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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**
**(Nineteenth session, 2-6 July 2001, agenda item 8 (d))**

# EXPLOSIVES, SELF-REACTIVE SUBSTANCES AND ORGANIC PEROXIDES

## Miscellaneous proposals

## UN 3242 - Amendment to Special Provision 215

## Transmitted by the International Council of Chemical Associations (ICCA)

### Background

1. Azodicarbonamide (AC) is widely used in industry as a cellular blowing agent for polymers.

2. Technically pure AC and its formulations are classified for transport as dangerous goods of Class 4 Division 4.1. The substance and its formulations with a self-accelerating decomposition temperature (SADT) of 75 °C or less, and an energy of decomposition of 300 J/g or more, are classified under one of the generic entries for self-reactive substances of this Division, but those with an SADT above 75 °C are classified as desensitised explosive under AZODICARBONAMIDE UN 3242, in accordance with Special Provision 215.

3. In the past it has generally been the practice for technically pure azodicarbonamide and high concentration formulations to be supplied to manufacturers of cellular plastics who then blend them with a polymer. It is however becoming increasingly common for the polymer blends themselves to be manufactured and transported. Such mixtures contain relatively low levels of AC and do not present a hazard of Division 4.1 during transport.

4. The purpose of this paper is to propose, for consideration by the Committee, a limiting concentration of azodicarbonamide in AC formulations below which a formulation is not considered a dangerous good of UN 3242 for the purposes of transport, based on the principles of classification contained in the *Model Regulations* and the *Manual of Tests and Criteria*. Formulations meeting the criteria of a self-reactive substance are not affected by the proposed change.

**Proposal**

5. Add the following text to special provision 215:

"Homogeneous mixtures containing not more than 40% by weight azodicarbonamide, and for which the acceptance procedure for Class 1 explosives need not be applied (see paragraph 2.4.2.4.2 a) and Appendix 6, paragraph 3.3 of the *Manual of Tests and Criteria,*), are not subject to these Regulations provided they do not meet the established defining criteria of any other class or division."

**Justification**

6. The principles of classification for an azodicarbonamide based formulation of UN 3242 in Division 4.1 are set out in paragraph 2.4.2.4.2 of the Model Regulations and Special Provision 215 applies.

Paragraph 2.4.2.4.2 states:

> *"Substances that:*
>
> *(a) have been provisionally accepted into Class 1 according to Test Series 1 and 2 but exempted from Class 1 by Test Series 6;*
> *(b) are not self-reactive substances of Division 4.1;*
> *(c) are not substances of Class 5;*
>
> *are also assigned to Division 4.1: UN 2956, UN 3241, UN 3242 and UN 3251 are such entries."*

and Special Provision 215 of UN 3242 (AZODICARBONAMIDE) states:

> *" This entry only applies to the technically pure substance or to formulations derived from it having an SADT higher than 75 ºC and therefore does not apply to formulations which are self-reactive substances. (For self-reactive substances see 2.4.2.3.2.3)."*

As with the other substances to which paragraph 2.4.2.4.2 refers, assignment of an AC based mixture to this division implies that it was initially considered as candidates for Class 1, but excluded on the basis of Test Series 6.

7. AC formulations containing not more than 40% by weight of azodicarbonamide with at least 60% inert have an energy of decomposition of less than 500 J/g (see Annex). Mixtures with such low energies of decomposition are not required to be considered as candidates for Class 1 (*Manual of Tests and Criteria*, Appendix 6: "Screening procedures for substances that may have explosive properties", paragraph 3.3(c)). Paragraph 3.3(c) of Appendix 6 states:

> *"When the organic substance or a homogenous mixture of organic substances contain chemical groups associated with explosive properties but the exothermic decomposition energy is less than 500 J/g and the onset of exothermic decomposition is below 500 ºC. (The temperature limit is to prevent the procedure being applied to a large number of organic materials which are not explosive but which will decompose slowly above 500ºC to release more than 500 J/g). The exothermic decomposition energy may be determined using a suitable calorimetric technique (see 20.3.3.3);...."*

8. An AC based formulation with an energy of decomposition of less than 500 J/g is not required to be considered as a candidate for Class 1. Such a formulation would not therefore meet criterion (a) of paragraph 2.4.2.4.2 and would not be subject to the requirements of the Model Regulations, providing it does not meet the criteria or definition of another Class or Division of dangerous good. Consequently it is proposed to limit the application of UN 3242 to high strength formulations by the application of the new wording of Special Provision 215.

9. The concept of a limiting concentration below which a substance is not considered to present a hazard during transport is widely applied in the Model Regulations and, of the other entries cited in paragraph 2.4.2.4.2 of the Model Regulations, Special Provision 226 applies a concentration limit (of 70%) to formulations containing isosorbide-5-mononitrate (UN 3251).

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**Annex**

**Data for azodicarbonamide formulations containing different diluents and activator systems plotted as Heat (Energy) of Decomposition versus Azodicarbonamide (AC) Content (Weight %)**

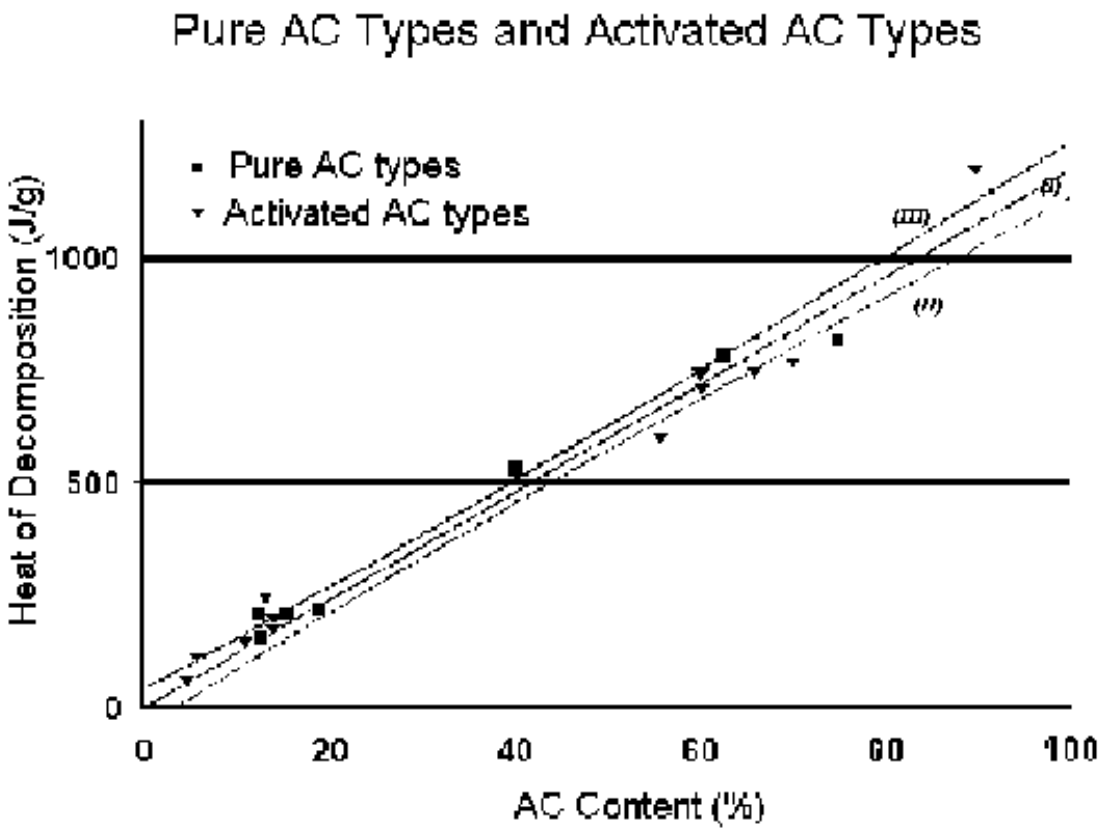


**Figure 1: Graph showing the correlation between the energy of decomposition and AC content**

| | | |
|---|---|---|
| **Samples:** | Pure azodicarbonamide in formulation: | 9 |
| | Activated azodicarbonamide in formulation: | 12 |
| | Total: | 21 |

**Lines:** (I) Regression line
(II) and (III) 95% confidence limits

The graphical plot shows that the 500 J/g threshold for the energy of decomposition occurs when the azodicarbonamide content is 40% by weight.

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# Thermal Properties of Azodicarbonamide Formulations

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Report No.:98/10547 Thermal Properties of Azodicarbonamide Formulations

# Safety Assessment

Dr. D. Heitkamp

## 1. Assessment Task

A wide range of azodicarbonamide (AC) formulations were to be tested with respect to their thermal properties. The influence of their ingredients on the decomposition behavior was to be studied, and a correlation between the azodicarbonamide content and the decomposition energy was to be found.

## 2. Assessment

This is a short version (summary) of the study report for public purposes (presentation to the UN). All confidential information is disclosed.

The 22 formulations investigated cover a wide range of AC concentrations, activators and inert material (inorganic, organic, polymer). The overall decomposition energy was obtained from DSC measurements using the same machine (see below) and plotted against the known AC content. Activated and non-activated AC formulations were first treated separately.

A linear regression was performed on each group with the y intercept set to zero. The upper and lower confidence limits (95 % probability) were calculated and added to the plot.

The data obtained are as follows:

Correlation: (Decomposition energy) [J/g] = slope * (AC content) [%]

| | Pure AC formulations | Activated AC formulations | All AC formulations |
|---|---|---|---|
| Observations | **10** | **12** | **22** |
| Multiple correlation coeff (R) | **0,982** | **0,987** | **0,985** |
| R^2 | **0,965** | **0,974** | **0,971** |
| Intercept (set) | **0** | **0** | **0** |
| Slope | **11,8** | **12,0** | **11,9** |
| Standard error (regression) | **52,8** | **58,4** | **54,9** |
| Analysis of variation (ANOVA) | | | |
| Sums of squares (regression) | **684012** | **1413343** | **2099992** |
| Sum of squares (residue) | **25072** | **37507** | **63315** |
| Aver. sum of quares (residue) | **2786** | **3410** | **3015** |
| Standard error (slope) | **0,38** | **0,35** | **0,25** |
| Lower 95 % (slope) | **10,9** | **11,3** | **11,4** |
| Upper 95 % (slope) | **12,6** | **12,8** | **12,5** |

Since no significant differences between the 2 groups could be detected, they were united and a third regression calculation was performed. The results are given in the table. The corresponding plot is shown in diagram 3.

The regression line may be calculated from the formula

**(Decomp. energy) [J/g] = 11,9 * AC content [%].**

Upper (UCL) and lower (LCL) confidence limits are obtained from the following equation

**UCL = (Decomp. energy) + 2,08 * $(cl)^{0,5}$**

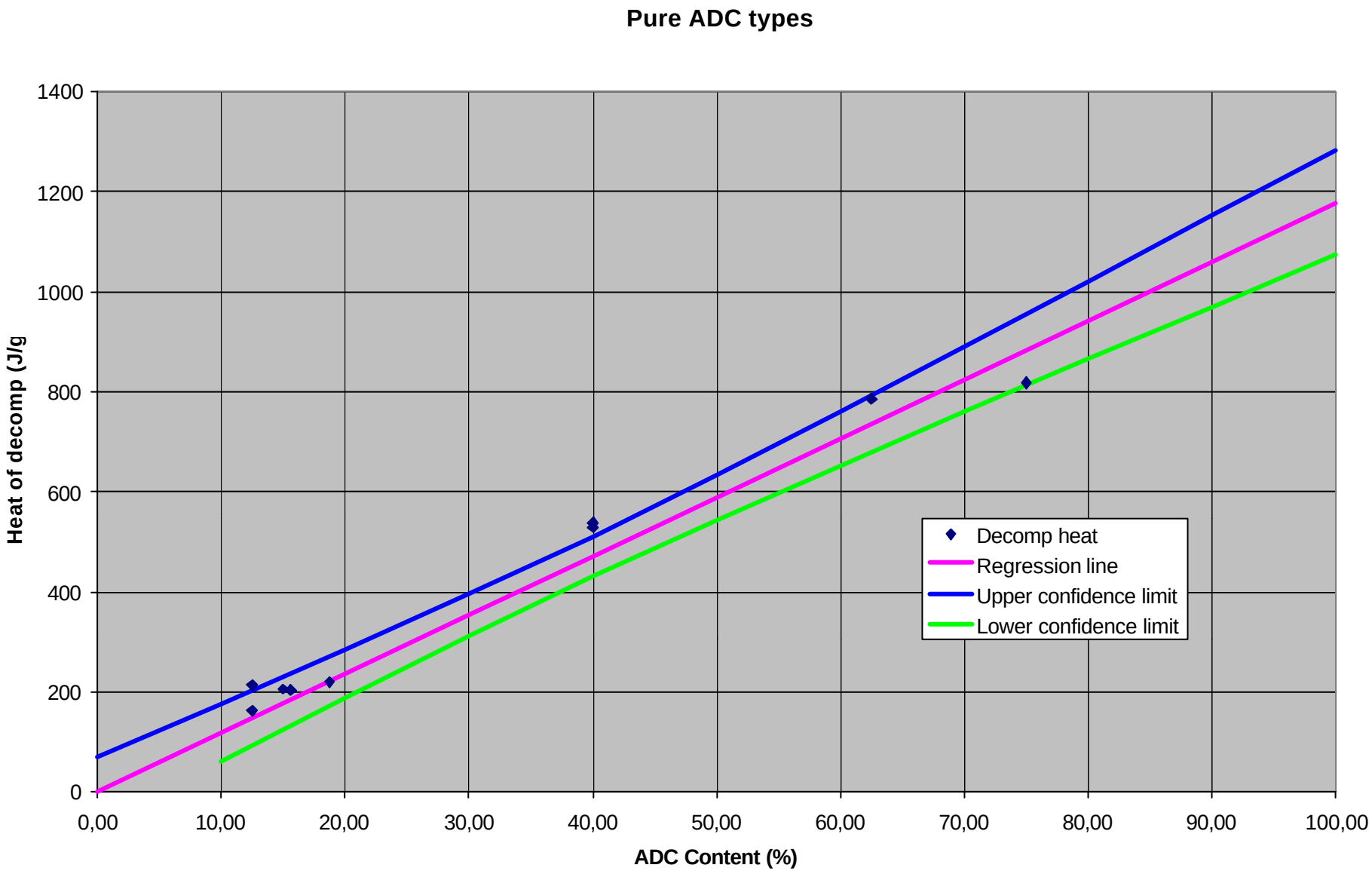
**LCL = (Decomp. energy) - 2,08 * $(cl)^{0,5}$** , with

**$(cl) = 3015 * (1/21 + ((AC\ content) - 37,773)^2 / 16508,2)$**

From these data one may calculate that for AC formulations containing less than 40 % AC, the decomposition energy will not exceed 500 J/g. According to the UN Manual of Tests and Criteria, Appendix 6, paragraph 3.3, for such formulations the acceptance procedure for Class 1 explosives need not be applied.

## 3. Notes

All measurements were performed on a DTA apparatus of Bayer's own development that had previously been carefully calibrated.


Pure ADC types
Heat of decomp (J/g
1400
1200
1000
800
600
400
200
0
0,00
10,00
20,00
30,00
40,00
50,00
60,00
70,00
80,00
90,00
100,00
ADC Content (%)
Decomp heat
Regression line
Upper confidence limit
Lower confidence limit

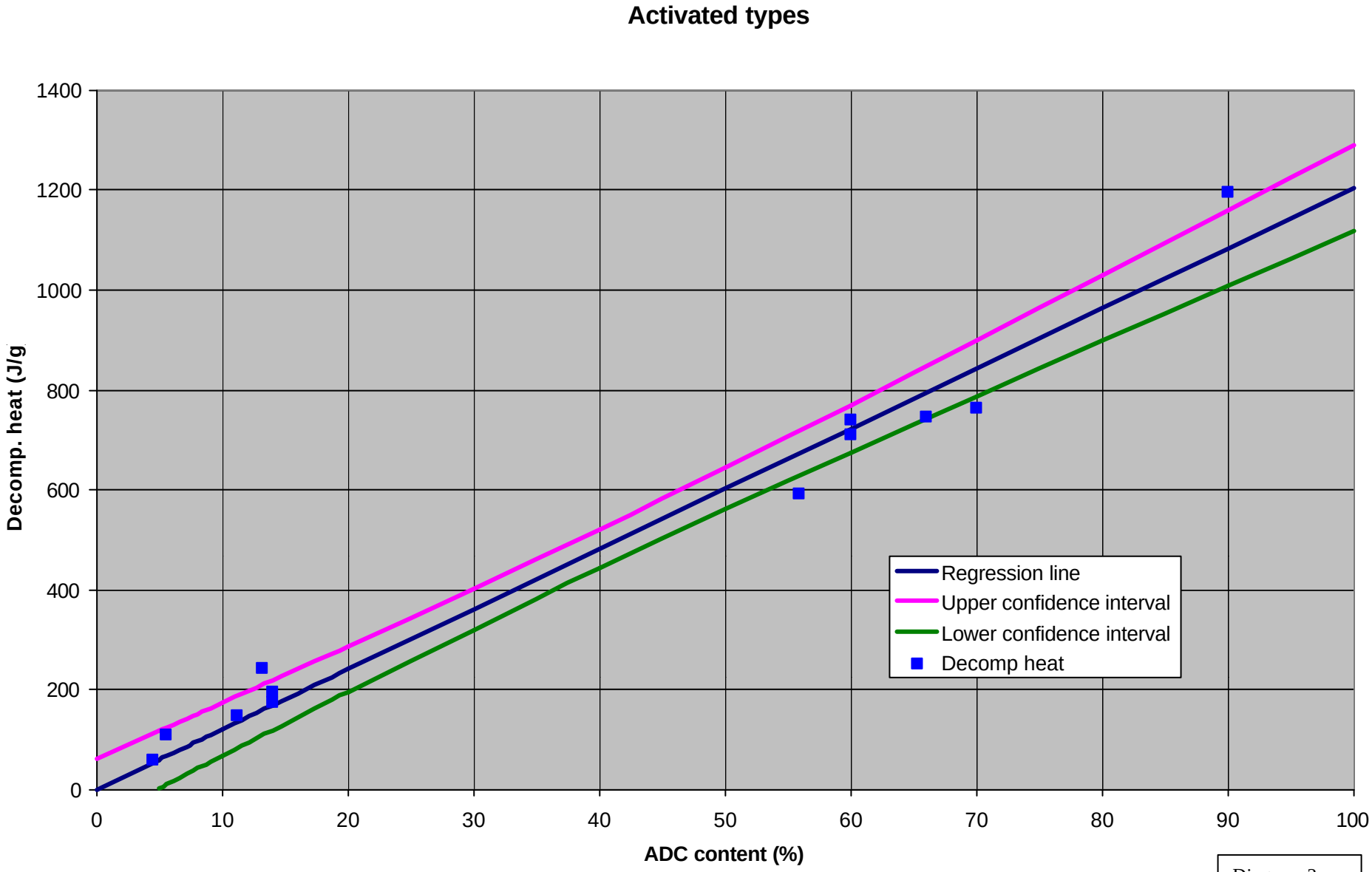

Activated types
Decomp. heat (J/g
1400
1200
1000
800
600
400
200
0
0
10
20
30
40
50
60
70
80
90
100
ADC content (%)
Regression line
Upper confidence interval
Lower confidence interval
Decomp heat

Diagram 2

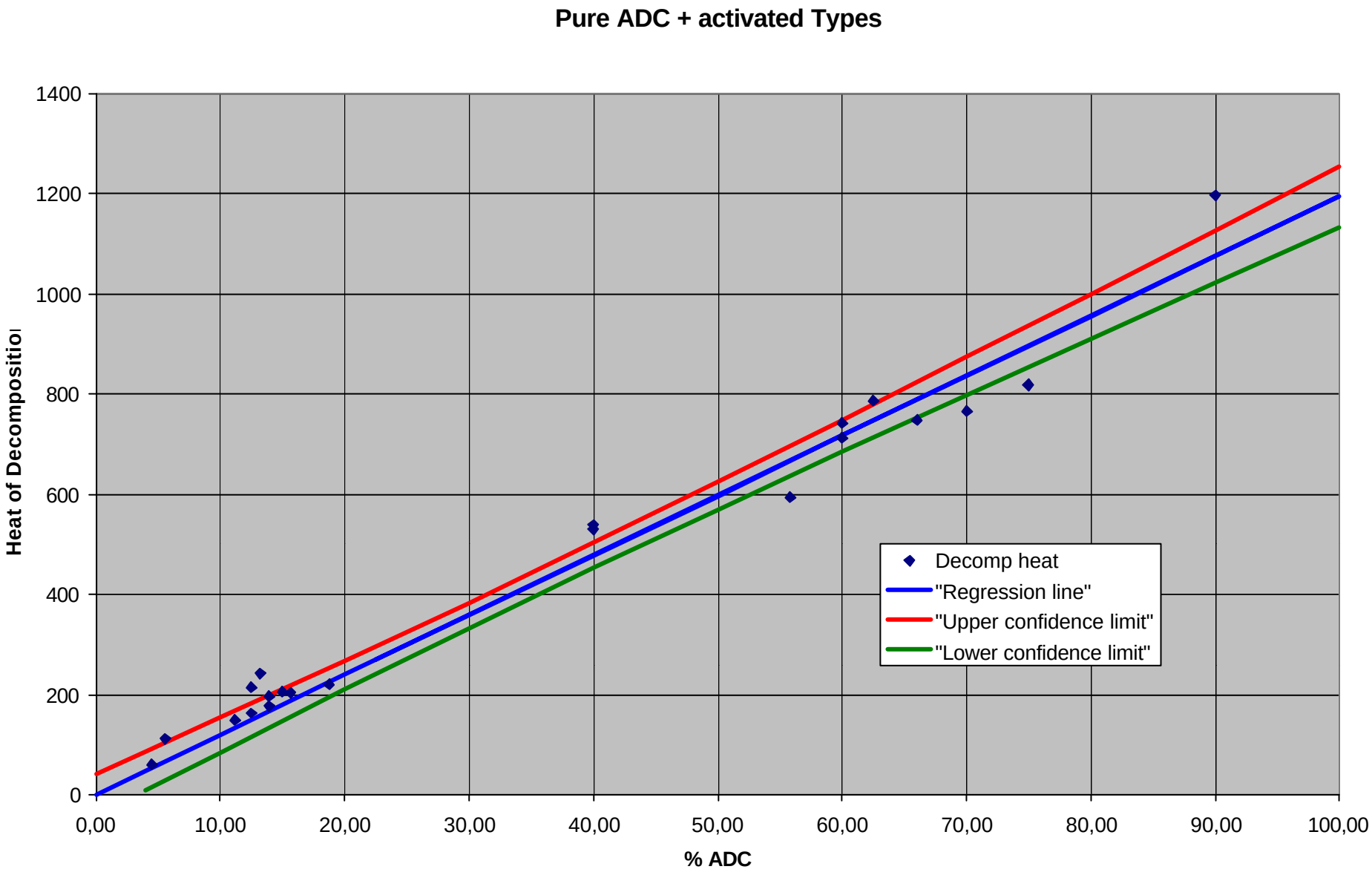

Pure ADC + activated Types
Heat of Decompositio
1400
1200
1000
800
600
400
200
0
0,00
10,00
20,00
30,00
40,00
50,00
60,00
70,00
80,00
90,00
100,00
% ADC
Decomp heat
"Regression line"
"Upper confidence limit"
"Lower confidence limit"

Diagram 3