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**COMMITTEE OF EXPERTS ON THE TRANSPORT OF
DANGEROUS GOODS AND ON THE GLOBALLY
HARMONIZED SYSTEM OF CLASSIFICATION
AND LABELLING OF CHEMICALS**

Sub-Committee of Experts on the
Transport of Dangerous Goods

Twenty-fifth session, 5-14 July 2004
Item 6 of the provisional agenda

LISTING, CLASSIFICATION AND PACKING

Proposal to amend the proper shipping name of Crotonaldehyde (UN 1143)

Transmitted by the International Council of Chemical Associations (ICCA)

Introduction

1. Crotonaldehyde is listed in the Dangerous Goods List under UN 1143 as “CROTONALDEHYDE, STABILIZED”.
2. According to this description, the substance can therefore only be transported in stabilized form. However the reason for this restriction may no longer be valid: indeed Crotonaldehyde, in its commercial pure form, has been handled and stored in large quantities in the process industry since many years, without any unintentional self-reaction.
3. The thermal stability of Crotonaldehyde (2-Butenal) is documented in the literature. The report on the environmentally relevant substance Crotonaldehyde (BUA-Stoffbericht 98, Gesellschaft Deutscher Chemiker, S. Hirzel Wissenschaftliche Verlagsgesellschaft, 1993) states that commercial pure Crotonaldehyde does not show a significant thermal decomposition below 275 °C. Heavy metal salts may catalyze the oxidation of Crotonaldehyde forming the corresponding acid.

Re-investigation of the thermal stability of Crotonaldehyde

4. The thermal stability of Crotonaldehyde was reinvestigated. A commercial grade sample was used with a purity of > 99,0 % by mass. Main impurity was water (150 ppm). All other constituents were below 100 ppm. A test procedure was chosen following closely the test method H.2 of the UN Manual of Tests and Criteria, fourth edition, 2003. The study was extended by differential scanning calorimetry (DSC) of the used Crotonaldehyde (see **Annex**).

5. The results of these investigations are:
- DSC-measurements: Crotonaldehyde shows a decomposition reaction above 200 °C with an exothermic energy of – 900 J/g. The heat release is spread over a wide temperature range from 200 to 400 °C.
 - Adiabatic storage test following closely test H.2: This test was performed following closely the test procedure H.2 but under confined conditions to avoid any heat loss by evaporation and in a full adiabatic mode. For the same reason the external heater was excluded and the thermal isolation measured with the substance in the Dewar vessel during heating up period (see Annex on the determination of the SADT of Crotonaldehyde). The experiments demonstrate that self accelerating decomposition can be excluded as long as the storage temperature does not exceed 85 °C. For the heat loss of the portable tank a heat loss rate of 2 mW/kg/K was assumed (table 28.3: heat loss per unit mass from packages; Manual of Tests and Criteria). The temperature of the TMR₂₄ (Time to maximum rate for a period of 24 hours) was evaluated from the data to be above 130 °C.
 - The tests do not give any evidence that the substance may have explosive properties although the heat of decomposition is high.
6. According to these new results the transport of Crotonaldehyde, in its commercial pure form, does not require to be stabilized. Therefore this proposal will not lead to a decrease in the level of safety.
7. Crotonaldehyde with a lower technical purity, or formulations derived from it, should be transported in accordance with the classification resulting from the determination of its dangerous properties. This lower grade of Crotonaldehyde is being transported in much smaller quantities than the pure grade and can therefore be transported, if required, under an appropriate n.o.s. entry.

Proposal

8. Remove “STABILIZED” from the name and description for UN 1143 in column 2 of the Dangerous Goods List of Chapter 3.2 so that it becomes “CROTONALDEHYDE”.
9. As a consequential amendment, the alphabetical index of substances and articles is to be amended accordingly.

Annex (Figures in English only)

Results of the kinetic study on the thermal stability of Crotonaldehyde

10. The thermal stability of Crotonaldehyde was reinvestigated in the test laboratories of Siemens Axiva GmbH, 65926 Frankfurt, Industriepark Höchst, C 487, Germany.

11. The used sample matched the commercial grade quality and was taken without further purification. The sample had a purity of > 99,0 % by weight with water as the main impurity (150 ppm) and all other impurities below 100 ppm.

Differential Scanning Calorimeter

12. The thermal stability was first screened by Differential Scanning Calorimetry (DSC). 10 mg of the substance were sealed into a glass sample holder and heated with a rate of 3 K/min up to 450 °C. The decomposition begins at a temperature of 200 °C releasing an energy of -900 J/g (mean value of several measurements), **Figure 1**. The decomposition extends over a wide temperature range between 200 and 400 °C with the maximum at 310 °C.

Heat accumulation test

13. The test was performed following closely the procedure of test H.2 of the UN Manual on Tests and Criteria. To improve the thermal isolation of the sample the Dewar was set into an autoclave which was afterwards tightly closed. Thermal couples were located in the centre of the sample and in the mantle of the autoclave. A pressure transducer measured the pressure inside the autoclave. The autoclave was homogeneously heated by an aluminium block oven. The temperature gradient at starting temperature was less than 0.5 K from top to bottom of the autoclave and proved to be negligible regarding the sensitivity of the measuring system. The system was totally closed, only the cable of the thermal couple and the pressure transducer were connected to the data recording system. For the same reasons any device to preheat the sample was not used. Due to the thermal isolation of the Dewar the time to get a temperature equilibrium in the system is in the order of 48 h. The Dewar had a volume of 200 ml and was filled with about 140g Crotonaldehyde.

14. In order to improve the sensitivity of the test procedure the autoclave temperature followed the sample temperature once the sample temperature exceeded ambient temperature by self-heating. The study was done under totally adiabatic conditions to match the required sensitivity for the assessment of the results.

15. Two runs were carried out. The first one was started at a temperature of 142 °C. At this temperature the Crotonaldehyde shows self-heating, **Figure 2**. The second run was started at 100°C. After 50 h, where no self-heating was detected, the ambient temperature was raised in 10 K steps. At 140°C self-heating was strong enough to switch the system into the adiabatic mode, **Figure 3** with test 1 in comparison.

16. Both runs differ by the thermal stress of the substance during which the sample may be altered without any detectable heat release. Tempering the sample should have endorsed any auto catalytic process but it seems that tempering suppresses any slow thermal decomposition of an impurity. (The DSC diagram, Figure 1, shows a minor reaction at the beginning of the decomposition indicating a complex reaction mechanism.).

17. In order to evaluate the influence of tempering on the thermal stability of Crotonaldehyde, the measured self-heating rates of both experiments are plotted in the form of an Arrhenius plot in **Figure 4**. The first run without tempering shows a "pre"-reaction which slows down at higher temperatures. The

second run with tempering seems to be thermally more stable at lower temperatures but follows the same decomposition kinetics at higher temperatures. It is obvious that tempering increases the thermal stability significantly. Prolonged exposure to higher temperature is more likely under transport conditions in portable tanks due to the thermal inertia of such tanks.

18. A zero order kinetic model was fitted to the data for both runs in the temperature range of low consumption of product. For run 1 the temperature range was limited between 140 and 170 °C, for run 2 (tempered sample) the model was adjusted to the data in the range between 150 and 185 °C. The fits to the data lead to activation energies of 100 kJ/mol for run 1 and 102 kJ/mol for run 2.

19. On the basis of these best fits the SADT was evaluated according to test method H.2 (Manual of Tests and Criteria). A constant specific heat of 2500 kJ/kg/K was assumed for the whole temperature range. The specific heat was experimentally determined by DSC at 140 °C.

Gas production

20. The exothermic reaction shows a pressure increase detectable at about 140°C with a very low rate of about $1 \cdot 10^{-2}$ ℓ/kg/min. Above 300°C the gas production has a maximum with 10 ℓ/min/kg. These data were estimated on the basis of a free gas volume of 0.5 ℓ in the autoclave.

Determination of “Time to Maximum Rate” (TMR₂₄) for the induction period of 24 hours

21. The TMR (Time to maximum rate) is defined as the time gap at the given temperature to the point of the maximum decomposition reaction. Plotting the measured induction times as a function of the sample temperature allows an extrapolation to the induction time of 24 h which is frequently used as a reference value for the communication of data on thermal stability, **Figure 5**. Given are only the data for the run with the lower SADT temperature, run 1. Run 2 would result in a higher value for the TMR at a selected temperature. Based on the results of run 1 an adiabatic induction time of 24 h is confirmed for a sample temperature of 134 °C.

Determination of the Self Accelerating Decomposition Temperature (SADT)

22. The Self Accelerating Decomposition Temperature (SADT) is derived from the best fit of the kinetic model to the decomposition reaction as shown in figure 4. The reaction power is calculated from the measured rate of temperature increased using the measured specific heat of 2500 J/kg/K of Crotonaldehyde at 140 °C following the procedure as given in the description of test H.2, **Figure 6**. Both runs differ due to the increase in the thermal stability with tempering.

23. The limiting temperature for safe storage is given by the intersection of the tangent to the self-heating rate with the x-axis. The SADT is then derived by rounding the temperature of the intersection point to the next higher number which can be divided by 5.

24. The heat loss of a portable tank (20 000 l) is assumed to be 2 mW/kg/K (Table 28.3 of the Manual of Tests and Criteria).

25. The critical ambient temperature is determined to be 84 °C (run 1) respectively 99 °C (run 2). The SADT temperature for a portable tank container would then be 85 °C following this procedure and taken into account the worst case conditions.

26. The SADT of a portable tank filled with Crotonaldehyde is above 75 °C, the border line for any substance following into the class 4.1 “self-reactive substances”.

27. The results of the experiments are summarized in the table:

Run	Sample size Crotonaldehyde	Ambient temperature	Time to maximum rate TMR ₂₄	Temp. max /	Pressure max	Activation Energy - "pre"reaction - main reaction
	[g]	[°C]	[°C]	[°C]	[bar]	[kJ/mol]
1	143	142	134	293	80	100
2	141	100 to 130 140	148	310	114	102

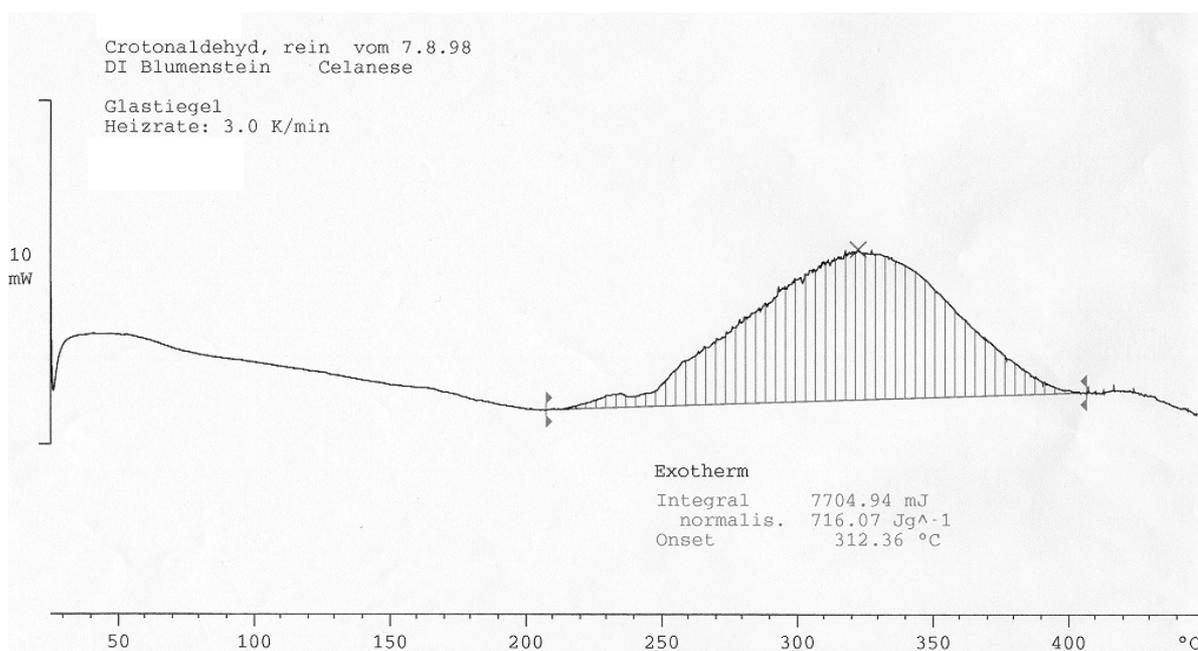


Figure 1: Differential scanning calorimetry of crotonaldehyde (Glas pan, heating rate 3K/min)

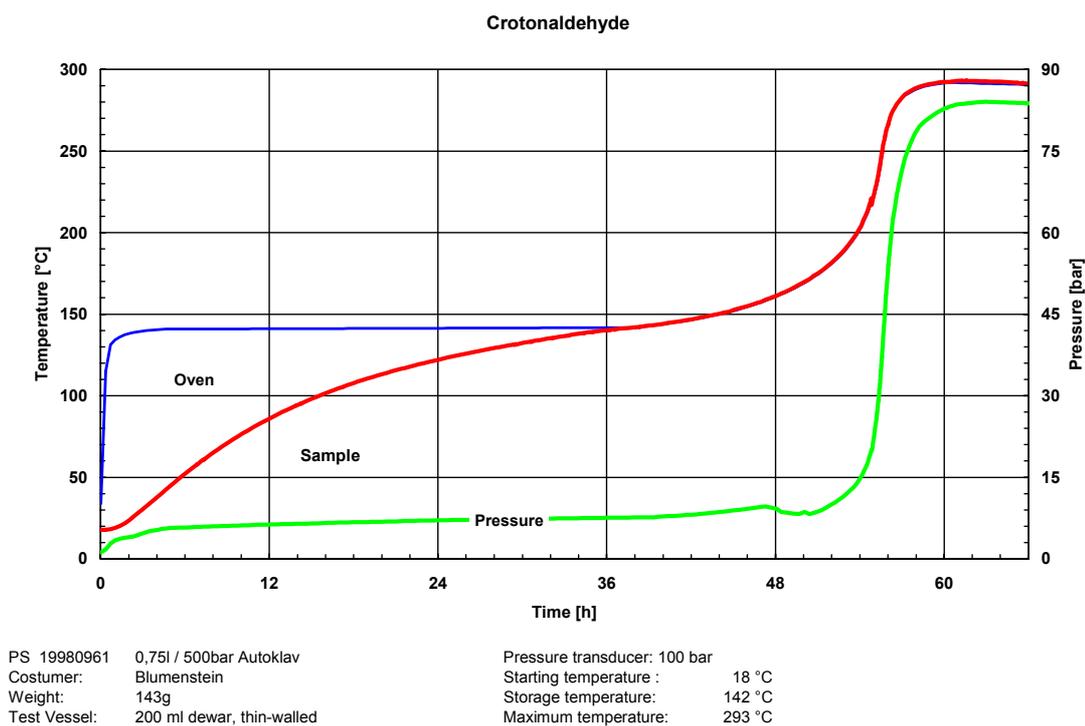


Figure 2: Temperature / Pressure plot of experiment run 1.

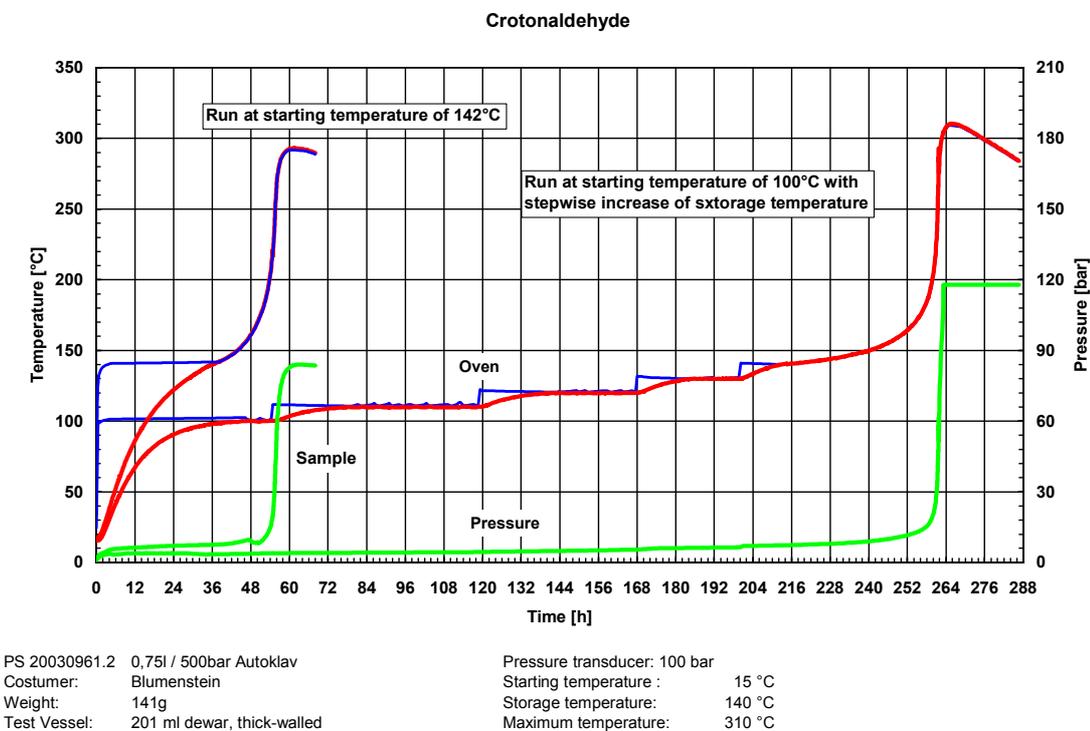


Figure 3: Temperature / Pressure plot of experiment run 2 in comparison with run 1

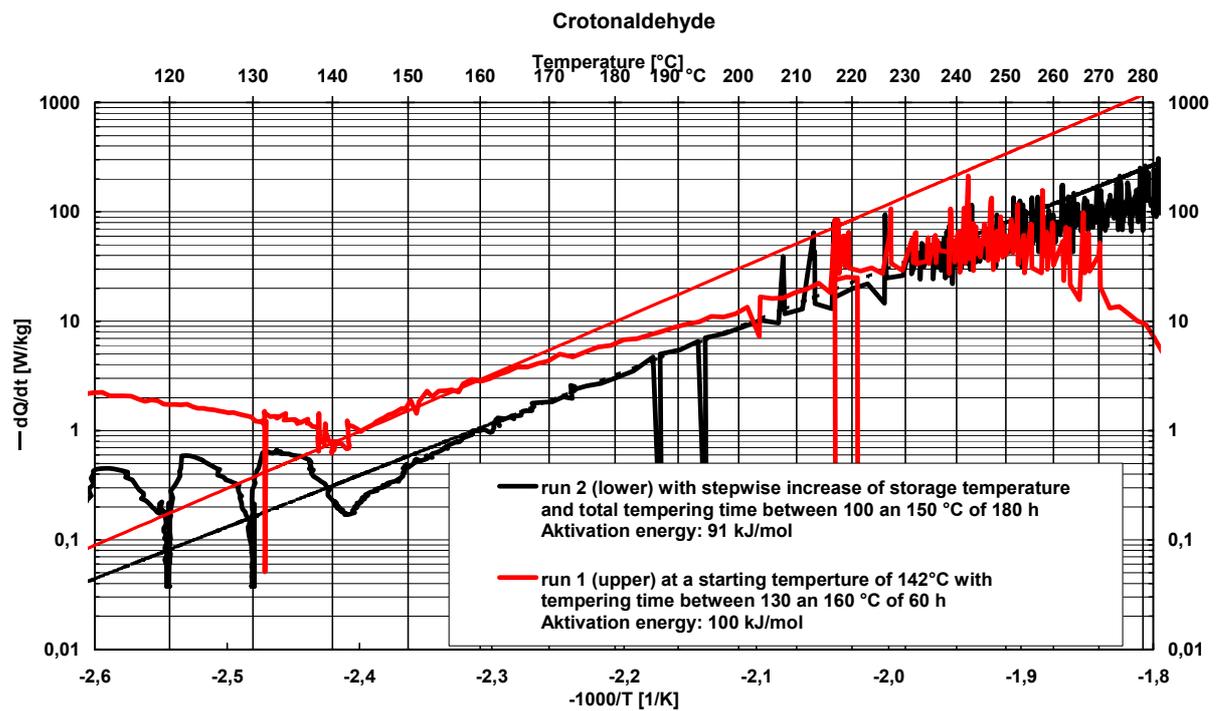
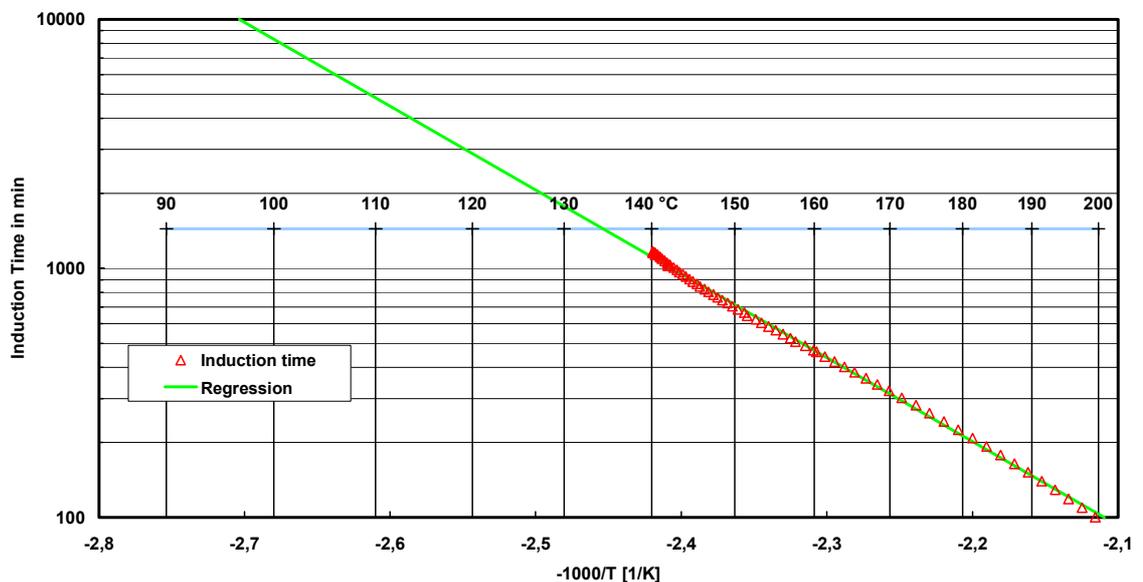


Figure 4: Arrhenius plot of the self-heating rate and fitted zero order kinetic model
Crotonaldehyde



Ergebnis: AZT24 = 134 °C

Regression: $\log(\text{TMR})[\text{min}] = A + (-B / T[\text{K}])$

PS 19980961 0,75l / 500bar Autoklav

Costumer: Blumenstein

Weight: 143g

Test Vessel: 200 ml dewar, thin-walled

A = -5,10242

B = -3366,66

Ea = 64 kJ/mol

Pressure transducer: 100 bar

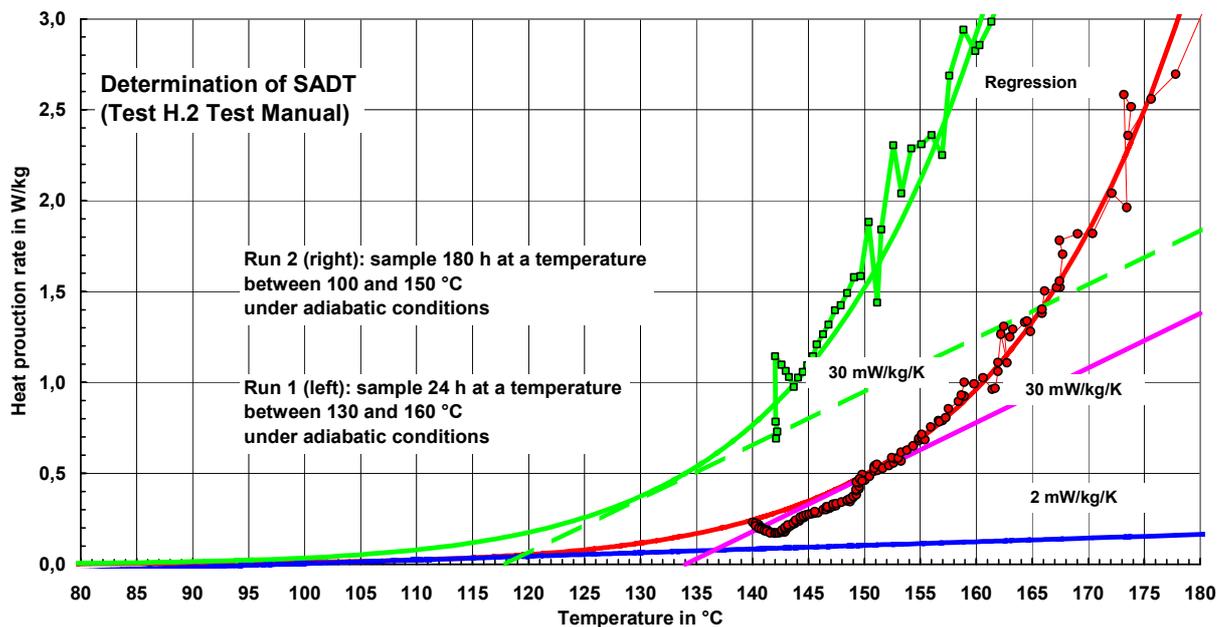
Starting temperature : 18 °C

Storage temperature: 142 °C

Maximum temperature: 293 °C

Figure 5: Time to maximum rate

Crotonaldehyde



Schnittpunkt mit der x-Achse = 99 °C
 PS 20030961.2 0,75l / 500bar Autoklav
 Costumer: Blumenstein
 Weight: 141g
 Test Vessel: 201 ml dewar, thick-walled

Pressure transducer: 100 bar
 Starting temperature : 15 °C
 Storage temperature: 140 °C
 Maximum temperature: 310 °C

Figure 6: Self Accelerating Decomposition Temperature for a portable tank with a heat of 2 mW/kg/K

**DATA SHEET TO BE SUBMITTED TO THE UNITED NATIONS
FOR NEW OR AMENDED CLASSIFICATION OF SUBSTANCES**

Submitted by **International Council of Chemical Associations**Date **1 March 2004**

Supply all relevant information including sources of basic classification data. Data should relate to the product in the form to be transported. State test methods. Answer all questions - if necessary state "not known" or "not applicable" - If data is not available in the form requested, provide what is available with details. Delete inappropriate words.

Section 1. SUBSTANCE IDENTITY

- 1.1 Chemical name **CROTONALDEHYDE**
- 1.2 Chemical formula **C₄H₆O contains 5% Cis- and 95% Trans-Crotonaldehyde**
- 1.3 Other names/synonyms **Propylene Aldehyde, 2-Butenal**
- 1.4.1 UN number**1143**
- 1.4.2 CAS number**4170-30-3 Commercial product**
- 1.5 Proposed classification for the Recommendations
- 1.5.1 proper shipping name (3.1.2¹) **CROTONALDEHYDE**
- 1.5.2 class/division **6.1**
- subsidary risk(s) **3**
- packing group **I**
- 1.5.3 proposed special provisions, if any
- 1.5.4 proposed packing instruction(s) **P001**

Section 2. PHYSICAL PROPERTIES

- 2.1 Melting point or range **-75 °C**
- 2.2 Boiling point or range **102 °C**
- 2.3 Relative density at :
- 2.3.1 15 °C
- 2.3.2 20 °C**0.8531**
- 2.3.3 50 °C
- 2.4 Vapour pressure at :
- 2.4.1 50 °C**9.3 kPa**
- 2.4.2 65 °C kPa
- 2.5 Viscosity at 20 °C² **0.82 (mPas) m²/s**
- 2.6 Solubility in water at 20 °C **15 g/100 ml**
- 2.7 Physical state at 20°C (2.2.1.1¹) **liquid**

1 *This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.*

2 *See definition of "liquid" in 1.2.1 of the Model Regulations on the Transport of Dangerous Goods.*

- 2.8 Appearance at normal transport temperatures, including colour and odour **Colourless liquid, clear, tar odour**
- 2.9 Other relevant physical properties **Changes colour when exposed to light or air**

Section 3. FLAMMABILITY

- 3.1 Flammable vapour
 - 3.1.1 Flash point (2.3.3¹) **10 °C cc**
 - 3.1.2 Is combustion sustained? (2.3.1.3¹) **yes**
- 3.2 Autoignition temperature **160 °C**
- 3.3 Flammability range (LEL/UEL) **2.0 / 30.0 %**
- 3.4 Is the substance a flammable solid? (2.4.2¹) **no**
 - 3.4.1 If yes, give details

Section 4. CHEMICAL PROPERTIES

- 4.1 Does the substance require inhibition/stabilization or other treatment such as nitrogen blanket to prevent hazardous reactivity ? **no**
If yes, state:
 - 4.1.1 Inhibitor/stabilizer used
 - 4.1.2 Alternative method
 - 4.1.3 Time effective at 55 °C.....
 - 4.1.4 Conditions rendering it ineffective
- 4.2 Is the substance an explosive according to paragraph 2.1.1.1? (2.1¹) **no**
 - 4.2.1 If yes, give details
- 4.3 Is the substance a desensitized explosive? (2.4.2.4¹) **no**
 - 4.3.1 If yes, give details
- 4.4 Is the substance a self-reactive substance? (2.4.1¹) **no**
If yes, state:
 - 4.4.1 exit box of flow chart... ..
What is the self-accelerating decomposition temperature (SADT) for a 50 kg package? **>110 °C**
Is the temperature control required? (2.4.2.3.4¹) **no**
 - 4.4.2 proposed control temperature for a 50 kg package °C
 - 4.4.3 proposed emergency temperature for a 50 kg package °C

1 This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.

- 4.5 Is the substance pyrophoric? (2.4.3¹) **no**
4.5.1 If yes, give details
- 4.6 Is the substance liable to self-heating? (2.4.3¹) **no**
4.6.1 If yes, give details
- 4.7 Is the substance an organic peroxide (2.5.1¹) **no**
If yes state:
4.7.1 exit box of flow chart...
What is the self accelerating decomposition temperature (SADT) for a 50 kg package?... °C
Is temperature control required? (2.5.3.4.1¹) yes/no
4.7.2 proposed control temperature for a 50 kg package °C
4.7.3 proposed emergency temperature for a 50 kg package °C
- 4.8 Does the substance in contact with water emit flammable gases? (2.4.4¹) **no**
4.8.1 If yes, give details
- 4.9 Does the substance have oxidizing properties (2.5.1¹) **no**
4.9.1 If yes, give details
- 4.10 Corrosivity (2.8¹) to:
4.10.1 mild steel mm/year at °C
4.10.2 aluminium mm/year at °C
4.10.3 other packaging materials (specify)
..... mm/year at °C
..... mm/year at °C
- 4.11 Other relevant chemical properties

Section 5. HARMFUL BIOLOGICAL EFFECTS

- 5.1 LD₅₀, oral (2.6.2.1.1¹) **206** mg/kg Animal species **rat**
- 5.2 LD₅₀, dermal (2.6.2.1.2¹) **380** mg/kg Animal species **rabbit**
- 5.3 LC₅₀, inhalation (2.6.2.1.3¹) .. mg/litre Exposure time **2** hours
or **200** ml/m³ Animal species **mouse**
- 5.4 Saturated vapour concentration at 20 °C (2.6.2.2.4.3¹) **38 (Chemsafe)** ml/m³

1 This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.

