Analysis	1334	260			Respirator was in use by operator
	6-24-77	Metric	Lois Caddie 233-66-5126	Outside Operator	Nitrogen Dioxide	Midget Impinger	Less than 3 mg/m3	9			
	6-24-77	Adipic Acid	O. C. Howard 458-62-3886	Outside Operator	Nitrogen Dioxide	Midget Impinger	1.3	9			
	6-27-77	Laboratory	John Ganske 466-78-0429	Instrument Lab Analyst	Benzene	SAC Charcoal Tubes GC Analysis	.1	3.2			
	6-28-77	Utilities	Courtney Grigsby 458-96-8980	Outside Operator	FeSO4	.5 Micron Filter Paper	.013	Not Established			

004918

Page 6 INDUSTRIAL HEALTH MONTHLY MONITORING SUMMARY

Sequence No. (Where Applicable)	Date	Unit	Employee Name (Social Security Number)	Job Description	Contaminant Monitored	Monitoring Method	8-Hour TWA Exposure Hg/H ₃	Acceptable TWA (Hg/H ₃)	Ceiling Level (Duration 10 Minutes) Hg/H ₃	Highest Concentration Detected Hg/H ₃	Comments
	6-28-77	Adipic Acid	Hugo Braithaupt 460-74-3028	Table Filters Operator	Nitrogen Dioxide	Midget Impinger	3.2	9 +			
	6-28-77	Laboratory	Thomas Moore 455-96-5283	Analyst	Benzene	SKC Charcoal Tubes GC Analysis	Less than .1	3.2			
	6-29-77	Analyzer Laboratory	---	Area Sample (Porch)	Sand Blasting Dust	.5 Micron Filter Paper				.02	There is a .05 mg/m ³ ceiling for silica
	6-29-77	Maintenance	Ricky Ellison 454-15-0071	To repair machines M-1253 & M-1252 in NS	Methanol	SKC Jumbo Alumina Tubes GC Analysis		260	1040 (15)	8300 for 180 min.	8 hour average exposure was 3100

004919

BASF Wyandotte Corporation



Wyandotte, Michigan 48192
313 282-3300

August 29, 1977

Mr. David Barrett
Celanese Chemical Company
Technical Center
P.O. Box 9077
Corpus Christi, Texas 78408

Dear Mr. Barrett:

Enclosed is a summary of the toxicity information on tri-phenylphosphine that we discussed in our telephone conversation last week. These studies were conducted in the BASF AG toxicology laboratories in Ludwigshafen, West Germany; and we translated the summary into English. The study is confidential (BASF AG) and should be treated as such. Please contact me or Sandi Reiss if you have any questions concerning this information.

*Will have
this been
cleared from
10/11*

Yours very truly,

A handwritten signature in cursive script that reads "Peter L. Lubs".

Peter L. Lubs
Industrial Toxicologist

mk
enc

004920

REPORT ON BIOLOGICAL TEST OF TRIPHENYLPHOSPHINE

Irritant action on skin and mucosa: dorsal skin, ear and eye of rabbits.

Acute and subacute toxicity: mice (s.c. and p.o.), rats (i.m. and p.o.), rabbits (i.m. and p.o.), cats (i.m. and p.o.), dogs (p.o.).

Inhalation of volatiles in mice, rats, rabbits, and cats.

Evaluation: As mentioned in a preliminary report, the product proved to be of little activity in the acute experiment with rodents.

Its irritant action is very slight: even a 50% suspension on the extremely sensitive dorsal skin of white rabbits is completely non-irritating. A 10% solution produces only minor inflammation symptoms in the rabbit eye.

After i.m. injection, some animals (rats) tolerate 2 g/kg, while even 3 g/kg is tolerated without intoxication symptoms after s.c. injection (mouse). Surprisingly, triphenylphosphine has a more potent action after oral application (dissolved in oil) than after injection, which may be explainable by a poorer absorption of triphenylphosphine from the oil depot based on the postmortem findings in rabbits.

Thus, while a single dose of triphenylphosphine seems to be relatively nontoxic, repeated applications produced pronounced damaging effects in the nervous system; in rabbits, even fractions of one gram applied repeatedly led to increasingly complete atonia of the entire body and characteristic paralysis signs of the hind legs up to death.

★
0.3 g / 100 g
The nerve damaging action of triphenylphosphine is still more evident in the experiments with cats and dogs: a single oral or i.m. dose of 300 mg/kg leads to grave and often lethal convulsions. Repeated oral doses first produce a certain degree of habituation, particularly with regard to the strychnine-like stimulant action of triphenylphosphine, so that somewhat higher doses are tolerated without marked symptoms. However, later, these doses lead to pronounced paralysis which are very similar to that produced by tri-o-cresyl phosphate, and like the latter, appear to be hardly reversible or perhaps irreversible (observation period of 3 months).

004921

- 2 -

Thus, like tr. o-cresyl phosphate, triphenylphosphine must be considered a potent nerve poison and it is entirely possible that even small quantities would lead to nerve damage also in man, particularly after repeated application. Since the product can probably also be readily absorbed from the skin because of its oil solubility, ~~prolonged contact with the skin, particularly in dissolved form, must be avoided as far as possible during handling of triphenylphosphine, even though it practically has no local irritant action on the skin. After any contact with the product, the most careful cleaning of skin and clothes must be urged.~~ Naturally, ~~contact of triphenylphosphine with mucous membranes, for example, through the hands, must be prevented in any case (washing of hands before eating).~~

The ~~risk of damage due to inhalation of triphenylphosphine vapor~~ is slight according to our preliminary experiments, since the product ~~is of low volatility even at elevated temperature (vapor pressure 5 mm Hg at 210°).~~

Translated from Summaries of German Reports.

Testing performed at BASF AG, Ludwigshafen, West Germany.

004922

Interoffice Memorandum

TO (Name and Location)	DATE
Mr. M. P. Neff - Bishop	9/14/77
FROM (Name and Location)	REFERENCE NO.
C. D. Barrett - CCCTC	CDB-80-77

Subject: BASF Wyandotte Report on Biological Test of Triphenylphosphine

I have attached summaries of the West German studies on triphenylphosphine. As the BASF Wyandotte cover letter indicates, this information is confidential.

Based on the West German studies, TPP appears to be a potent chronic nerve poison. Since the information in the summary is so limited, it is difficult to assess the inhalation hazard (refer to CDB-76-77). However, I think we must conclude that TPP is potentially toxic by all routes of entry.

Our use of TPP should be reviewed and exposure reduced to an absolute minimum.

I would like to review the job and discuss control procedures with you and Jim Jackson.

I'll be sending this information along with the other study to Judy Tins for review and comments. Hopefully, we can find some additional research studies that can clarify the toxicity of TPP.


C. D. Barrett, Industrial Hygienist

/mg
Attachment

cc: Mr. J. M. Jackson - Bishop
Mr. J. M. Ramey - NYO
Ms. J. A. Tins - NYO

004923

BASF Wyandotte Corporation



Wyandotte, Michigan 48192
313 282-3300

August 29, 1977

Mr. David Barrett
Celanese Chemical Company
Technical Center
P.O. Box 9077
Corpus Christi, Texas 78408

Dear Mr. Barrett:

Enclosed is a summary of the toxicity information on tri-phenylphosphine that we discussed in our telephone conversation last week. These studies were conducted in the BASF AG toxicology laboratories in Ludwigshafen, West Germany; and we translated the summary into English. The study is confidential (BASF AG) and should be treated as such. Please contact me or Sandi Reiss if you have any questions concerning this information.

Yours very truly,

A handwritten signature in cursive script that reads "Peter L. Lubs".

Peter L. Lubs
Industrial Toxicologist

mk
enc

004924

REPORT ON BIOLOGICAL TEST OF TRIPHENYLPHOSPHINE

Irritant action on skin and mucosa: dorsal skin, ear and eye of rabbits.

Acute and subacute toxicity: mice (s.c. and p.o.), rats (i.m. and p.o.), rabbits (i.m. and p.o.), cats (i.m. and p.o.), dogs (p.o.).

Inhalation of volatiles in mice, rats, rabbits, and cats.

Evaluation: As mentioned in a preliminary report, the product proved to be of little activity in the acute experiment with rodents.

Its irritant action is very slight: even a 50% suspension on the extremely sensitive dorsal skin of white rabbits is completely non-irritating. A 10% solution produces only minor inflammation symptoms in the rabbit eye.

After i.m. injection, some animals (rats) tolerate 2 g/kg, while even 3 g/kg is tolerated without intoxication symptoms after s.c. injection (mouse). Surprisingly, triphenylphosphine has a more potent action after oral application (dissolved in oil) than after injection, which may be explainable by a poorer absorption of triphenylphosphine from the oil depot based on the postmortem findings in rabbits.

Thus, while a single dose of triphenylphosphine seems to be relatively nontoxic, repeated applications produced pronounced damaging effects in the nervous system; in rabbits, even fractions of one gram applied repeatedly led to increasingly complete atonia of the entire body and characteristic paralysis signs of the hind legs up to death.

7325
The nerve damaging action of triphenylphosphine is still more evident in the experiments with cats and dogs: a single oral or i.m. dose of 300 mg/kg leads to grave and often lethal convulsions. Repeated oral doses first produce a certain degree of habituation, particularly with regard to the strychnine-like stimulant action of triphenylphosphine, so that somewhat higher doses are tolerated without marked symptoms. However, later, these doses lead to pronounced paralysis which are very similar to that produced by tri-o-cresyl phosphate, and like the latter, appear to be hardly reversible of perhaps irreversible (observation period of 3 months)

004925

Thus, like tri-o-cresyl phosphate, triphenylphosphine must be considered a potent nerve poison and it is entirely possible that even small quantities would lead to nerve damage also in man, particularly after repeated application. Since the product can probably also be readily absorbed from the skin because of its oil solubility, ~~prolonged contact with the skin, particularly in dissolved form, must be avoided as far as possible during handling of triphenylphosphine, even though it practically has no local irritant action on the skin. After any contact with the product, the most careful cleaning of skin and clothes must be urged. Naturally, contact of triphenylphosphine with mucous membranes, for example, through the hands, must be prevented in any case (washing of hands before eating).~~

The risk of damage due to inhalation of triphenylphosphine vapors is slight according to our preliminary experiments, ~~since the product is of low volatility even at elevated temperature (vapor pressure 5 mm Hg at 210°).~~

Translated from Summaries of German Reports.

Testing performed at BASF AG, Ludwigshafen, West Germany.

004926

Interoffice Memorandum

TO (Name and Location)	DATE
* As Listed	9-21-77
FROM (Name and Location)	REFERENCE NO.
M. P. Neff	MPN-225-77

* Messrs. John Hodges
Bill Meyer
Danny Walker
Buddy Cloud

Subject: Triphenylphosphine

Attached for your review are the Material Safety Data Sheets and the summary of the German Study on TPP.

I have also summarized the use of TPP as I understand it from our meeting. If there are any corrections or additions to the summary please point them out at the meeting on Wednesday.



M. P. Neff

MPN/ks

cc: Messrs. C. W. Lee
C. W. Harrison
P. J. Volpe
M. A. John
R. W. Swanbeck
J. M. Sawyer
N. J. Sternadel
R. N. Updike

004927

SEPTEMBER 20, 1977

TPP is received in flake or powder form from either BASF-Wyandotte or M & T Chemical Company for use in the OXO Unit. The dry product is stored in the Shipping Services area, transported by Maintenance, added to the system by both Operations and Maintenance Department Personnel and sometimes has sample work performed on it by Laboratory Personnel. Maintenance Department Personnel are exposed to the product during routine repairs to equipment and when the catalyst is drummed for shipment to an outside vendor for recovery operations.

On an annual basis the reactor system is dumped and then recharged with approximately 14,500 pounds of fresh TPP. This changing operation is usually handled by the Maintenance Department.

The next meeting will be held on Wednesday, September 28, at which time we will review draft procedures for the handling of TPP by each of the areas that have exposure opportunities.

Plans are to:

1. Have the Company Hygienist research for additional literature on toxicological testing of TPP.
2. Have Corporate Medical ascertain if there are medical tests available that can determine any medical problems associated with exposure to TPP and to recommend the proper medical surveillance program for the future.
3. Notify the Chemical Company Product Safety Committee and the Houston S & D group of the problems associated with TPP.
4. Determine what will be necessary to legally dispose of containers, coveralls, etc. that have been exposed to TPP. Mr. Jack Sawyer will handle this area.
5. Inform employees that have an opportunity for exposure to TPP of the possible hazards of the product and the steps necessary to protect themselves from contamination. This will not be started until written S.O.P.'s have been established and approved.

004928

Interoffice Memorandum

(Name and Location)

Mr. H. W. Head, Jr.

DM: (Name and Location)

J. M. Sawyer

DATE

September 23, 197

REFERENCE NO.

JMS-1000-

Triphenyl Phosphine

We use Triphenyl Phosphine (TPP) in our OXO Unit reactor here, and Bay City will use it when the recently approved OXO Unit is constructed there. We charge about 14,500 pounds of TPP to the reactor, and ~~add about 220 pounds per day to make up for losses in the liquid heavy ends stream burned in our boilers.~~

We have received information from Germany this week (see attachment) which tends to show that TPP is an accumulative nerve poison. If true, and we are using this assumption, our Industrial Hygiene-Safety Department is in the process of re-defining guidelines for handling TPP. One of the proposed guidelines is to provide workers with coveralls, gloves, and other protective equipment. We need to dispose of these used clothes.

The OXO reactor is emptied each year, and the contents are drummed, and shipped to Englehard in New Jersey for rhodium catalyst recovery. They recover the catalyst via a combustion process.

I'm sure you have anticipated my next questions: How do we dispose of the coveralls? How do we dispose of the 1000 50# plastics-lined bags we use? If we use drums (plastic lined), can we sell the drums? What responsibilities do we have in the Englehard catalyst recovery operation?

I would appreciate your comments.



J. M. Sawyer

kf

Attachment

cc: Messrs. Joe Schaefer
R. H. Maurer
M. P. Neff (w/o attach)

004929

Interoffice Memorandum

(Name and Location)	DATE
* As Listed	9-21-77
DM (Name and Location)	REFERENCE NO.
M. P. Neff	MPN-225-77

* Messrs. John Hodges
Bill Meyer
Danny Walker
Buddy Cloud

Subject: Triphenylphosphine

Attached for your review are the Material Safety Data Sheets and the summary of the German Study on TPP.

I have also summarized the use of TPP as I understand it from our meeting. If there are any corrections or additions to the summary please point them out at the meeting on Wednesday.



M. P. Neff

MPN/ks

cc: Messrs. C. W. Lee
C. W. Harrison
P. J. Volpe
M. A. John
R. W. Swanbeck
J. M. Sawyer
N. J. Sternadel
R. N. Updike

004930

SEPTEMBER 20, 1977

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On an annual basis the reactor system is dumped and then recharged with approximately 14,500 pounds of fresh TPP. This changing operation is usually handled by the Maintenance Department.

The next meeting will be held on Wednesday, September 28, at which time we will review draft procedures for the handling of TPP by each of the areas that have exposure opportunities.

Plans are to:

1. Have the Company Hygienist research for additional literature on toxicological testing of TPP.
2. Have Corporate Medical ascertain if there are medical tests available that can determine any medical problems associated with exposure to TPP and to recommend the proper medical surveillance program for the future.
3. Notify the Chemical Company Product Safety Committee and the Houston S & D group of the problems associated with TPP.
4. Determine what will be necessary to legally dispose of containers, coveralls, etc. that have been exposed to TPP. Mr. Jack Sawyer will handle this area.
5. Inform employees that have an opportunity for exposure to TPP of the possible hazards of the product and the steps necessary to protect themselves from contamination. This will not be started until written S.O.P.'s have been established and approved.

004931

Interoffice Memorandum

(Name and Location)	DATE
Mr. M. P. Neff - Bishop	9/14/77
DM (Name and Location)	REFERENCE NO.
C. D. Barrett - CCCTC	CDB-80-77

Subject: BASF Wyandotte Report on Biological Test of Triphenylphosphine

I have attached summaries of the West German studies on triphenylphosphine. As the BASF Wyandotte cover letter indicates, this information is confidential.

Based on the West German studies, ~~TPP appears to be a potent chronic nerve poison.~~ Since the information in the summary is so limited, it is difficult to assess the inhalation hazard (refer to CDB-76-77). ~~However, I think we must conclude that TPP is potentially toxic by all routes of entry.~~

Our use of TPP should be reviewed and exposure reduced to an absolute minimum.

I would like to review the job and discuss control procedures with you and Jim Jackson.

I'll be sending this information along with the other study to Judy Tins for review and comments. Hopefully, we can find some additional research studies that can clarify the toxicity of TPP.

C. D. Barrett

C. D. Barrett, Industrial Hygienist

/mg
Attachment

cc: Mr. J. M. Jackson - Bishop
Mr. J. M. Ramey - NYO
Ms. J. A. Tins - NYO

004932

BASF Wyandotte Corporation



Wyandotte, Michigan 48192
313 262-3300

August 29, 1977

Mr. David Barrett
Celanese Chemical Company
Technical Center
P.O. Box 9077
Corpus Christi, Texas 78408

Dear Mr. Barrett:

Enclosed is a summary of the toxicity information on tri-phenylphosphine that we discussed in our telephone conversation last week. These studies were conducted in the BASF AG toxicology laboratories in Ludwigshafen, West Germany; and we translated the summary into English. The study is confidential (BASF AG) and should be treated as such. Please contact me or Sandi Reiss if you have any questions concerning this information.

Yours very truly,

A handwritten signature in cursive script, reading "Peter L. Lubs".

Peter L. Lubs
Industrial Toxicologist

mk
enc

004933

REPORT ON BIOLOGICAL TEST OF TRIPHENYLPHOSPHINE

Irritant action on skin and mucosa: dorsal skin, ear and eye of rabbits.

Acute and subacute toxicity: mice (s.c. and p.o.), rats (i.m. and p.o.), rabbits (i.m. and p.o.), cats (i.m. and p.o.), dogs (p.o.).

Inhalation of volatiles in mice, rats, rabbits, and cats.

Evaluation: As mentioned in a preliminary report, the product proved to be of little activity in the acute experiment with rodents.

Its irritant action is very slight: even a 50% suspension on the extremely sensitive dorsal skin of white rabbits is completely non-irritating. A 10% solution produces only minor inflammation symptoms in the rabbit eye.

After i.m. injection, some animals (rats) tolerate 2 g/kg, while even 3 g/kg is tolerated without intoxication symptoms after s.c. injection (mouse). Surprisingly, triphenylphosphine has a more potent action after oral application (dissolved in oil) than after injection, which may be explainable by a poorer absorption of triphenylphosphine from the oil depot based on the postmortem findings in rabbits.

~~Thus, while a single dose of triphenylphosphine seems to be relatively nontoxic, repeated applications produced pronounced damaging effects in the nervous system, in rabbits, even fractions of one gram applied repeatedly led to increasingly complete atonia of the entire body and characteristic paralysis signs of the hind legs up to death.~~

The nerve damaging action of triphenylphosphine is still more evident in the experiments with cats and dogs: a single oral or i.m. dose of 300 mg/kg leads to grave and often lethal convulsions. Repeated oral doses first produce a certain degree of habituation, particularly with regard to the strychnine-like stimulant action of triphenylphosphine, so that somewhat higher doses are tolerated without marked symptoms. However, later, these doses lead to pronounced paralysis which are very similar to that produced by tri-o-cresyl phosphate, and like the latter, appear to be hardly reversible or perhaps irreversible (observation period of 3 months)

004934

~~Thus, like tri-o-cresyl phosphate, triphenylphosphine must be considered a potent nerve poison and it is entirely possible that even small quantities would lead to nerve damage also in man, particularly after repeated application. Since the product can probably also be readily absorbed from the skin because of its oil solubility, prolonged contact with the skin, particularly in dissolved form, must be avoided as far as possible during handling of triphenylphosphine, even though it practically has no local irritant action on the skin.~~ After any contact with the product, the most careful cleaning of skin and clothes must be urged. Naturally, contact of triphenylphosphine with mucous membranes, for example, through the hands, must be prevented in any case (washing of hands before eating).

The risk of damage due to inhalation of triphenylphosphine vapors is slight according to our preliminary experiments, since the product is of low volatility even at elevated temperature (vapor pressure 5 mm Hg at 210°).

Translated from Summaries of German Reports.

Testing performed at BASF AG, Ludwigshafen, West Germany.

004935

Safety Data Sheet

DATE 1/1/80
SAFETY
BILL MEYER
Ann Arbor, Mich 48102
313 282-3300

SECTION I

TRADE NAME	Triphenyl Phosphine	CHEMICAL NAME	Triphenyl Phosphine
SYNONYMS	Triphenyl	CHEMICAL FAMILY	Phosphines
FORMULA	(C ₆ H ₅) ₃ P	MOLECULAR WEIGHT	

SECTION II — HAZARDOUS INGREDIENTS

NAME	%	TLV UNITS	TOXICOLOGICAL DATA
Triphenylphosphine	100		Rat Oral LD ₅₀ 0.8-1.6 g/Kg

SECTION III — PHYSICAL DATA

Boiling Point - 760mm Hg > (360 °C)	711°		
Vapor Pressure, mm Hg @ 20° C. (210 °C)	5		
Specific Gravity (H ₂ O = 1) 25 °C	1.132		
Solubility in Water	Insol. sol. in alc. benzene, acetone CCl ₄		
Appearance and Odor	White crystalline solid		

SECTION IV — FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (TEST METHOD)	AUTOIGNITION TEMPERATURE		
FLAMMABILITY LIMITS IN AIR - % BY VOLUME	LOWER	UPPER	
EXTINGUISHING MEDIA	☒ WATER FOG ☒ FOAM (Type) ☒ CO ₂ ☐ DRY CHEMICAL ☐ OTHER		
SPECIAL FIRE-FIGHTING PROCEDURES	Explosion hazard slight, if vapor exposed to flame can react vigorously with oxidizing agents.		
UNUSUAL FIRE AND EXPLOSION HAZARDS			

EMERGENCY TELEPHONE NUMBER

004936

(201) 263-0200

This number is available days, nights, weekends, and holidays.

SECTION I — HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE Not established

EFFECTS OF OVEREXPOSURE Possible slight irritation to eyes, skin and mucous membranes. Repeated slight ingestion or absorption through mucous membrane or skin lead to nervous system damage. Possible paralysis.

FIRST AID PROCEDURES

EYES

FLUSH
WITH
FLOWING
WATER
AT
LEAST

MINUTES

Wash affected areas thoroughly with detergent and water. Consult a physician. Strict personal hygiene after each exposure greatly reduce possibility of harmful effects.

NEVER GIVE
FLUIDS OR
INDUCE VOMITING
IF PATIENT
IS UNCONSCIOUS
OR HAVING
CONVULSIONS

SECTION VI — REACTIVITY DATA

STABILITY	UNSTABLE	CONDITIONS TO AVOID
	STABLE	

INCOMPATIBILITY Oxidizing materials

HAZARDOUS DECOMPOSITION PRODUCTS Phosphine: PO_2 at high temperatures

HAZARDOUS POLYMERIZATION	MAY OCCUR	CONDITIONS TO AVOID
	DOES NOT OCCUR	

SECTION VII — SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE OF SPILLS

WASTE DISPOSAL METHOD

CONSULT LOCAL AND STATE LAWS

SECTION VIII — SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION

VENTILATION	LOCAL EXHAUST Preferred	SPECIAL
	MECHANICAL (General) Acceptable	OTHER

004937

PROTECTIVE CLOTHING Rubber gloves. Coveralls EYE PROTECTION

OTHER remove contaminated clothing and launder after exposure.

SECTION IX — SPECIAL PRECAUTIONS

PRECAUTIONARY LABELING

Triphenyl Phosphine

May cause irritation of skin eyes, nose and throat. Repeated absorption harmful.

Shipping regulation
ICC, CG, IATA.
Poison Label ←

HANDLING AND STORAGE CONDITIONS

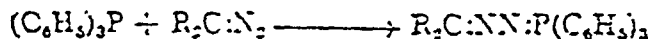
Avoid breathing dust.
Wash thoroughly before eating or smoking
Avoid contact with skin, eyes, and clothing.

004938

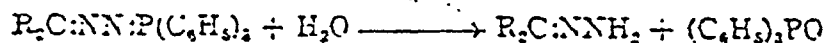
141 2 1

Addition Reactions

Addition to aliphatic diazo compounds to form phosphazines



Phosphazines are readily hydrolyzed into hydrazones:

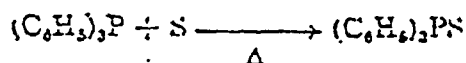


H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 2, 612-8 (1919).

M&T Triphenylphosphine adds one molecule of chlorine (or other halogen) to form triphenylphosphine dichloride (or other dihalide)



M&T Triphenylphosphine can be heated with sulfur to form triphenylphosphine sulfide



TOXICOLOGY:

Although M&T Triphenylphosphine is only slightly toxic by ingestion and slightly irritating to the skin, care should be taken to avoid accidental swallowing and contact with the skin and eyes. Because triphenylphosphine dust may be irritating, care should be taken to avoid breathing it.

SUGGESTED FIRST AID:

Persons exposed to an excessive amount of triphenylphosphine dust should be removed to a non-contaminated area. A physician should then be consulted.

In the event of skin contact, the exposed areas should be washed thoroughly with soap and water. Contaminated clothing should be removed and laundered before reuse.

In case of eye contact, flush eyes with copious amounts of water for 10 to 15 minutes. Then consult a physician.

For Industrial Use Only

M&T Chemicals Inc. gives no warranty, express or implied, and all products are sold upon condition that purchasers will make their own tests to determine the quality and suitability of the product. M&T Chemicals Inc. shall be in no way responsible for the proper use and service of the product. Any information or suggestions given are without warranty of any kind and purchasers are solely responsible for any loss arising from the use of such information or suggestions. No information or suggestions given by us shall be deemed to be a recommendation to use any product in conflict with any existing patent rights.

004939

CELANESE CHEMICAL COMPANY
TECHNICAL CENTER
Corpus Christi, Texas

To: As Listed*

From: C. D. Barrett

CDB-96-77

September 28, 1977

Subject: BASF Wyandotte Report on the Toxicology of Triphenylphosphine

Recently, Mr. M. P. Neff received a material safety data sheet on triphenylphosphine from BASF Wyandotte, the supplier. Triphenylphosphine is used along with rhodium as a catalyst in the Bishop OXO Unit. According to the data sheet, BASF Wyandotte had classified the compound as being a potentially toxic chronic nerve poison. Mr. Neff requested that I obtain additional toxicological information on TPP both from the supplier and from other sources. The following information on TPP has been obtained and forwarded to Corporate Medical and to Mr. Neff:

1. The BASF Wyandotte classification of TPP as a chronic nerve poison is based on a series of sub-acute animal toxicity studies conducted in Germany by BASF AG toxicology laboratories. A confidential summary of these studies has been obtained for our review. According to the summary, the German group has conducted a series of acute and subacute toxicity studies by various routes of administration to mice, rats, rabbits, cats and dogs. Based on these studies several conclusions have been drawn:

- a. TPP is generally non-toxic in short-term experiments with rodents. The compound has a higher order of acute toxicity in rabbits, cats and dogs.
- b. Repeated applications of TPP to test animals, especially among non-rodents, results in paralysis and various other damaging effects to the nervous system. The mode of action is believed to be cholinesterase inhibition. Furthermore, the effects of chronic TPP exposure are considered by BASF Wyandotte to be comparable to that of tri-o-cresyl phosphate, a well documented nerve poison. They have concluded that TPP should be handled as a "potent nerve poison" and that human exposure by any route should be controlled to a very low level.

2. M. & T. Chemical Company, our other supplier of TPP, has conducted only short-term animal toxicity studies and has concluded that the compound has a very low order of toxicity. Similar findings are published in Industrial Hygiene and Toxicology by Frank A. Patty, 1967. In addition, M. & T. is not aware of any occupational health problems among their employees who have worked in TPP manufacturing areas since the 1960's. However, cholinesterase testing has not been conducted.

004940

September 28, 1977

3. Du Pont's Haskell Laboratories conducted TPP acute and sub-acute inhalation toxicity studies in rats in 1975. There was no indication of nerve damage or any other cumulative toxic effect.

CONCLUSIONS

The BASF German studies raise serious questions concerning the toxicity of TPP. BASF Laboratories is the only research group that we are aware of which has used non-rodents as experimental animals. We are in the process of obtaining a complete translation of these studies.

In the meantime, our Company position should be to handle TPP as a hazardous material. We have no indication at the present time that our handling of TPP has resulted in any health problems. Bishop is presently reviewing work procedures and personal protective equipment requirements to further assure employee protection. Employees handling TPP will be informed in a low-key manner of the potential hazard. Furthermore, we will be reviewing along with Corporate Medical the complete translation of the German studies.

We will keep you well informed of any new information or safe handling recommendations concerning TPP. The information in this report should be treated as confidential, pending release from BASF.



C. D. Barrett, Industrial Hygienist

/mg

004941

MATERIAL SAFETY DATA SHEET

F 1570

SECTION I

MANUFACTURER'S NAME BASF AG Ludwigshafen, West Germany		EMERGENCY TELEPHONE NO.
ADDRESS (Number, Street, City, State, and ZIP Code)		
CHEMICAL NAME AND SYNONYMS Triphenylphosphine		TRADE NAME AND SYNONYMS
CHEMICAL FAMILY Triarylphosphin	FORMULA C ₁₈ H ₁₅ P	

SECTION II HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TLV (Units)
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					
HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES				%	TLV (Units)

SECTION III PHYSICAL DATA

BOILING POINT (°F.) °C	377	SPECIFIC GRAVITY (H ₂ O = 1)	1.194
VAPOR PRESSURE (mm Hg.)	< 1	PERCENT VOLATILE BY VOLUME (%)	< 1
VAPOR DENSITY (AIR = 1)		VAPORATION RATE (_____ = 1)	
SOLUBILITY IN WATER	unsoluble		
APPEARANCE AND ODOR	colorless crystals, inherent odor		

SECTION IV FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used) 180°C. ASTM open cup	FLAMMABLE LIMITS	Lel	Uel
EXTINGUISHING MEDIA CO ₂ - and powder extinguisher			
SPECIAL FIRE FIGHTING PROCEDURES			
UNUSUAL FIRE AND EXPLOSION HAZARDS			

004942

SECTION V HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE

0

EFFECTS OF OVEREXPOSURE

it is no known that TPP is injurious to human health, also in acute animal trials nearly unotoxicological. Injuries only if repeatedly consumed in higher quantities

EMERGENCY AND FIRST AID PROCEDURES

SECTION VI REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	X	
INCOMPATIBILITY (Materials to avoid) oxidation materials, like chlorine			
HAZARDOUS DECOMPOSITION PRODUCTS none			
HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
WASTE DISPOSAL METHOD

SECTION VIII SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type)		
VENTILATION	LOCAL EXHAUST	SPECIAL
	MECHANICAL (General)	OTHER
PROTECTIVE GLOVES		EYE PROTECTION
OTHER PROTECTIVE EQUIPMENT no special protective clothing		

SECTION IX SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING	please avoid contact with skin
for a longer period of time	
OTHER PRECAUTIONS	keep working - clothing clean

004943

Interoffice Memorandum

TO (Name and Location)	J.A. BOUSQUET	DATE	October 13, 1977
FROM (Name and Location)	JAMES M. RAMEY	REFERENCE NO.	jmr/574/77

CONFIDENTIAL

SUBJECT: TRIPHENYLPHOSPHINE (TPP) TOXICITY

A summary of a phone call with Dave Bouchard of BASF is attached which confirms the information given us previously. In essence, Mr. Bouchard stated that TPP must be considered a potent nerve poison, based on animal test data. Exposure by any route must be minimized. After any contact with the product, the affected area should be thoroughly washed. Contaminated clothing should be either discarded or laundered. BASF also lifted the "confidentiality" from the toxicity summary and recommended we discuss the report with customers and/or suppliers.

BASF also recommended that triphenylphosphine oxide (TPPO) be considered a nerve toxin, even though they have very limited data on this chemical.

As you know, TPP and TPPO are present in the oxo-Butanol process at Bishop and will be present in the Bay City process coming on stream in mid-78. We have had limited useage of TPP at CCCTC but none at the present time I am told.

There are several actions which should or have been taken:

1. Bishop should immediately impose work practice controls to include compulsory use of protective equipment to reduce employee exposure to TPP to an absolute minimum. Mike Neff has outlined appropriate procedures in a letter which will issue this week. These procedures have been reviewed and approved by the Division Industrial Hygienist.
2. Bishop should immediately initiate an industrial hygiene survey to determine airborne concentrations of TPP and TPPO. If the measurements show a significant potential for exposure, engineering controls should be implemented.
3. Dr. Dixon should make a recommendation on medical surveillance for employees potentially exposed to TPP and TPPO i.e. should we set up a program to monitor for cholinesterase inhibition?
4. I have discussed reporting requirements under Section 8(e) of TOSCA (Substantial Risk), with the Law Department. They agreed we can wait until BASF makes a decision on whether or not TPP qualifies under the present definition of Substantial Risk. If they report, then we are relieved of the responsibility. If they do not, then we have a decision to make.

004944

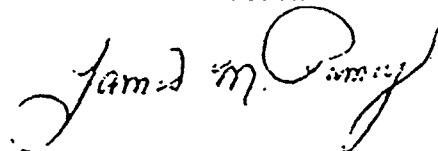
CONFIDENTIAL

J.A. Bousquet

-2-

October 13, 1977
JMR/574/77

5. We should pass on toxicity information on TPP to Engelhard Industries immediately. This should be handled by F.J. Girolamo or someone in Division Central Purchasing. After Engelhard has had a chance to review the data, we probably need to schedule a meeting with them several weeks in advance of the next scheduled catalyst recovery operation.
6. Bishop should determine if the Butanol Heavy Ends stream which we are now selling contains significant levels of TPP or TPP0.
7. We will receive the complete toxicity report on TPP from BASF in about 2 weeks. This should be reviewed by the Corporate Director of Toxicology and the appropriateness of our action reassessed.

JMR/to
enc.

cc: C.D. Barrett
W.M. Brown
Dr. E.M. Dixon
R.D. Damron Corpus Christi
W. Harrison Bishop
P.E. Hime Bishop
J.C. Martin
B.R. Miller
M. Neff ✓ Bishop
Dr. L. Starr
R.E. Suggs
P.J. Volpe Bishop
F.J. Girolamo Houston S&D
Dr. E.N. Wheeler

004945

Received a phone call from Dave Bouchard of B.A.S.F. on 10/11/77 relative to the toxicity of triphenylphosphine (TPP). The substance of his call was:

1. He released us from the "confidentiality" assigned to the toxicity summary on TPP provided previously by BASF. After reviewing the toxicity test data with the West German laboratory which performed the study, BASF reaffirmed its position that TPP "must be considered a potent nerve poison" based on the animal test data. Exposure by any route must be minimized. After any contact with the product, the affected area should be washed thoroughly and contaminated clothing either discarded or laundered.
2. Triphenylphosphine oxide (TPPO) should also be considered to be a nerve toxin, even though toxicity data on TPPO is very limited.
3. BASF has provided M&T Chemical Company (our major supplier of TPP) with complete toxicity information. I assume this relieves us of any responsibility of discussing with M&T.
4. BASF has not observed any medical problems in employees exposed to TPP in the manufacturing process. (They have been manufacturing TPP for over 10 years.)

Mr. Bouchard did not have specific data on exposure levels. BASF has not run cholinesterase inhibition tests on employees exposed to TPP.

5. BASF lawyers have not reached a decision on whether or not the neurotoxic properties of TPP should be reported to EPA under the "substantial risk" clause in Section 8(e) of The Toxic Substances Control Act.

004946

Interoffice Memorandum

TO (Name and Location)	DATE
Mr. B. R. Miller - NYO	October 14, 1977
FROM (Name and Location)	REFERENCE NO.
C. D. Barrett - CCCTC; M. P. Neff - Bishop	CDB-109-77
	MPN-244-77

Subject: Informing Employees of the Toxicity of Triphenylphosphine

Based on the toxicity information recently supplied by BASF Wyandotte, Bishop employees will be informed (per Policy-Hazardous Chemicals, April 15, 1977) of the possible toxicity of triphenylphosphine. The attached information will be appropriately communicated to employees. Comments should be submitted to M.P. Neff.

C. D. Barrett
 C. D. Barrett, Industrial Hygienist

M. P. Neff by CDB
 M. P. Neff, Safety Supervisor

/mg
 Attachment

cc: E. M. Dixon, M. D. - NYO
 J. A. Bousquet - NYO
 Dr. E. N. Wheeler - NYO
 Dr. L. Starr - CCCTC
 Mr. J. M. Ramey - NYO

004947

ATTACHMENT A1

TOXICITY INFORMATION

As a Company, we are not aware of any related health problems among employees handling triphenylphosphine (TPP) as a catalyst in the OXO Unit. Similarly, our two suppliers of TPP (M. & T. Chemical Company and BASF Wyandotte Corporation) are not aware of any health problems among their employees handling TPP. Despite this seemingly good experience with the material, we have recently received the results of some animal toxicity tests conducted in West Germany that raise serious questions about the toxicity of TPP.

When animals were exposed to TPP under laboratory conditions, the compound proved to be highly toxic by affecting the nervous system. After studying these animal test results, we have concluded that TPP and triphenylphosphine oxide (TPPO) may be potentially toxic in humans. The compound may act as a nerve poison and thus affect the nervous system. Even though the dust or vapor is nonirritating to the skin or eyes, ~~the TPP can be readily absorbed through the skin. The compound can also enter the body through the lungs~~

Therefore, we need to eliminate both skin contact and exposure to the dust as well as practice good personal hygiene.

MATERIAL SAFETY DATA SHEET (Attachment A2)

MEDICAL SURVEILLANCE

(Dr. E. M. Dixon will provide medical procedures.)

Employees who have been exposed to TPP in the past will be requested to undergo a simple medical exam consisting of a series of blood tests. The tests will indicate if the TPP has had any detectable effect on the nervous system.

INDUSTRIAL HYGIENE MONITORING

An air sampling study will be conducted to determine the amount of dust or TPP vapor in the work areas. Test results will be used to determine the need for control procedures.

STANDARD OPERATING PROCEDURES FOR HANDLING TPP (& TPPO)

(S.O.P's will be reviewed)

QUESTIONS & ANSWERS

004948

Safety Data Sheet

BASF Wyandotte Corporation

Wyandotte, Mich. 48192
313 282-3300

SECTION I

TRADE NAME	Triphenyl Phosphine	CHEMICAL NAME	Triphenyl Phosphine
SYNONYMS	Triphenyl	CHEMICAL FAMILY	Phosphines
FORMULA	(C ₆ H ₅) ₃ P	MOLECULAR WEIGHT	

SECTION II — HAZARDOUS INGREDIENTS

NAME	%	TLV UNITS	TOXICOLOGICAL DATA
Triphenylphosphine	100		Rat Oral LD ₅₀ 0.8-1.6 g/Kg

SECTION III — PHYSICAL DATA

Boiling Point - 760mm Hg >(360 °C)	711°		
Vapor Pressure, mm Hg @ 20° C. (210 °C)	5		
Specific Gravity (H ₂ O = 1) 25 °C	1.132		
Solubility in Water	Insol. sol. in alc. benzene, acetone C Cl ₄		
Appearance and Odor	White crystalline solid		

SECTION IV — FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (TEST METHOD)	AUTOIGNITION TEMPERATURE		
FLAMMABILITY LIMITS IN AIR - % BY VOLUME	LOWER	UPPER	
EXTINGUISHING MEDIA	☒ WATER FOG ☒ FOAM (Type) ☒ CO ₂ ☐ DRY CHEMICAL ☐ OTHER		
SPECIAL FIRE-FIGHTING PROCEDURES	Explosion hazard slight, if vapor exposed to flame can react vigorously with oxidizing agents.		
UNUSUAL FIRE AND EXPLOSION HAZARDS			

EMERGENCY TELEPHONE NUMBER

004949

(201) 263-0200

This number is available days, nights, weekends, and holidays.

SECTION V — HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE Not established

EFFECTS OF OVEREXPOSURE Possible slight irritation to eyes, skin and mucous membranes. Repeated slight ingestion or absorption through mucous membrane or skin lead to nervous system damage. Possible paralysis.

FIRST AID PROCEDURES

EYES

FLUSH
WITH
FLOWING
WATER
AT
LEAST

MINUTES

Wash affected areas thoroughly with detergent and water. Consult a physician. Strict personal hygiene after each exposure greatly reduce possibility of harmful effects.

NEVER GIVE
FLUIDS OR
INDUCE VOMITING
IF PATIENT
IS UNCONSCIOUS
OR HAVING
CONVULSIONS

SECTION VI — REACTIVITY DATA

STABILITY	UNSTABLE	CONDITIONS TO AVOID	
	STABLE		
INCOMPATIBILITY Oxidizing materials			
HAZARDOUS DECOMPOSITION PRODUCTS Phosphine: PO _x at high temperatures			
HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	DOES NOT OCCUR		

SECTION VII — SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE OF SPILLS

WASTE DISPOSAL METHOD

CONSULT LOCAL AND STATE LAWS

SECTION VIII — SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION

VENTILATION	LOCAL EXHAUST Preferred	SPECIAL
	MECHANICAL (General) Acceptable	OTHER

004950

PROTECTIVE CLOTHING Rubber gloves. Coveralls EYE PROTECTION

OTHER remove contaminated clothing and launder after exposure.

SECTION IX — SPECIAL PRECAUTIONS ✓

PRECAUTIONARY
LABELING

Triphenyl Phosphine

Shipping regulation
ICC, CG, IATA.
Poison LabelMay cause irritation of skin eyes, nose and
throat. Repeated absorption harmful.HANDLING AND
STORAGE CONDITIONSAvoid breathing dust.
Wash thoroughly before eating or smoking
Avoid contact with skin, eyes, and clothing.

004951