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TSCA HEALTH & SAFETY STUDY COVER SHEET

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1.0 SUBMISSION TYPE ☒ *Contains CBI*

☒ 8(d) ☐ 8(e) ☐ FYI ☐ 4 ☐ OTHER: Specify____________________

☒ Initial Submission ☐ Follow-up Submission ☐ Final Report Submission

Previous EPA Submission Number or Title if update or follow-up: ____________________ Docket Number, if any: # ________________

ITC Submission ☐ Yes ☒ No

☐ continuation sheet attached

2.1 SUMMARY/ABSTRACT ATTACHED (may be required for Sec. 8(e); optional for Secs. 4, 8(d) & FYI) ☒ Yes ☐ No

2.2 SUBMITTER TRACKING NUMBER OR INTERNAL ID 01R

2.3 FOR EPA USE ONLY

2.4 Study 1 **of** 21

3.0 CHEMICAL/TEST SUBSTANCE IDENTITY ☐ *Contains CBI*

Reported Chemical Name (specify nomenclature if other than CAS name): Formaldehyde

CAS# 50 - 00 - 0

Purity _______%

☐ Single Ingredient

☒ Commercial/Tech Grade

☐ Mixture *Trade Name:* ________________________ *Common Name*: _________________________

–

Other chemical(s) present in tested mixture

CAS Number	*NAME*	*% WEIGHT*

☒ continuation sheet attached

4.0 REPORT/STUDY TITLE ☐ *Contains CBI* Physical Properties of Formaldehyde Products

☐ continuation sheet attached

5.1 STUDY/TSCATS INDEXING TERMS

[CHECK ONE]

HEALTH EFFECTS (HE):______ ENVIRONMENTAL EFFECTS (EE):______ ENVIRONMENTAL FATE (EF): X

5.2 STUDY/TSCATS INDEXING TERMS (see instructions for 4 digit codes)

STUDY TYPE: PCHE | SUBJECT ORGANISM (HE, EE only):_______ | ROUTE OF EXPOSURE (HE only):______ | VEHICLE OF EXPOSURE (HE only)_____

*Other:*____________ *Other:*_________________________ *Other:* ____________________ *Other:*__________________

6.0 REPORT/STUDY INFORMATION ☒ *Contains CBI* ☐ Study is GLP

Laboratory [redacted]

Report/Study Date 10/11/88

Source of Data/Study Sponsor (if different than submitter) ______________________________________ Number of pages 11

☐ continuation sheet attached

7.0 SUBMITTER INFORMATION ☒ *Contains CBI*

Submitter: [redacted] Title: [redacted] Phone: [redacted]

Company Name: [redacted] Company Address: [redacted]

____ Submitter Address (if different):

Technical Contact: [redacted] Phone: [redacted]

☐ continuation sheet attached e-mail address [redacted]

8.0 ADDITIONAL COMMENTS ☒ *Contains CBI*

[redacted]

☐ continuation sheet attached **Submitter Signature:** [redacted] Date:___________________

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TSCA HEALTH & SAFETY STUDY COVER SHEET

9.0 CONTINUATION SHEET

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Submitter Tracking Number/Internal ID

01R

CONTINUED FROM COVER SHEET SECTION # 3.0

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Formaldehyde (18% wt)/Methanol (7% wt)
Formaldehyde (28% wt)/Methanol (0.5% wt)
Formaldehyde (30% wt)/Methanol (1% wt)
Formaldehyde (37% wt)/Methanol (1% wt)
Formaldehyde (37% wt)/Methanol (3% wt)
Formaldehyde (37% wt)/Methanol (7% wt)
Formaldehyde (37% wt)/Methanol (9-12% wt)
Formaldehyde (37% wt)/Methanol (12-15% wt)
Formaldehyde (40% wt)/Methanol (1.5% wt)
Formaldehyde (44% wt)/Methanol (1.5% wt)
Formaldehyde (44% wt)/Methanol (6% wt)
Formaldehyde (45% wt)/Methanol (1.5% wt)
Formaldehyde (46.5% wt)/Methanol (1.5% wt)
Formaldehyde (46.5% wt)/Methanol (12% wt)
Formaldehyde (50% wt)/Methanol (1.5% wt)
Formaldehyde (52% wt)/Methanol (1.5% wt)
Formaldehyde (43% wt)/Methanol (47% wt)
Formaldehyde (55% wt)/Methanol (35% wt)
Formaldehyde (40% wt)/n-Butyl Alcohol (53% wt)
Formaldehyde (40% wt)/i-Butyl Alcohol (53% wt)
Formaldehyde (53% wt)/Methanol (34% wt)/Acetic Acid (3% wt)
Formaldehyde (15% wt)/ Acetic Acid (60% wt)
Paraformaldehyde (91-93% wt)
Paraformaldehyde (95-97% wt)

[redacted]

To: [redacted] November 10, 1988

From: [redacted] HRG-366-88

Physical Properties of Formaldehyde Products

ABSTRACT

At the request of the SHE Group in [redacted], we have developed more accurate physical properties information for each of our formaldehyde products. This report summarizes the most reliable data on boiling point, specific gravity, vapor pressure, vapor density and flash points and documents their sources.

It is recommended that this information be used to correct discrepancies and/or deficiencies in our Material Safety Data Sheets (MSDSs).

KEYWORDS
MSDS
Physical
Properties
Formaldehyde
Formcel
SHE
Paraform
Mixture
1988
S-2966

INTRODUCTION

In late 1986, the Safety, Health, and Environment (SHE) Group in [redacted] requested we develop accurate physical properties information for each of our formaldehyde products (1). The purpose was to correct discrepancies and/or deficiencies in our MSDSs. A plan was agreed upon and we proceeded to obtain the necessary data from a variety of sources as well as to make some experimental determinations (2). The purpose of this report is to convey the requested information and document its sources.

DISCUSSION

The [redacted] SHE Group in [redacted] noted a number of discrepancies in the MSDSs for our formaldehyde products (1). The area of concern is the physical properties; i.e., boiling point, specific gravity, vapor pressure, vapor density, and flash point. At the request of the SHE Group, we have developed reasonably accurate information for all the products in question. This report summarizes our work.

RESULTS

Sources of Information

A substantial part of the vapor pressure data was supplied by Mr. [redacted] of [redacted] (3). These data were obtained from a VLE computer program developed at Dortmund University. Where we could make a comparison, the VLE program gives somewhat higher partial pressures of formaldehyde than the observed values reported by Green and Vener (4) and Walker (5). Not knowing the source of information in the data base and how the computer program works, we cannot comment on the reasons for the differences. However, it is well known that discrepancies in formaldehyde VLE data obtained by different researchers are due to the type of distillation apparatus, its mode of operation, and the age of the formaldehyde solution. Weighing all the factors, we believe that the data calculated by the VLE program give the maximum partial pressures of formaldehyde that would be observed under a variety of conditions. In my opinion, these data represent the best available input to our MSDSs.

Some vapor pressure data were determined experimentally at [redacted]. This was done for formaldehyde solutions containing i-butyl alcohol, n-butyl alcohol, or acetic acid (2). No prior data existed for these mixtures.

Flash points were obtained from a list of tag open cup (TOC) and tag closed cup (TCC) flash points compiled by Havlik (6). The other source is our MSDSs. For mixtures where no data were available, the flash points were calculated by a computational procedure discussed in the Appendix. This method is judged to be satisfactory, because, for mixtures with flash points reported in the above sources, the calculated value is within ±5°C of the experimental value for all but two. In these cases, the calculated value was 7 and 9°C lower than the literature.

Specific gravities were taken from pounds per gallon tables supplied by the [redacted] plant (7).

Upper and lower flammable limits for pure components were taken from several sources (8,9,10).

Tabulation of Data

The physical property data for all formaldehyde products are given in Table I. The following is a brief explanation of each column in the table. For convenience, temperatures are reported in both °C and (°F).

PBT

This is a code which identifies each [redacted] MSDS.

Composition

The weight percent of each organic component in the mixture is given. The balance is water.

Storage Temperature

Storage temperatures are typical temperatures at which the product is stored and shipped.

Boiling Point

Boiling points for a number of mixtures were calculated by Mr. [redacted] (3) using a VLE program. Values for intermediate compositions were estimated by interpolation. Boiling points for mixtures containing the butyl alcohols or acetic acid were determined at the Technical Center (2).

Specific Gravity

Specific gravity is the density (g/ml) of the mixture at storage temperature divided by the density of water at 4°C (1.00 g/ml).

Vapor Pressure

Vapor pressure is given as millimeters of mercury absolute (mmHgA). The values are the partial pressures of each component in the mixture. The total vapor pressure of the mixture (not given) is the sum of the partial pressures. Data for a number of the mixtures were supplied by Mr. [redacted] (3) using the VLE program. Data for intermediate compositions were estimated by interpolation using nearby compositions. Data for compositions containing the butyl alcohols or acetic acid were determined experimentally (2).

Vapor Density

Vapor density was calculated from the liquid composition in column 2. To calculate this value, it was assumed that the mixture was completely vaporized in a closed system. The average molecular weight of the gas was calculated and divided by 29 (the average molecular weight of the components in dry air). This calculation conforms to the procedure given by OSHA for MSDSs.

Flash Point

Flash points are given in two columns. Where available, values from the literature are given. In most cases the values were determined using the tag closed cup method (TCC). In two cases (mixtures containing butyl alcohols), the flash points were determined by the tag open cup method (TOC). TCC values are more appropriate for MSDSs, because they represent a flammable mixture in a closed storage tank.

Calculated flash points are given in the last column. As discussed earlier, comparison of the two columns shows the reliability of the flash point calculation.

Flammable Limits

It was not feasible to determine the upper and lower flammable limits for these mixtures. In any case, such measurements for these mixtures would not be meaningful and would be subject to misinterpretation. As an alternative, the upper and lower flammable limits for the pure components in these mixtures are given at the bottom of the Table.

CONCLUSIONS

Physical properties for all [redacted] products containing formaldehyde have been updated with the most reliable and current data available. These were obtained from recent literature, [redacted], computer programs, and [redacted] plant documents or determined experimentally. Sources of information are documented.

RECOMMENDATIONS

It is recommended that this information be used to update the MSDSs for these products.

FUTURE WORK

With the information compiled, it will be possible to supply physical properties data for many formaldehyde mixtures not yet produced. We expect to supply this information as needed.

[redacted]

[redacted]

REFERENCES

1. [redacted], "Physical Properties-Formaldehyde Products," JDW-120-86, November 25, 1986.

2. [redacted], "Vapor-Liquid-Equilibrium Data for Formaldehyde Solutions," HRG-362-88, and ESS, September 9, 1988.

3. [redacted], Letter from [redacted], November 2, 1987.

4. Green, S. J. and R. E. Vern, I&EC 47, 103(1955).

5. Walker, J. F., Formaldehyde, Robert E. Krieger Publishing Co., Inc., Huntington, New York, 1964, p. 92.

6. Havlik, L. D., "HM-102-FLAMMABLE, COMBUSTIBLE, AND PYROFORIC LIQUIDS," LDH-121-72, July 24, 1972.

7. [redacted], "Pounds per Gallons Table," [redacted].

8. NFPA Fire Protection Guide on Hazardous Materials, 9th Edition, 1987.

9. Zabetakis, M. G., Flammability Characteristics of Combustible Gases and Vapors, Bureau of Mines Bulletin 627, U.S. Dept. of the Interior, 1965.

10. MSDS for Glacial Acetic Acid, [redacted], January 1, 1988.

11. Product Bulletin for Formaldehyde, [redacted], ca. 1975.

12. Product Bulletin for Formcel Solutions, [redacted].

TABLE I

TABLE I

UPDATED PHYSICAL PROPERTIES DATA FOR [redacted] FORMALDEHYDE PRODUCTS

PBT	Composition, wt%		Storage Temp °C/(°F)	BP (760 mmHgA) °C/(°F) (a)	SpGr (H2O=1) @ Stor. Temp	Vapor Pressure mmHgA (b)	Vapor Density (Air=1) (c)	Flash Point, TCC (i) Literature	Flash Point, TCC (i) Calcd. (j)
102	HCHO CH3OH	18 7	60 (140)	96.7 (206)	1.021 (n)	PW=128 PF=12 PM=17	0.73		71 (160)
103	HCHO CH3OH	28 0.5	60 (140)	98.2 (209)	1.062 (n)	PW=126 PF=17 PM=0.5	0.74		78 (172)
115	HCHO CH3OH	30 1	60 (149)	98.2 (209)	1.068 (n)	PW=123 PF=17 PM=2	0.63		75 (167)
47C	HCHO CH3OH	37 1	60 (140)	98.3 (209)	1.090 (m)	PW=118 PF=20 PM=2	0.79	85 (f) (185)	76 (169)
98	HCHO CH3OH	37 3	60 (140)	98.0 (208)	1.084 (n)	PW=116 PF=20 PM=5	0.79	78 (d) (173)	74 (165)
45	HCHO CH3OH	37 7	60 (140)	97.3 (207)	1.072 (m)	PW=113 PF=20 PM=11	0.81	69 (156)	69 (156)
45B	HCHO CH3OH	37 9-12	60 (140)	96.9-96.2 (206-205)	1.064-1.053 (m)	PW=110-107 PF=21 PM=16-24	0.81-0.83	64-58 (d) (148-137)	67-63 (152-145)
46	HCHO CH3OH	37 12-15	60 (140)	96.2-95.6 (205-204)	1.053-1.047 (m)	PW=106-102 PF=22 PM=24-32	0.83-0.85	61 (f) (141)	63-59 (145-138)
116	HCHO CH3OH	40 1.5	65 (149)	98.4 (209)	1.094 (n)	PW=148 PF=27 PM=3	0.79	82 (e) (179)	75 (167)
47B	HCHO CH3OH	44 1.5	65 (149)	98.6 (210)	1.102 (m)	PW=142 PF=29 PM=3	0.81	74 (r) (165)	74 (165)
99	HCHO CH3OH	44 6	65 (149)	97.9 (208)	1.089 (m)	PW=135 PF=30 PM=12	0.83	66 (r) (150)	68 (154)
47A	HCHO CH3OH	45 1.5	65 (149)	98.7 (210)	1.105 (m)	PW=141 PF=29 PM=3	0.81	74 (r) (165)	74 (165)
47F	HCHO CH3OH	46.5 1.5	65 (149)	98.9 (210)	1.109 (m)	PW=138 PF=30 PM=3	0.82	74 (e) (165)	73 (163)
??	HCHO CH3OH	46.5 12	65 (149)	97.1 (207)	1.071 (n)	PW=117 PF=33 PM=33	0.82		61 (142)
47D	HCHO CH3OH	50 1.5	65 (149)	99.1 (210)	1.119 (m)	PW=134 PF=31 PM=3	0.83	70 (f) (158)	72 (162)
47E	HCHO CH3OH	52 1.5	65 (149)	99.3 (211)	1.125 (m)	PW=131 PF=32 PM=3	0.84	70 (r) (158)	72 (162)

TABLE I CONTINUED

TABLE I (cont)

UPDATED PHYSICAL PROPERTIES DATA FOR [redacted] FORMALDEHYDE PRODUCTS

PBT	Composition, wt%		Storage Temp °C/(°F)	BP (760 mmHgA) °C/(°F) (a)	SpGr (H2O=1) @ Stor. Temp	Vapor Pressure mmHgA (b)	Vapor Density (Air=1) (c)	Flash Point, TCC (i) Literature	Calcd. (j)
109	HCHO CH3OH	43 47	40 (104)	88.0 (190)	0.977 (m)	PW=12 PF=15 PM=60	1.03	30 (s) (87)	33 (91)
49	HCHO CH3OH	55 35	40 (104)	91.6 (197)	1.051 (m)	PW=10 PF=15 PM=35	1.02	44 (f) (112)	41 (106)
48	HCHO n-BuOH	40 53	40 (104)	104.5 (1) (220)	0.963 (m)	PW=26 (1) PF=7 PB=9 PM=1	1.81	74 (k) (166)	41 (106)
??	HCHO i-BuOH	40 53	40 (104)	102.7 (1) (217)	0.958 (o)	PW=29 (1) PF=6 PB=10 PM=1	1.81	67 (k) (152)	43 (109)
50	HCHO CH3OH HOAc	53 34 3	40 (104)	96.4 (1) (206)	1.050 (n)	PW=13 (1) PF=10 PM=34 PA=0.1	1.05		43 (109)
44	HCHO HOAc	15 60	20 (68)	101.0 (1) (214)	1.099 (p)	PW=10 (1) PF=1 PA=7	1.55		54 (129)
69	Paraform	91-93		Decomposes	Solid	PF = 1.45 (g) @ 25°C	1.03 (q)	70 (f,h) (158)	
70	Paraform	95-97		Decomposes	Solid	PF = 1.45 (g) @ 25°C	1.03 (q)	69 (f,h) (157)	
71	Paraform	95-97		Decomposes	Solid	PF = 1.45 (g) @ 25°C	1.03 (q)	69 (f,h) (157)	

PW = P_{H2O} PF = P_{HCHO} PM = P_{CH3OH} PB = P_{i-BuOH} or P_{n-BuOH} PA = P_{HOAc}

Compound	Flammable Limits, mol% Lower	Upper	Reference
Formaldehyde	7.0	73	(8)
Methanol	6.7	36	(9)
n-Butyl Alcohol	1.4	11.2	(8)
i-Butyl Alcohol	1.7	10.6	(8)
Acetic Acid	5.3	16.6	(10)

TABLE I CONTINUED

TABLE I (Footnotes)

(a) Calculated from boiling points of similar mixtures...data supplied by Mr. [redacted] of [redacted] (3), unless otherwise specified.
(b) Calculated from VLE data at the specified storage temperature...data supplied by Mr. [redacted] of [redacted] (3), unless otherwise specified.
(c) Calculated from the liquid composition. Assumes complete vaporization of product.
(d) Data taken from Ref. (5).
(e) Interpolated from the data for 37 and 50 weight percent formaldehyde in Ref. (6).
(f) Data taken from Ref. (6).
(g) Data taken from Ref. (5).
(h) The lower explosion limit for paraformaldehyde dust is 0.04 oz/cu ft or 3.4 wt% in air (5).
(i) All flash points are given as Tag Closed Cup (TCC), unless otherwise specified.
(j) Calculated by the procedure described in the Appendix.
(k) Tag Open Cup (TOC) from Ref. (6).
(l) Experimentally determined at [redacted] (2).
(m) Taken from pounds per gallon Tables used at the Chemcel Plant in [redacted] (7).
(n) Obtained by interpolation or extrapolation of experimental data in this Table.
(o) Estimated from a [redacted] Product Bulletin for i-Butyl Formcel (12).
(p) Experimentally determined at [redacted]. See Laboratory Notebook No. 35935, p. 21.
(q) Calculated as the ratio of molecular weights of formaldehyde and air (30/29 = 1.03).
(r) Information taken from [redacted] Product Bulletin (11).
(s) Determined by extrapolation of data in Ref. (6).

APPENDIX

Calculation of Flash Points

Flash points were calculated for all liquid mixtures. This was done, assuming that the lower flammable limit (L_f) of the vapor above the liquid mixture is equivalent to the TCC flash point. The experimental methods differ only in how the vapor is introduced into the apparatus. In the TCC method the liquid mixture is gradually heated in a closed chamber with air. The gaseous mixture is repeatedly tested for flammability with a spark until it ignites. The temperature of the liquid at which ignition occurs is the flash point. In methods to determine the lower flammable limit, synthetic gas mixtures containing air are fed into a closed chamber, until one is found which can be ignited with a spark.

Zebetakis (9) defines a procedure for calculating the L_f of a mixture, when the L_fs of each pure component are known. The formula given is:

$$\frac{1}{L_f(\text{mixture})} = \frac{n_1}{L_{f1}} + \frac{n_2}{L_{f2}} + \frac{n_3}{L_{f3}} \ldots \qquad 1$$

when n_i is the mole fraction of component i. For example, consider a vapor mixture containing 60 mole % methanol (L_f = 6.7%), 30% formaldehyde (L_f = 7.0%), and 10 mole % acetic acid (L_f = 5.3%). The calculation gives

$$\frac{1}{L_f(\text{mixture})} = \frac{0.6}{6.7} + \frac{0.3}{7.0} + \frac{0.1}{5.3}$$

and L_f(mixture) = 6.6%.

This means that when the composition of the three components in air exceeds a total of 6.6 mole%, the mixture will be flammable.

The vapor composition of each mixture was calculated for numerous temperatures until the temperature was found that gives a flammable composition per equation 1. In effect we simulated the TCC experiment using the computational method.

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