UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

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MEMORANDUM

SUBJECT: Review of "A Study of Formaldehyde Exposures from Metalworking Fluid Operations Using Hexahydro-1,3,5-Tris (2-Hydroxyethyl)-S- Triazine

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This memo is a review of the above mentioned study which was submitted by the Troy Corporation on 1/29/2008 in support of the HHT RED. This study was conducted in 1993 by Howard Cohen, Ph. D., CIH on behalf of the Triazine Joint Venture. The purpose of the study was to measure formaldehyde exposures arising from the use of triazine biocides in metal working fluids. This was done to determine if exposures exceeded 100 ppb as an eight hour time weighted average, which would require special labeling, exposure monitoring and hazard communication training, under the OSHA formaldehyde standard.

Introduction

This study was conducted at a triazine formulation facility and at seven different manufacturing facilities that used triazine to treat metal working fluids (MWF). A description of the sites sampled is included in Table 1.

Table 1 – Sites Sampled in the Triazine MWF Study

Site	Description
1 Triazine Formulation Facility	Specialty chemical facility that blended several formulations of triazine. Triazine was transferred from 55 gallon drums into the reactor using a vacuum hose. Several additives were charged into the reactor and combined with triazine and then the product was gravity fed into 55 gallon drums.
2. Steel Rolling Mills	Consisted of two steel rolling mills (A and B) that were both located in a large steel building with general ventilation
3. Automotive Transmission Plant	Consisted of two areas (A and B) located in different buildings. Area A was crowded and had poor ventilation with a decay like odor which triggered employee complaints. Area B was less crowded, had windows which could be opened, and had fewer complaints. 16 gallons of triazine was added once weekly in Area A and 2 gallons were added daily in Area B.
4. Manufacturer of Large Industrial Machinery	Consisted of two areas (A and B) located in one building. All machines were well enclosed. Area A had natural ventilation with 20 ft ceilings, Area B had air conditioning.
5. Manufacturer of Medium Sized Industrial Machinery	Most machining operations were enclosed except for the grinders and machine operators #1 and #2. Machine operator #1 had particularly prominent overspray. Two background samples were taken in the same building but neither sampling location was adjacent to the operations monitored.
6. Automobile Manufacturer	Consisted of two areas (A and B) located in one large building. Area A had a very high ceiling but no local exhaust on machines. The afternoon workload was low and workers took breaks away from the work area. Area B had a lower ceiling and local exhaust over each machine.
7. Aluminum Can Manufacturer	Visible coolant overspray, return flumes uncovered.
8. Aluminum Can Manufacturer	Consisted of three D & I machining lines all on the same platform. Line #1 was supported by a 4000 gallon Delaval filtering system that was continuously fed triazine at 4 gallons per day. Lines #2 and #3 were supported by a 6000 gallon Schneider filter system that is normally fed 6 gallons of triazine per day, however, no triazine was fed on the day of the study because the plant chemist decided that the triazine levels were adequate.

Sampling Strategy

Personal breathing zone (PBZ) air samples were collected on the workers as they conducted normal production operations such as tool setup, machining, grinding, steel rolling and aluminum can drawing and ironing using MWF treated with triazine. Samples were also taken during the addition of triazine which typically occurred in the middle of the shift. The sample durations were 3 to 4 hours during production operations and 10 to 20 minutes during triazine addition. Area samples were taken in the workareas near the employees and source samples were taken near potentially high exposure areas such as MWF sumps and return flumes. Background samples were also taken in areas such as adjacent office spaces to determine ambient formaldehyde levels that were not associated with MWF operations. Metal working fluid samples were taken from the sumps at each facility before and after triazine addition and were analyzed for triazine.

Sample Collection and Analysis Methods

The PBZ samples were collected either with SKC silica gel tubes and/or GMD 570 passive badge dosimeters both of which were treated with 2, 4-dinitrophenylhydrazine (DNPH). In many cases duplicate samples were taken using both methods. The tubes were used with a personal sampling pump that was operated at 0.1 liters per minute and the badges were assumed to have a flow rate of 0.0252 liters per minute based on manufacturer testing. The samples were taken for 120 to 240 minutes each during MWF operations before and after triazine addition and for 5 to 27 minutes during triazine addition. Area, source and background samples were also collected also using midget impingers operated at a flow rate of 1 LPM in addition to the silica gel tubes and passive dosimeters. The samples were analyzed by two laboratories which were accredited by the American Industrial Hygiene Association (AIHA). The tubes were analyzed using EPA Method #T011 and the impinger samples were analyzed using NIOSH Method #3500. The badge samples were analyzed by eluting acetonitrile and analyzing with HPLC and UV detection. The limit of quantification (LOQ) for a 4 hour sample was 17 ppb, 18 ppb and 27ppb for the impingers, tubes and badge dosimeters, respectively. The LOQ for a 15 minute sample was 270 ppb, 297 ppb and 426 ppb.

Field recovery samples were generated by spiking with known amounts of a solution of one microgram formaldehyde per microliter of water to approximate the quantities expected from a four hour sample at 100 ppb. The results as shown in Table 2 indicated generally good recoveries with the exception of the badge dosimeters from site 3B which indicated an excessive recovery of 272%. This recovery was greater than the recovery of 103 % from site 3A or the average recovery of 113 % from all of the sites combined. There were only a few recoveries that were less than 90% and these include the two badge spikes from site 1 (58% and 64%) and 2 tube spikes from site 4 (67% and 80%).

Table 2 – Field Fortification Recoveries

Site	Media	Fortification (ug)	Corresponding Formaldehyde Air Concentration (ppb)	N	Mean Percent Recovery	SD
5	Badge	1	136	4	133	43
2A	Badge	1	136	1	150	N/A
2B	Badge	1	136	3	117	19
3A	Badge	1	136	10	103	12
3B	**Badge**	**1**	**136**	**5**	**272**	**206**
4 Control	Badge	1	136	1	140	N/A
4 Sump	Badge	1	136	2	150	N/A
4A	Badge	1	136	2	105	N/A
5 Control	Badge	1	136	1	90	N/A
5 Sump	Badge	1	136	2	120	N/A
1	Badge	18.5	2507	1	58	N/A
1	Badge	37	5014	1	69	N/A
Badge Average (All Included)				33	137	104
Badge Average (Site 2B Excluded)				28	113	30

Table 2 – Field Fortification Recoveries						
Site	**Media**	**Fortification (ug)**	**Corresponding Formaldehyde Air Concentration (ppb)**	**N**	**Mean Percent Recovery**	**SD**
1	Impinger	18.5	63	1	91	N/A
2A	Impinger	30	102	2	153	N/A
2B	Impinger	30	102	2	123	N/A
5	Impinger	33	112	4	104	5
3A	Impinger	33	112	4	119	4
3B	Impinger	33	112	4	121	22
4 Sump	Impinger	33	112	2	173	N/A
4B	Impinger	33	112	2	122	N/A
1	Impinger	37	125	1	91	N/A
Impinger Average (All Included)				22	123	28
5	Tube	3	102	10	105	16
2A	Tube	3	102	6	121	8
2B	Tube	3	102	4	114	8
3A	Tube	3	102	9	113	16
3B	Tube	3	102	9	115	39
4 Addition	Tube	3	102	1	127	N/A
4 Sump	Tube	3	102	2	74	N/A
4A	Tube	3	102	2	110	N/A
4B	Tube	3	102	5	105	14
1	Tube	18.5	627	1	129	N/A
1	Tube	37	1253	1	125	N/A
Tube Average (All Included)				50	111	23

Summary of Results

A summary of the reported results for the PBZ samples is included in Table 3. These results were not corrected for field recovery or background levels. In cases where duplicate samples were taken using tubes and badges, only the highest results are shown. The results for the production operations ranged from non-detect to a maximum of 490 ppb and many exceeded the 100 ppb level of concern. The highest results were from Site 3B which had good ventilation and few worker complaints. Although most of the Site 3B samples were taken with badges that had excessive field recovery, a few were taken with tubes, which had normally field recovery, and indicated similar exposure levels. The PBZ samples for triazine addition were all less than the LOQ which ranged from 165 ppb to 930 ppb due the short sampling times. The background samples ranged from non-detect to 118 ppb with the highest levels measured at sites 5 and 7. The results of the area and source samples are included in Table 4. These results were generally similar to or lower than the PBZ results with exception that some of the source samples taken near the sumps were greater than the corresponding PBZ samples. This was particularly true for site 5 where the sump was located below ground level outside of the manufacturing building and only had minimal ventilation.

Table 3 - Formaldehyde PBZ Air Concentrations Measured on Workers Using Triazine Treated MWF						
Site	**Operation**	**MWF Triazine Level (ppm)**	**N**	**Duration (Minutes)**	**Reported Values (ppb)**	**Background Level (ppb)**
1	Charging Reactor Drumming Triazine	N/A	1 1	80 264	130 28	Not Measured
2A	Operator and Helper	Prior - 550	3	205 to 223	<19 to <29	<20
2A	Operator and Helper	After - 1240	3	182 to 184	<23 to <35	<20
2B	Operator and Helper	Prior - 0	2	205, 223	<21, <22	<20
2B	Operator and Helper	After - 220	3	179 to 181	<31 to **110**	<20
3A	Heat Treat Operator Lathe Operator Grinder Machining Operator	Prior - 0	1 1 3 4	174 172 137 to 172 146 to 166	<26 <26 <37 to <47 <28 to <44	<18
3A	Heat Treat Operator Lathe Operator Grinder Machining Operator	After - 400	1 1 3 4	117 127 110 to 119 109 to 121	<55 <36 <39 to <58 <37 to <56	<18
3B	Machining Operator Maintenance Helper Pipefitter	Prior - 1300	4 1 2	194 to 212 206 47, 223	**160 to 470** **250** **140, 162**	<18
3B	Machining Operator Maintenance Helper Pipefitter	After - 1400	4 1 1	144 to 157 146 157	**140 to 490** **410** **340**	<18
4A	Worker in General Area Machinery Operator	Prior - 1045	1 1	242 211	52 **154**	28
4A	Worker in General Area Machinery Operator	After -1685	1 1	162 161	**106** **257**	28
4B	Machinery Operators	Prior - 1045	3	172 to 236	**122 to 137**	28
4B	Machinery Operators	After - 1685	3	153 to 154	**102 to 163**	28
5	Grinder Operators Machine Operators	Prior - 586	2 5	217, 220 197 to 218	**110, 130** **55 to 207**	78
5	Grinder Operators Machine Operators	After - 1107, 839 After - 1012	2 5	171, 195 189 to 196	**170, 196** **119 to 250**	78
6A	Machine Operator Setup Operator	Prior - 169	2 2	232, 236 236, 237	<18, <30 <18, <19	26
6A	Machine Operator Setup Operator	After - 1894	2 2	160, 171 108, 171	**140, 160** **140**, 59	26
6B	Grinder Operator	Prior - 301	2	208, 207	36, <30	26
6B	Grinder Operator	After - 1847	2	175, 178	58, 56	26
7	D& I Operator Washer Operator	Prior - 997	4 1	195 to 209 194	**143 to 196** **175**	118
7	D & I Operator Washer Operator	After - 1160	4 1	262 to 277 284	**123 to 165** **127**	118
8	D & I Operator Line 1	Prior - 975	2	434, 464	**123, 170**	50
8	D & I Operator Line 3	After - 1823	3	421 to 458	**151 to 209**	50

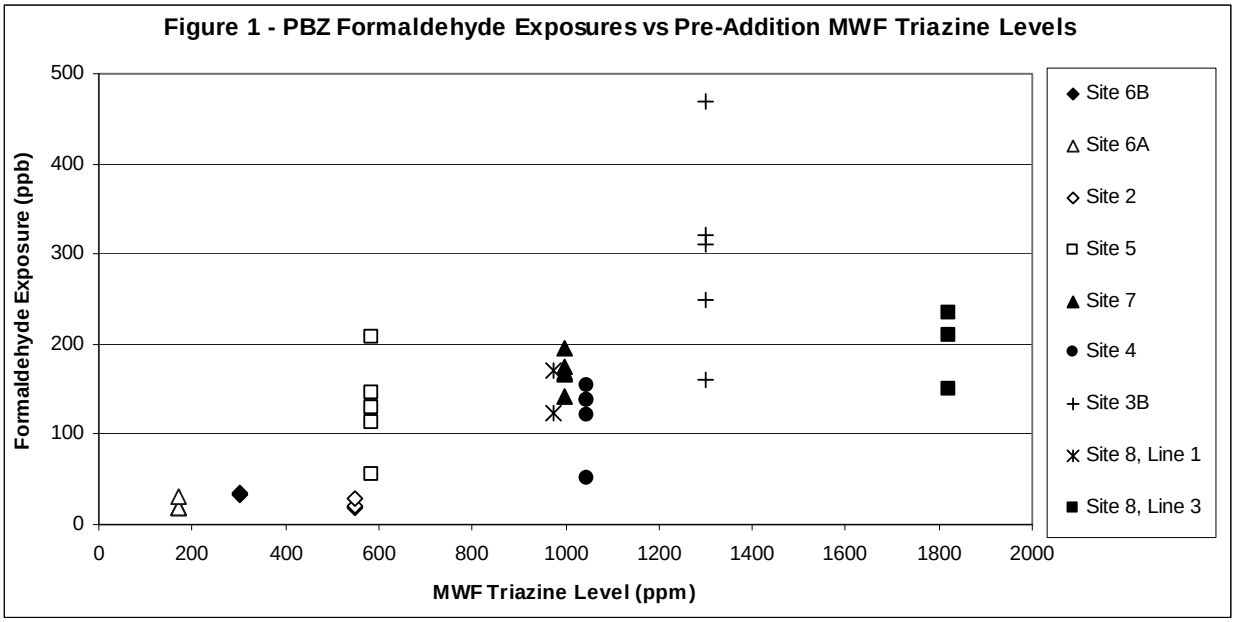
*** Results highlighted in bold font exceed 100 ppb**

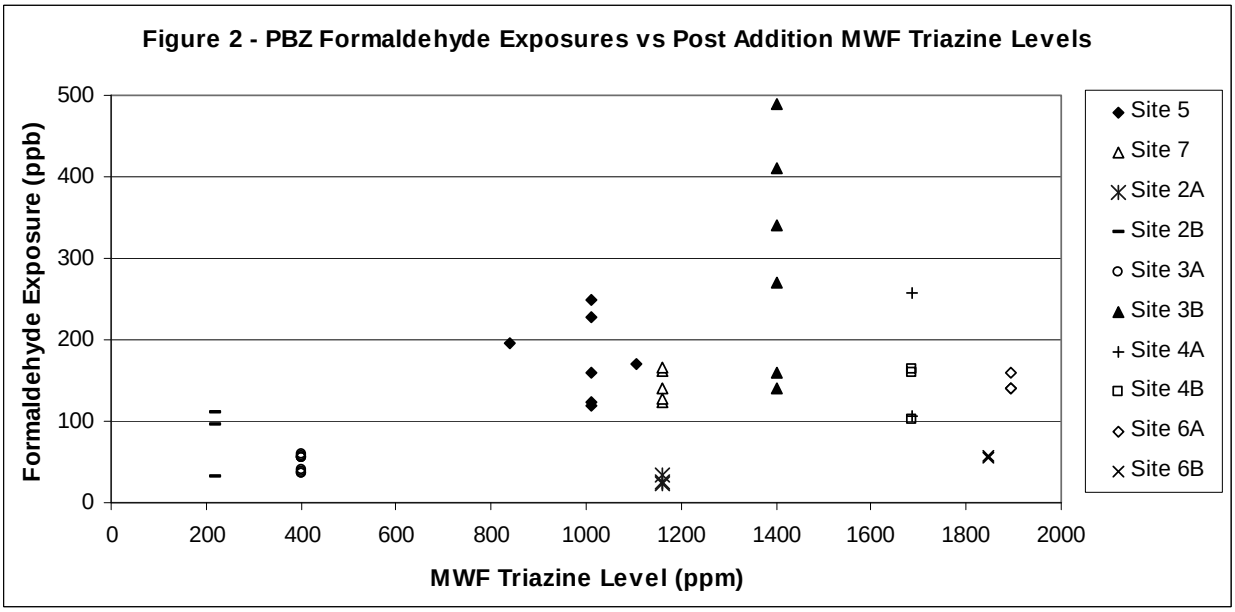
Table 4 - Formaldehyde Area and Source Air Concentrations							
Site	**Sample Type**	**Sample Location**	**MWF Triazine Level (ppm)**	**N**	**Duration (Minutes)**	**Reported Values (ppb)**	**Background Level (ppb)**
1	Area Area Source	Over drum being washed At drum weigh station On top of Triazine Drum	N/A	2 3 2	54, 251 165, 235 58, 65	**210**, 62 <28 <44	Not Measured
2A	Source	Directly over sump Directly over sump	550 1240	1 1	213 213	39 70	ND
2B	Source	Next to sump Next to sump	0 220	1 1	216 200	<20 23	ND
3A	Area	Near central sump Near central sump	0 400	1 1	143 112	<31 69	ND
3A	Source	Directly over sump next to updraft	0 400	1 1	138 112	71 **180**	ND
3B	Area	Near machine operator 1 and 2	1300 1400	1 1	200 147	**280** **320**	ND
3B	Area	Furthest point from sump	1300 1400	1 1	196 139	**178** **260**	ND
3B	Source	At sump directly over return flume	1300 1400	1 1	196 143	**270** **440**	ND
4A	Area	10 feet from a machine	1045 1685	1 1	208 202	83 33	28
4B	Area	Ground level 4 ft above open flume	1045 1685	1 1	194 194	61 26	28
5	Area	Operator's desk 5 feet from machine	586 1012	1 1	163 208	30 43	78
5	Area	5 feet above return flume grating	586 1012	1 1	163 205	62 **104**	78
5	Source	Inside central sump 5 feet above flume	586 1012	1 1	164 269	**707** **1012**	78
6A	Area	Aisleway near operator #1	169 1894	1 1	189 175	<34 **140**	26
6A	Source	Inside sump room	169 1894	1 1	196 196	<28 **320**	26
6A	Area	Behind operator #1 grinders	301 1847	1 1	194 169	39 **150**	26
6B	Source	Inside sump area 3 ft from flume	301 1847	1 1	196 170	36 <32	26
7	Area	Platform over draw machine	997 1160	1 1	190 290	**294** **360**	118
7	Source	Directly over sump	997 1160	1 1	191 296	78 83	118
7	Source	Next to Schneider Filters	997 1160	1 1	195 299	**208** 58	118
8	Area	At Delaval filter Press, Line #1	975	1	377	**162**	50
8	Area	At Schneider filter press, Line #2	1823	1	374	**126**	50
8	Area	On D& I Platform	1823	1	371	**107**	50

***Results highlighted in bold font exceed 100 ppb.**

Relationship Between Triazine Levels and Formaldehyde Exposures

The results of the PBZ samples for production operations were compared to the levels of triazine measured in the MWF samples to determine if there was a relationship between triazine levels and formaldehyde exposures. Regression analysis of the exposure data taken prior to the addition of triazine as shown in Figure 1 indicates that the coefficient of determination (R^2) is 0.48 and the coefficient of correlation (R) is 0.70. Regression analysis of the exposure data taken after the addition of triazine as shown in Figure 2 indicates a less significant relationship ($R^2 = 0.13$, $R = 0.36$). It is suspected that this is due to a lag time between triazine addition and formaldehyde emissions.





Study Acceptability, Data Limitations and Recommendations for Future Studies

This study meets the series 875 guidelines and the data are adequate for use in risk assessment. There are some limitations; however, which make it somewhat difficult to compare the results of this study to the EPA level of concern of formaldehyde which is 100 ppb as a ceiling value.

The first limitation is that the sampling times generally ranged from 3 to 4 hours while ceiling exposures are normally measured with sampling times of 15 minutes or less. Since many of these results exceed the level of concern of 100 ppb as a 3 to 4 hour average; however, it can be assumed that 15 minute samples taken within the same 3 to 4 hour time period would have also exceeded 100 ppb. It is also possible that the 3 to 4 hour samples which were below 100 ppb contained one or more 15 minute periods of exposure that exceeded 100 ppb.

The second limitation is that analytical methods were not capable of measuring exposure levels at or below 100 ppb if the sampling times were less than one half hour. This was observed in the samples taken during triazine addition where the sample durations ranged from 5 to 27 minutes and no formaldehyde residues were detected with LOQs that ranged <930 ppb to <165 ppb.

Since the time that the study was completed (1993), the sampling and analytical methods have improved and it is now possible to measure formaldehyde levels of less than 100 ppb with 15 minute samples. As discussed in the second edition of EPA Method TO-11A (EPA, 1999), the commercially available sampling cartridges now have a lower pressure drop and can be used at flowrates of up to 2 liters per minute which is much greater than the flowrate of 0.1 lpm that was used in this study. These cartridges also have a lower and more consistent background of <0.15 ug/cartridge. The NIOSH methods for formaldehyde have also been updated and the documentation for Method #2016 (NIOSH, 2003) indicates that the working range is 12 to 2000 ppb for a 15 liter sample with a flow rate of 0.03 to 1.5 liters per minute. This means that 12 ppb could be quantified in a ten minute sample if the flowrate was 1.5 liters per minute.

Exposure Reduction Recommendations Based on this Study

Although this study was conducted at a variety of workplaces which had various configurations of engineering controls such as machine enclosure, local exhaust ventilation and general ventilation the only factor that seemed to have any consistent effect on exposure is the amount of triazine added to the MWF. Therefore, based on this study, the only way to reduce exposures would be to reduce the working concentration of triazine in the MWF. The study also indicated that exposures tended to be lower if the triazine were added in smaller increments which provided a more consistent triazine concentration in the MWF.

Comparison to more recent studies on formaldehyde in MWF

Linnainmaa, 2003 measured formaldehyde exposures in machine shops using triazine as part of a study designed to evaluate the effects of triazine use and machine enclosures, including recirculating air cleaners, on workers exposure to bacterial endotoxins and formaldehyde originating from triazine. This study was conducted in 8 workplaces where hard metal or stellite blades were ground and 10 workplaces where general machining operations, such as grinding, turning, drilling, sawing and milling, were done. Seven different types of recirculating local

exhaust ventilation systems were tested by measuring endotoxin concentrations in the exhaust air during the normal operation of the machines. Both personal and area samples were collected for formaldehyde using Waters Sep Pak silica cartridges treated with DNPH at a flow rate of 0.1 LPM for 2 to 4 hours. The concentration of triazine in the MWF was also measured in conjunction with the air sampling. Twenty one personal samples were collected and the formaldehyde air concentrations ranged from 8.1 ppb to 179 ppb with a mean of 42 ppb and a median of 20 ppb. Twenty seven area samples were collected and the air concentrations ranged from 6.5 ppb to 195 ppb with a mean of 45 ppb and a median of 17 ppb. The concentrations of triazine in the MWF ranged from <0.5 to 3500 ppm with a mean of 470 ppm and a median of 4 ppm. The concentrations of triazine in the MWF correlated well with the formaldehyde concentrations in the air near the machines (n=23) with a correlation coefficient (R) of 0.69. The authors concluded that the triazine levels should be kept above 500 ppm to prevent bacterial growth and that overdosing should be avoided to keep airborne formaldehyde levels low.

References:

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