Thermochimica Acta, 202 (1992) 181-189
Elsevier Science Publishers B.V., Amsterdam

Thermogravimetric analysis of urea-formaldehyde polycondensates [1]

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(Received 10 September 1991)

Abstract

A simple thermogravimetric method was performed on eight samples of urea-formaldehyde polycondensates; five samples were uncured glues from CHEMKO. A linear relationship between the temperatures of the characteristic peaks of the DTG curves and the sample weights of these polycondensates was found. The gradient of this line was closely related to the molecular structures of the above-mentioned polycondensates, and with the reactivities of the uncured glues, i.e. with their condensation ability.

INTRODUCTION

Urea-formaldehyde polycondensate (UFPC) products have found a wide range of applications, particularly as wood adhesives, in fertilizers containing slow-release nitrogen, in insulation materials and as chemical agents in paper technology. There is, however, no adequate thermoanalytical description of these compounds to evaluate their importance and exploitation in industry, although DTA [1,2,5] and TGA [3,5] have already been applied to the study of the thermolysis mechanism of UFPCs.

The existing literature reveals that the first endothermic peak of UFPC decomposition in DTA can be recorded as early as in the temperature range 80-100°C [2,6], the second within the temperature range 105-130°C [1,2,5,6], and the third at 230-255°C [1,5,6]; last but not least, the fourth may occur within the range 270-310°C [5]. According to Nakamura [1] it is possible to estimate the molar ratio of formaldehyde to urea in the corresponding UFPC from endotherms at temperatures above 200°C.

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[1] Presented in part at the 12th Conference on Thermal Analysis, TERMANAL 91, Slovak Chemical Society Meeting, Slovak Technical University, Bratislava, 26-28 June 1991.

EXPERIMENTAL

Apparatus

All the measurements were performed with TGA 7 (Perkin–Elmer) apparatus, operating at a rate of temperature increase of 20°C min^{-1}, with weighed samples of up to 7 mg, thermolysed in a nitrogen atmosphere.

Samples

A survey of UFPC samples (mostly products from CHEMKO) is shown in Table 1. In the following, individual samples are characterized in greater detail.

Adhesive LP is a solution of a multicomponent polycondensate, for production of agglomerated materials, of emission category E0 at 170–210°C.

Adhesive 3T is a three-component polycondensate, for production of agglomerated materials, emission category E1 at 90–210°C.

Diakol DM is an adhesive which is meant for veneering at 140–150°C.

Diakol M is an adhesive for production of agglomerated materials within the range 50–150°C.

Diakol F is meant for glueing current furniture items at normal temperatures.

Pergopak M2 is a cured urea-formaldehyde polycondensate (Ciba–Geigy), applied as a chemical agent in paper technology.

Chemoform is a linear UFPC, used as a chemical agent in paper technology, as an anticaking ingredient in crystalline compounds, as a component of fertilizers etc.

Methylenebisurea was prepared according to the method described in ref. 7 and was recrystallized once from distilled water.

Adhesive 3T and the Diakols were applied in the form of dry substances prepared by vacuum evaporation of water from them at 30°C.

Table 1 also shows the nitrogen contents of separate UFPC samples. For uncured polycondensates (glues), Table 1 also contains data on the condensation ability (KS_{100}) of glues at 100°C, set by the Czechoslovak State Standard [8]. This is defined as the time in which the sample of a given glue passes into gel form in a mixture with the curing agent.

RESULTS AND DISCUSSION

Examples of the results from TGA of the set of urea–formaldehyde polycondensates are shown in Figs. 1–4: Figures 1 and 2 show the influence of the weights of Adhesive LP on the peaks of the DTG curve in the corresponding TGA records. A common feature of the records obtained is

TABLE 1

Survey of the urea–formaldehyde polycondensates studied

Sample no. [a]	Urea–formaldehyde polycondensate	Nitrogen content (wt.%)	Condensation ability at 100°C KS_{100} (s)	Coefficients of eqn. (1)		
				A (°C mg^{-1})	B (°C)	Correlation coefficient
1	Adhesive LP	36.7	80–86	1.81 ± 0.22	304.55 ± 0.96	0.9851
2	Adhesive 3T	35.7	70–75	3.47 ± 0.60	301.35 ± 2.95	0.9717
3	Diakol M	28.7	60–68	4.33 ± 0.79	309.50 ± 2.48	0.9838
4	Diakol DM	25.6	Max. 55	5.37 ± 0.89	312.87 ± 2.39	0.9734
5	Diakol F	24.2	Max. 40	5.31 ± 1.77	310.66 ± 6.40	0.9043
6	Pergopak M2	33.5		11.58 ± 2.64	303.88 ± 6.82	0.9517
7	Chemoform	36.2		5.85 ± 0.54	307.55 ± 2.09	0.9836
8	Methylenebisurea	42.4		3.31 ± 1.87	299.47 ± 4.30	0.8701

[a] Samples 1–5 and 7 are products from CHEMKO.

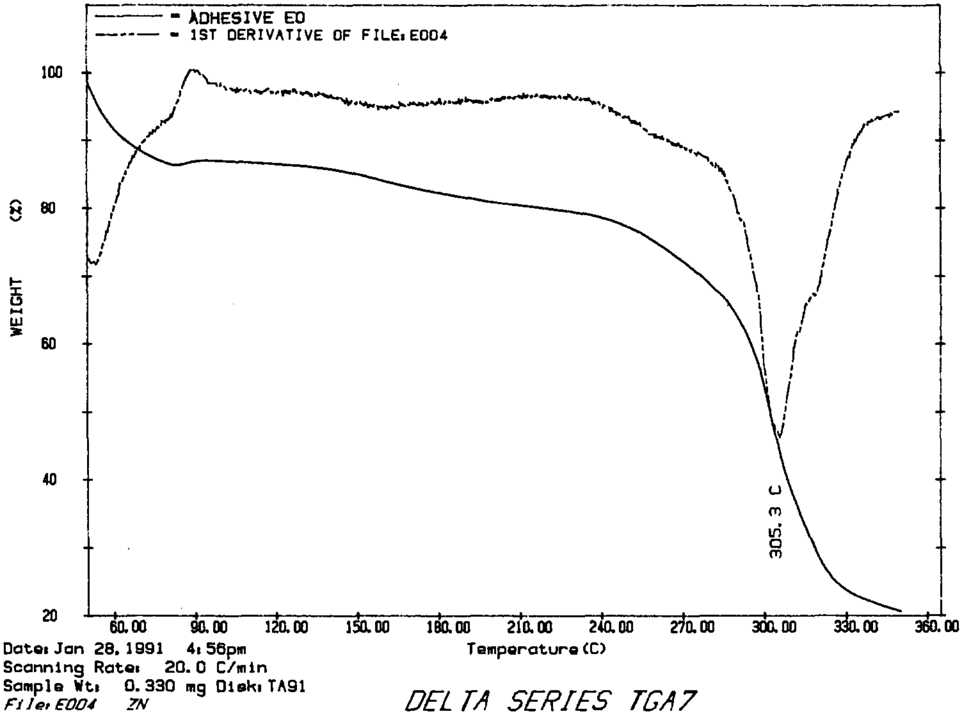

Fig. 1. TGA record of the thermolysis of Adhesive LP (E0 emission category) with a sample weight of 0.330 mg.

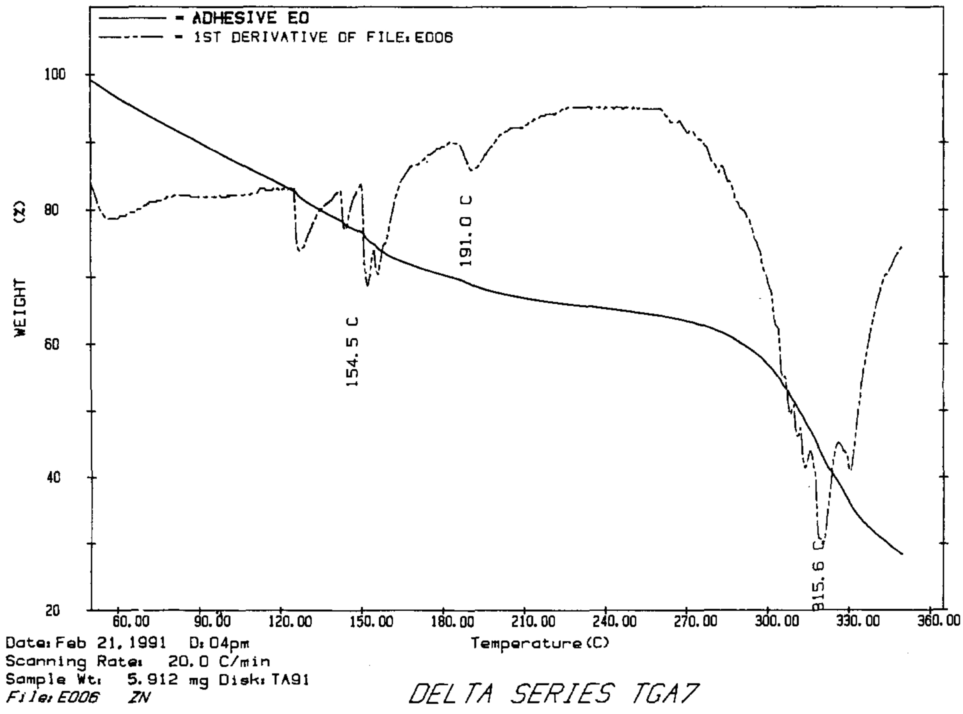

Fig. 2. TGA record of the thermolysis of Adhesive LP (E0 emission category) with a sample weight of 5.912 mg.

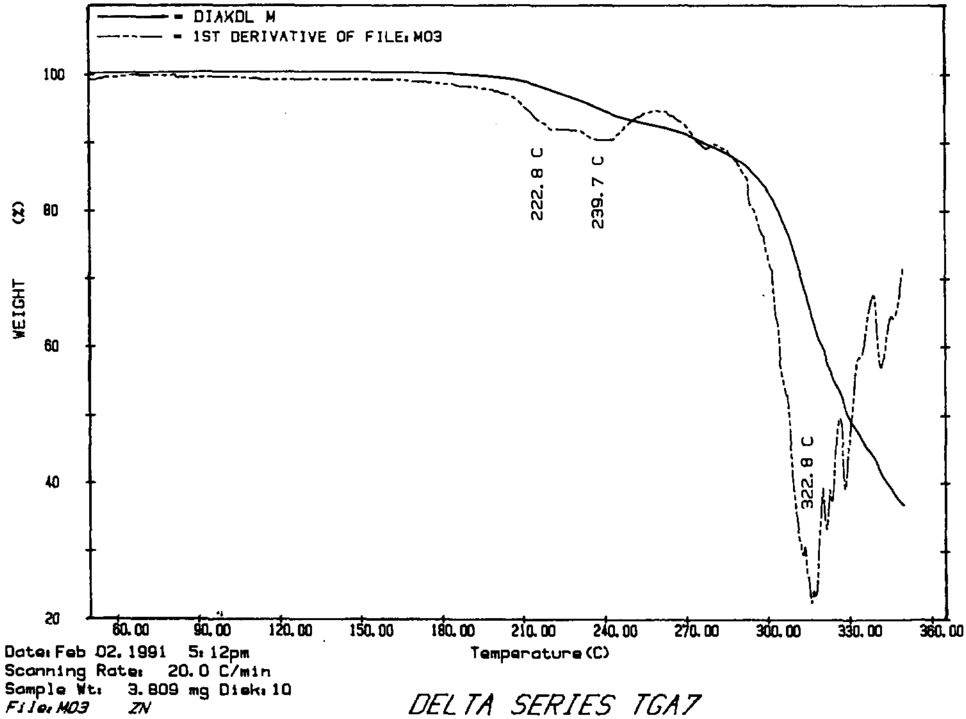

Fig. 3. TGA record of the thermolysis of Diakol M with a sample weight of 3.809 mg.

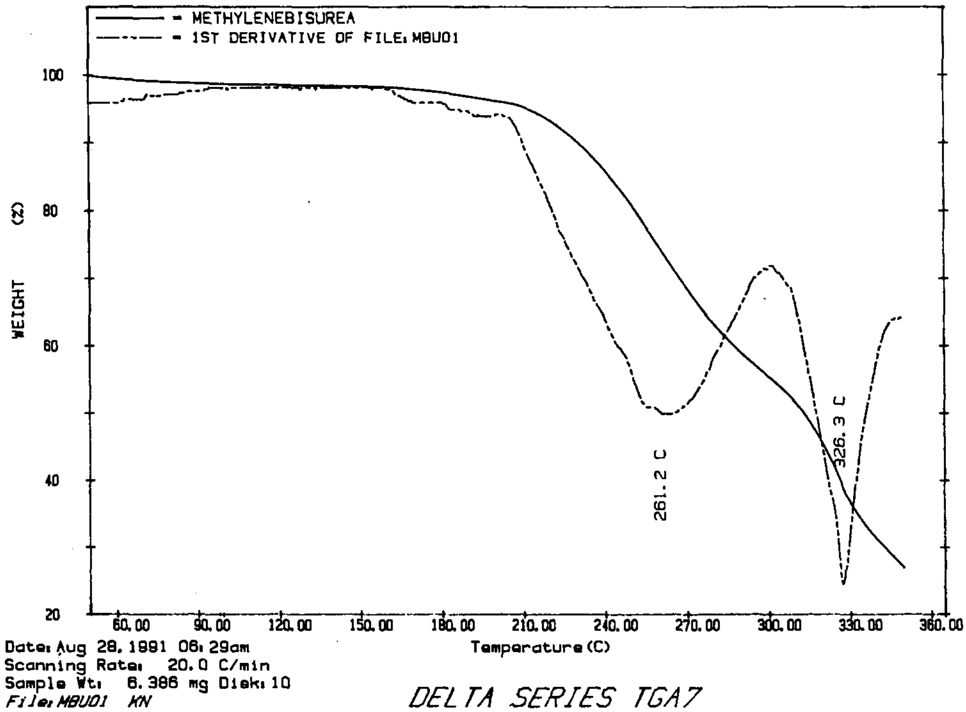

Fig. 4. TGA record of the thermolysis of methylenebisurea with a sample weight of 6.386 mg.

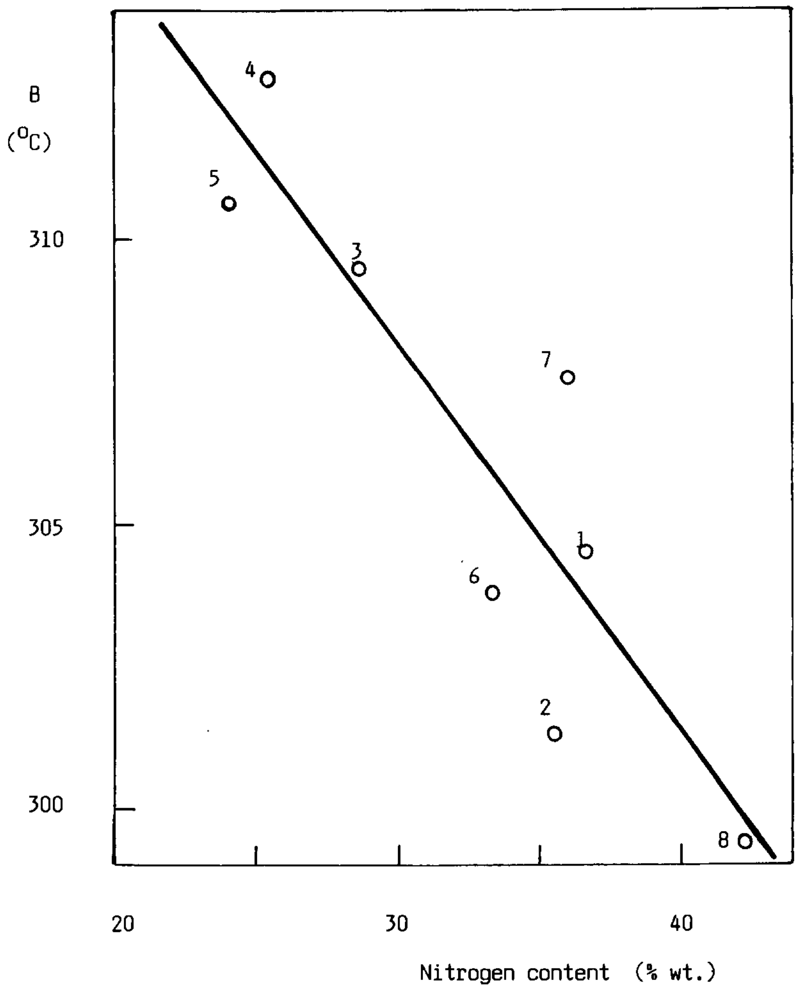

Fig. 5. The relationship between the value of the coefficient B in eqn. (1) and the nitrogen content in the corresponding UFPC. Correlation coefficient $r = -0.8924$.

that the DTG curves usually show peaks in three temperature regions, i.e. 180–225°C, 245–275°C and 300–345°C. The peaks in the last temperature range proved to be characteristic of those for UFPCs. By comparing the positions of typical peaks and the weights for various UFPCs we obtained the linear relationship

$$P = An + B \tag{1}$$

where P is the position of the peak in °C and n is the weight in milligrams. Coefficients of eqn. (1) are shown in Table 1.

The next analysis revealed that coefficient B of eqn. (1) is correlated with the nitrogen content of UFPCs as shown in Fig. 5.

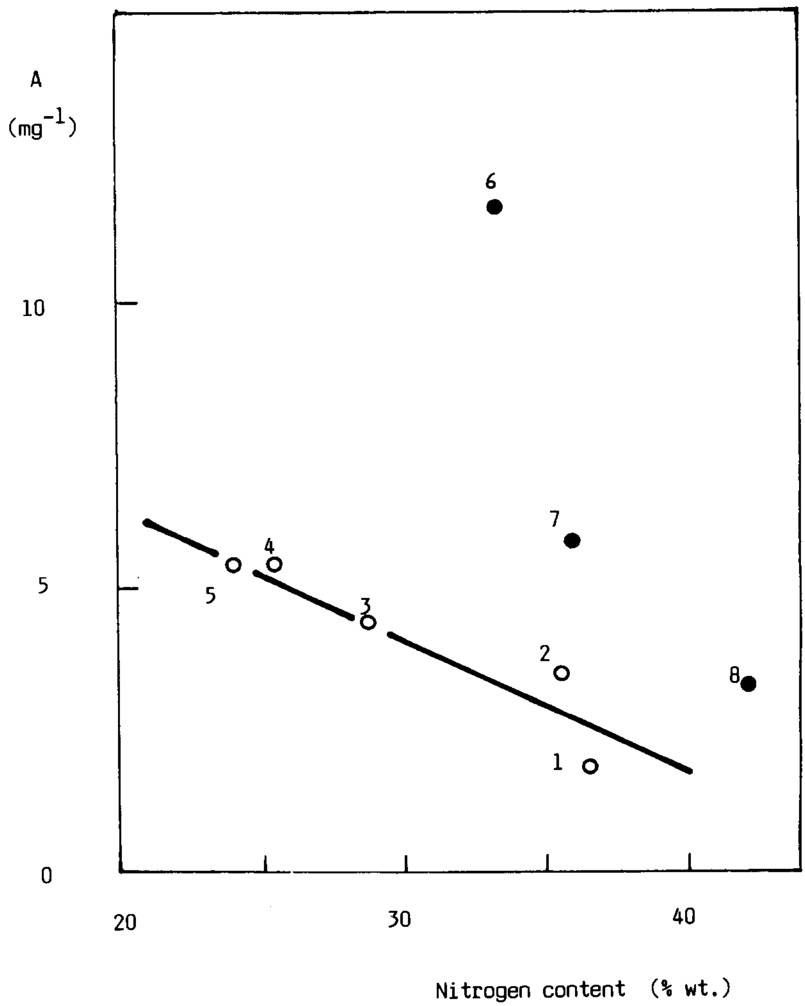

Fig. 6. The relationship between the value of the gradient A of eqn. (1) and the nitrogen content in the corresponding UFPC. Points • do not correlate. Correlation coefficient $r = -0.9354$.

For coefficient A in eqn. (1), there is an analogous correlation only for the uncured adhesives 1–5, as shown in Fig. 6.

Sample 6 is a cured UFPC; samples 7 and 8 are linear urea–formaldehyde condensates.

It follows from what has just been said that the gradient A in eqn. (1) is closely related to the details of the molecular structures of the UFPCs, and also with their reactivities. From this point of view, the existence of a relationship between the condensation ability KS_{100} of adhesives 1–5 and the corresponding gradient A is understandable; this relationship is shown in Fig. 7.

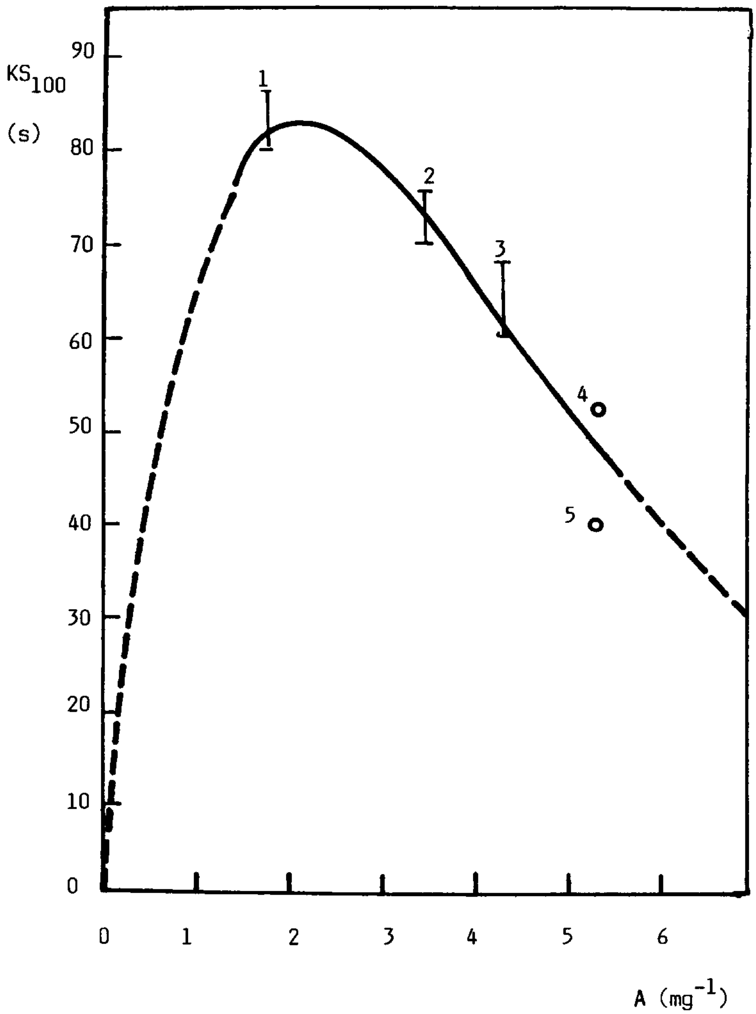

Fig. 7. The relationship between the value of the gradient A of eqn. (1) and the condensation ability KS_{100} of adhesives 1–5. This relationship is represented by the equation $KS_{100} = 105.82A\ \exp(-0.4628A)$, with $r = -0.9876$.

CONCLUSIONS

Under the conditions of the experiments, i.e. at a linear rate of temperature increase of 20°C min^{-1} and weighed amounts of samples of up to 7 mg, the DTG curves of urea–formaldehyde polycondensates (within the temperature range 300–345°C) exhibit characteristic peaks. The positions of these peaks (within this temperature range) show a linear dependence on the weighed amounts of the samples. The gradient of this relationship is closely related to the molecular structure of the UFPC. From this point of view, the correlation between this gradient for uncured urea–formaldehyde adhesives possessing valid characteristics and their condensation ability at 100°C can be understood.

REFERENCES

1 T. Nakamura, Iwate Diagaku Kogakuba Kenkyu Hokoku, 15 (1962) 115; Chem. Abstr., 57 (1962) 13 964f.
2 B. Chabert, Bull. Inst. Text., 22 (1962) 385.
3 G. Camino, L. Operti, L. Costa and L. Trossarelli, in B. Miller (Ed.), Proc. 7th Int. Conf. Thermal Anal., Vol. 2, Wiley, Chichester, 1982, p. 1144.
4 G. Camino, L. Operti and L. Trossarelli, Polym. Degrad. Stab., 5 (1983) 161.
5 E.P. Trub, E.N. Boytsov, A.G. Koryakin and T.L. Pripisnova, Khim. Promst. (Moscow), (1989) 22.
6 S. Zeman, unpublished results for DTA of UFPC, January 1982.
7 H. Kadowaki, Bull. Chem. Soc. Jpn., 11 (1936) 248.
8 Czechoslovak State Standard CSN 66 86 29.