Journal of Thermal Analysis, Vol. 36 (1990) 721-732

THERMAL ANALYSIS OF DISAZO PIGMENTS
I. Derivatives of 1,4-bis(5'-hydroxy-7'-sulpho-2'-naphthyl)-benzenediamine

G. Simeonov, A. Draganov and *D. Rustschev*

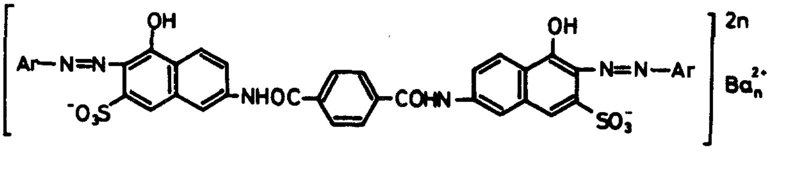
HIGHER INSTITUTE OF CHEMICAL TECHNOLOGY, DEPARTMENT OF TECHNOLOGY OF ORGANIC SYNTHESIS AND FUELS, 1156 SOFIA, BULGARIA

(Received April 6, 1989; in revised form January 9, 1990)

The differential-thermal and thermogravimetric analysis of eight derivatives of 1,4-bis-(5'-hydroxy-7'-sulpho-2'naphthyl)-benzenediamide showed that these compounds have a marked exothermic effect, with maxima in the temperature range 280-330°C. The derivative of 4-nitroaniline-2-sulphonic acid were found to undergo a blast-like decomposition in the temperature intervals 255-265 °C and 285-290 °C, which is reflected by large steps in their TG curves.

The thermal analysis of disazo pigments permits determination of their applicability at higher temperatures.

This work analyses the processes occurring during the thermal decomposition of disazo pigments, derivatives of 1,4-bis-(5'-hydroxy-7'-sulpho-2'naphthyl)-benzenediamide, with the following general structural formula:



John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

where Ar designates the residues of the aromatic amines used as disazo components.

Products with this structure have been obtained by Draganov and Simeonov through multistage synthesis [1]. The structure of the compounds comprises a chain of aromatic nuclei interconnected by means of amide and azo groups. The presence of these groups determines their thermal stability. The heating of such azo compounds to 300-400° for 1-2 min results in breaking of the azo bond, with formation of the respective amines; the nitro groups present in the molecule do not change and the thermal decomposition leads to formation of the initial amines [2].

The thermal destruction of azo dyes at 700°, combined with gas-chromatographic and mass-spectroscopic analysis, is recommended as a better method for investigation of these compounds than direct determination of the mass-spectra of the dyes, because it can lead to the distinction of isomeric azo dyes and the isomerism may be judged on the basis of the type of the decomposition products [2].

Skutial and Gasparic [3] studied the thermal decomposition of primary amides to nitriles. Rode *et al.* [4, 5] investigated the processes of thermal destruction of aromatic polyamides obtained by condensation of the acid chloride of terephthalic acid with 9,9-bis-(4-aminophenyl)-fluorene and anilinephthalein, and found that the amide bond in the aromatic polyamides is the weakest point; the destruction of the amide bonds at 350-400° is therefore determined by hydrolytic processes. Moreover, the oxygen present in the system does not initiate the process, but participates in the oxidation of the polymer in the second stage of the decomposition (above 400°), which is accompanied by homolytic processes of breaking of the amide bonds, resulting in the formation of fragments of tertiary amides and amides, and cross-linking of the polymer chains.

Krasnov, Aksyonova and Harkov [6] studied the processes of thermal decomposition in vacuum of aromatic polyamides obtained through condensation of the acid chloride of terephthalic acid and diamines of the diphenyl series, and reached the conclusion that the amide bond is the weakest point in the polyamide chain, its decomposition in the temperature range 360-500° leading to the formation of considerable amounts of CO_2, H_2O, benzene, nitriles, etc.

The thermal stability of the polyamides decreases perceptibly after the $-CH_2-$ and $-O_2-$ groups are introduced as linking elements between the phenyl nuclei in the polymer chain. The thermal stability of the isomeric aromatic polyamides is found to be influenced by the isomeric forms of both phenyldiamine and dicarbonic acid. Polyamides with para-para positions of the amide bonds have higher thermal stabilities than those of the remaining isomers [7, 8].

Masaro, Hironori and Teijiro [9] determined the thermal stabilities of organic pigment derivatives of 3-hydroxy-2-methyl-4-carboxyquinolone by means of thermal analysis.

The results of the thermal analysis of disazo pigments may be used to obtain useful information about their thermal stability, and also to determine the temperature range in which they can be used without changes in their colour, composition or properties.

Experimental

The experiments were carried out with several disazo pigments, which are listed in Table 1.

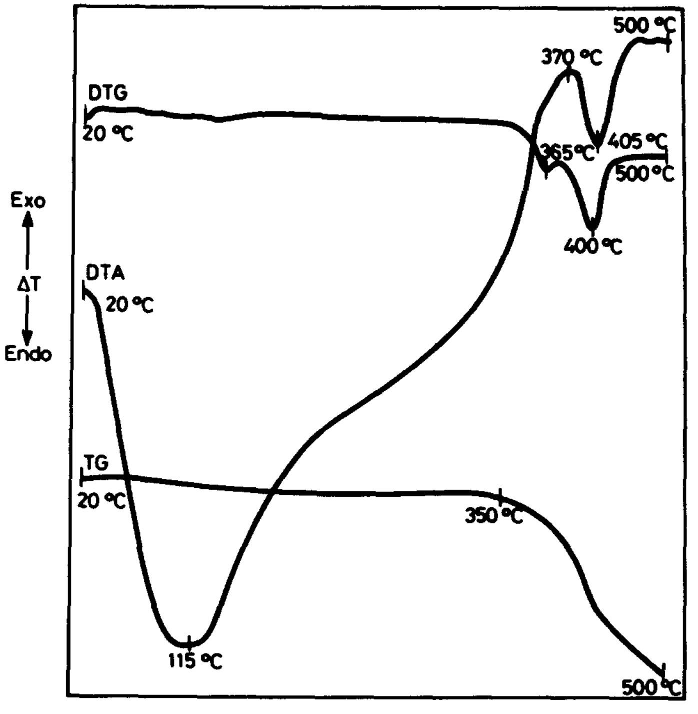


Fig. 1 DTA, DTG and TG curves of 1,4-bis-(5'-hydroxy-7'-sulpho-2'-naphthyl)-benzenediamide (a)

Table 1 Amount of volatile pyrolysis products (%) at different temperatures

Pigment	Azo and diazo components	Volatile pyrolysis products at temperature, °C									
		50	100	150	200	250	300	350	400	450	500
a	1,4-bis-(5'-hydoxy-7'-sulpho-2'naphthyl)-benzenediamine	0	0.3	1.0	1.3	1.3	1.3	2.6	13.1	22.9	–
b	2-aminobenzoic acid	0.5	3.0	8.1	10.6	12.2	17.2	20.3	24.9	29.4	33.5
c	4-nitroaniline	0.5	3.1	8.1	11.7	13.2	49.7	51.8	54.8	58.9	61.0
d	4-aminobenzenesulphonic acid	0.5	3.5	9.1	13.2	15.2	21.3	23.3	26.9	31.4	35.5
e	4-nitroaniline-2-sulphonic acid	0.5	3.0	8.1	10.7	12.2	45.2	46.7	49.8	53.8	56.9
f	aniline	0	0	0.5	1.4	1.9	2.4	8.1	10.3	15.1	21.0
g	2,5-dichloroaniline	0	2.1	5.5	8.3	8.9	13.8	17.9	24.1	30.3	35.8
h	2-aminonaphthyl-4,8-di-sulphonic acid	0	0	0.7	1.3	2.3	3.0	9.2	13.2	17.8	21.7
i	1-aminonaphthyl-5-sulphonic acid	0	0	0	0.6	0.7	2.0	5.2	10.4	15.3	19.0

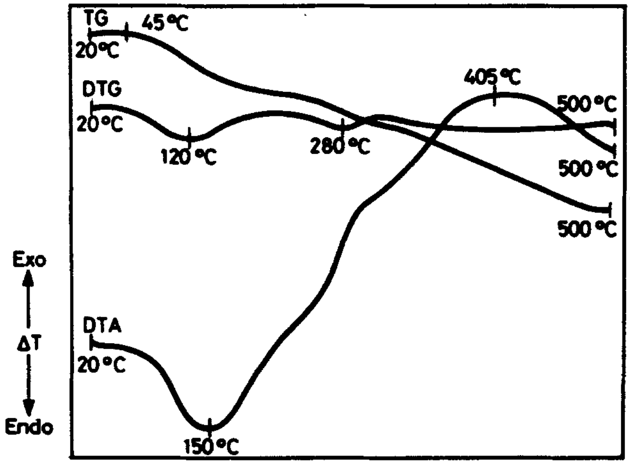


Fig. 2 DTA, DTG and TG curves of pigment b

The pigments were obtained by using the method described by Draganov and Simeonov [1]. The synthesized pigments were tested for thermal stability by determining their DTA and TG curves. Thermal analysis was performed with a QD-102 derivatograph (MOM, Hungary) under the following conditions: heating rate - 10 deg/min, uncontrolled air medium - final temperature 500°, reference material - Al_2O_3, sample quantity - about 1 g, DTA - 1/20, DTG - 1/10.

Results and discussion

Figure 1 shows the DTA, DTG and TG curves of 1,4-bis-(5'-hydroxy-7'-sulpho-2'naphthyl)-benzenediamide, while Figs 2-9 depict the DTA, DTG and TG curves of the pigments obtained from it. Table 1 shows the disazo components (Ar) and the quantities of the volatile pyrolysis products for the pigments synthesized from them. The compounds studied were found to undergo some common thermochemical reactions. Three characteristic conversion intervals were observed. In the interval up to 200°, an endothermic process with a maximum mass loss rate occurs at 120-130°. The peak temperature of the DTA curve is at 100-150°.

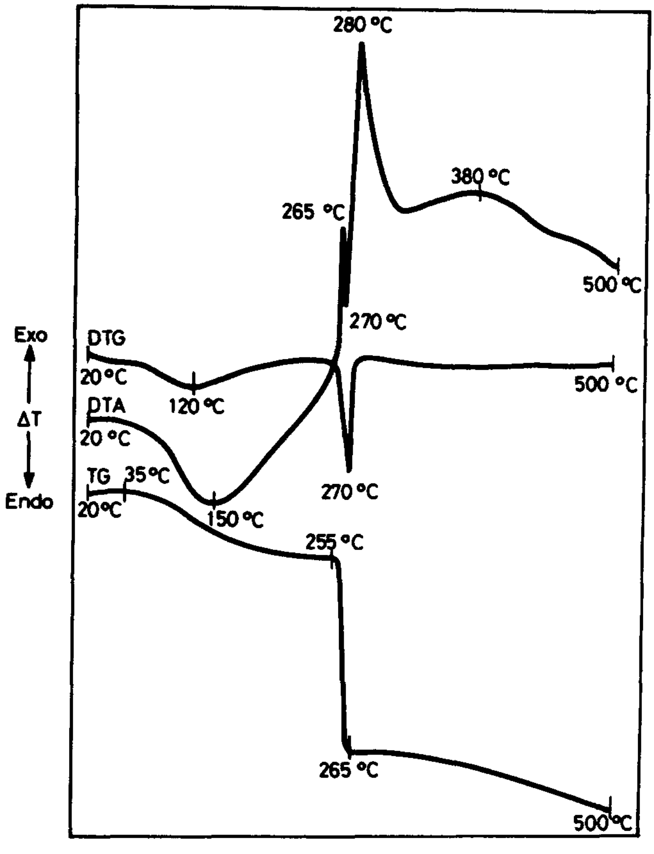


Fig. 3 DTA, DTG and TG curves of pigment c

The mass losses at the maximum rate are about 5-6%, reaching 11% at the end of the interval under consideration (200°). In order to throw light on the reasons for the loss of mass in this interval, spectrophotometric analysis was performed in the visible part of the spectrum in dimethylformamide solution, after samples of the substances were heated to 200°. Since the spectral curves showed no deviation from the curves of the substances determined prior to their heating, it may be assumed that the mass loss was due to the release of crystallization water from the crystal lattice, when the compounds are sedimented as barium salts. In the interval 200-260°, the compounds do not change, whereas exothermic processes take place between 260° and 320°, resulting in sharp changes in the mass of the sample. These sharp

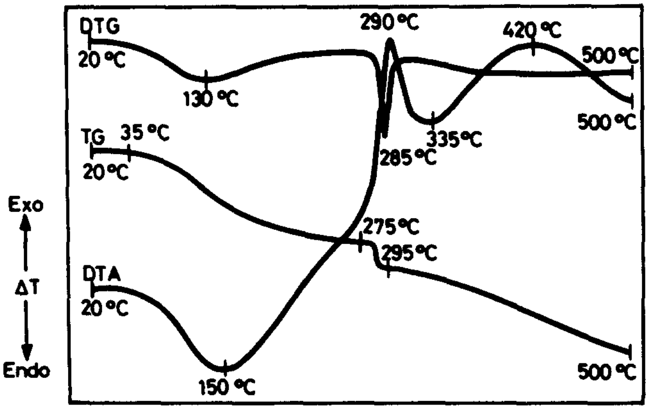


Fig. 4 DTA, DTG and TG curves of pigment d

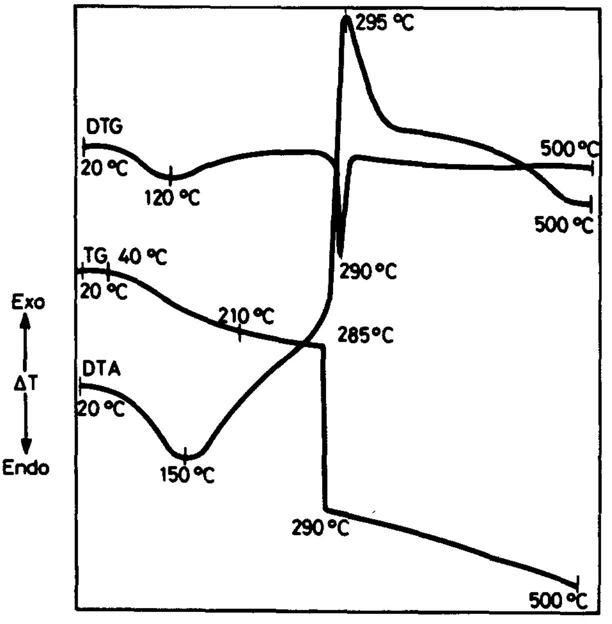


Fig. 5 DTA, DTG and TG curves of pigment e

changes are particularly substantial for the TG curves of pigments *c* and *e*, which contain nitro groups (Fig. 3). The azo groups are probably decomposed at these temperatures and the resulting nitro compounds, which have a lower boiling temperature, are evaporated and burnt. This step is much less manifested in the compounds containing salt-forming groups in the molecules of the disazo components from which they are synthesized. When the samples are heated to temperatures exceeding 320°, the decrease in their mass is relatively more uniform. Different reactions are observed for compounds *h* and *i*, obtained from diazonium salts of aminonaphtholsulphonic acids. The changes in their TG curves in the interval below 260° are insignificant (Figs 8 and 9). Upon increase of the number of sulpho groups in compound *h*, the initial temperature for a change in mass to occur rises to 315°.

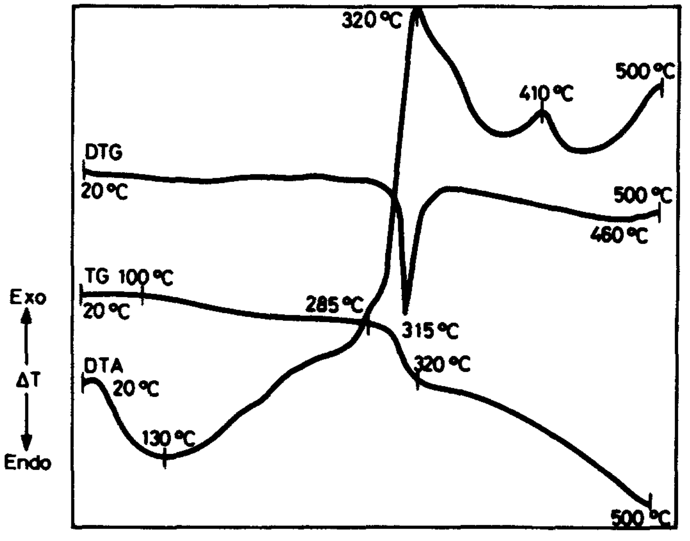


Fig. 6 DTA, DTG and TG curves of pigment f

From the TG curve of the azo compound (Fig. 1), it can be seen that no changes are observed below 330°, with the exception of insignificant mass losses (about 1%) at 120°. However, the DTA curve displays a considerable endothermic peak at 115°, not accompanied by loss of mass, which shows that the thermochemical changes in the molecule of the pigments do not involve breaking of the amide bonds.

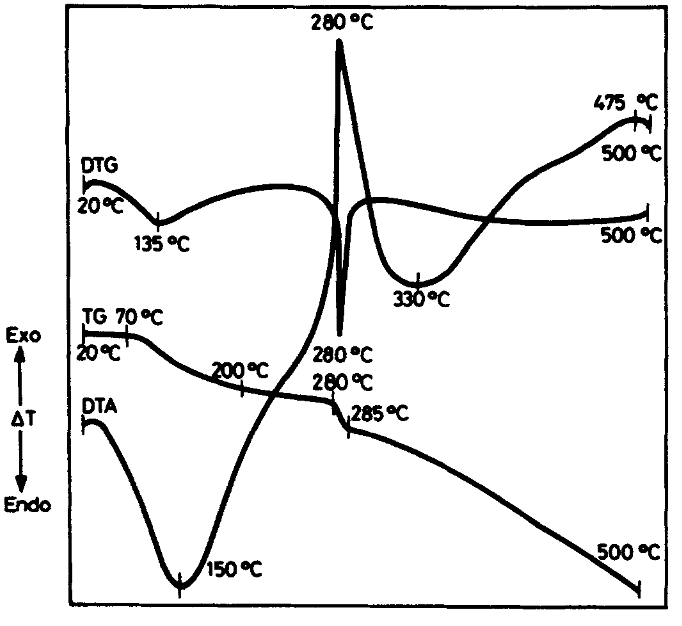


Fig. 7 DTA, DTG and TG curves of pigment g

The DTA curves are characterized by a clear exothermic effect with a maximum in the temperature range 280-330°. For the initial 1,4-bis-(5'-hydroxy-7'-sulpho-2'naphthyl)-benzenediamide (a), this maximum is registered at a relatively high temperature (375°), whereas pigment *b*, obtained from the diazonium salt of anthranilic acid, does not exhibit a marked exothermic effect (Figs 1 and 2).

The thermal stabilities of the compounds studied are best illustrated by the TG curves. The most stable compound is 1,4-bis-(5'-hydroxy-7'-sulpho-2'naphthyl)-benzenediamide (Fig. 1), whereas the least stable compound is pigment *c*, obtained from the diazonium salt of 4-nitroaniline, which undergoes a blast-like destruction at 255-265° (Fig. 3). Pigments *f*, *h* and *i* proved to have the highest thermal resistance, releasing 2.4%, 3% and 2% pyrolysis products. Pigments *c* and *e* possess the lowest resistance, releasing 41.4 and 45.2% volattile pyrolysis products up to 300° (Table 1).

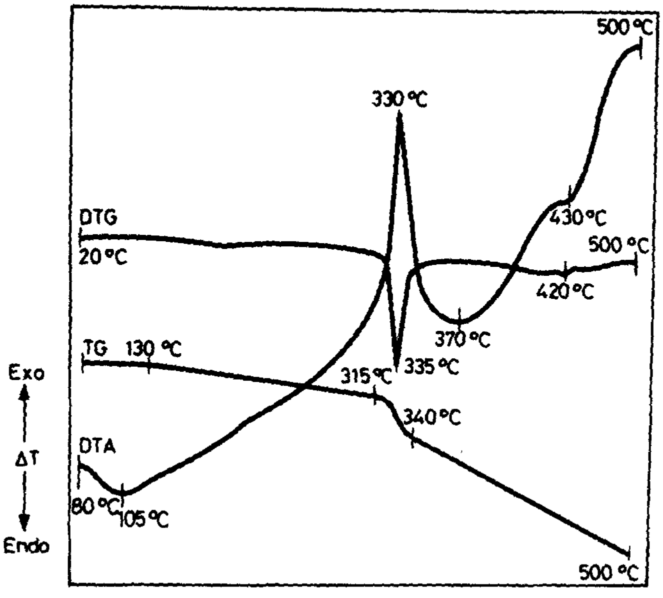


Fig. 8 DTA, DTG and TG curves of pigment h

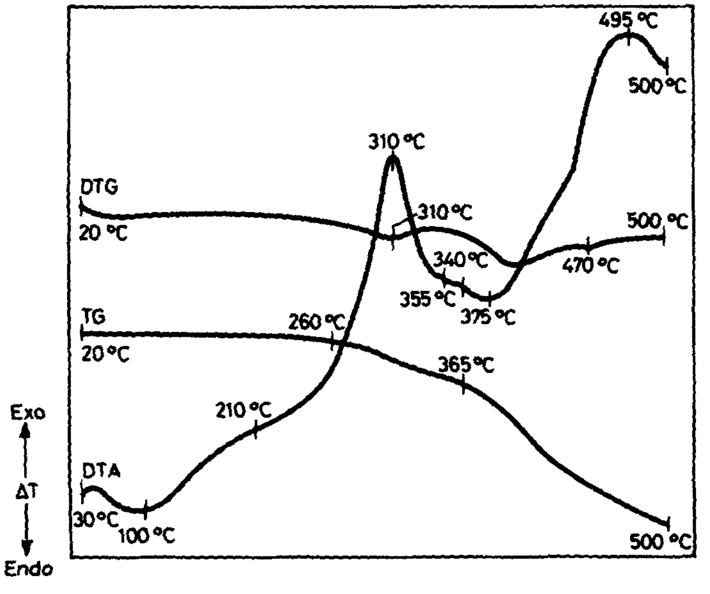


Fig. 9 DTA, DTG and TG curves of pigment i

The DTA and TG studies on disazo pigments which are derivatives of 1,4-bis-(5'-hydroxy-7'-sulpho-2'naphthyl)-benzenediamide show that some of them can be used for the mass-dying of polymer fibres, which requires thermal stability up to 250°.

Conclusions

1. The DTA and TG analysis of eight derivatives of 1,4-bis-(5'-hydroxy-7'-sulpho-2'naphthyl)-benzenediamide showed that these compounds have a marked exothermic effect, with maxima in the temperature range 280-330°.

2. The TG curves revealed that the derivatives of aniline and 1-aminonaphthyl-5-sulphonic acid have the highest thermal stability, releasing only 21% and 19% pyrolysis products, respectively, up to 500°. At this temperature, the derivatives of 4-nitroaniline and 4-nitroaniline-2-sulphonic acid release almost three times more volatile substances (61% and 56.9%, respectively).

3. The derivatives of 4-nitroaniline and 4-nitroaniline-2-sulphonic acid undergo a blast-like decomposition in the temperature interval 255-265° and 285-290°, respectively, which is reflected by large steps in their TG curves.

4. Thermal analysis permits the selection of suitable disazo pigments for the mass-dying of synthetic fibres.

References

1 Al. Draganov and G. Simeonov, Avt. sv. (1986), NRB No 40866, No 40877.
2 K. Venkataraman, Analiticheskaya khimiya sinteticheskih kresiteley, khimiya (Analytical Chemistry of Synthetic Pigments), Leningrad, 1979, p. 297 (in Russian).
3 I. Skutil and I. Gasparic, Mikrochim. Acta, (1974) 791.
4 V. V. Rode, P. N. Gribkova, Ya. S. Vygodskii, S. V. Vinogradova and V. V. Koršak, Izv. AN SSSR, Ser. Khim., (1969) 85.
5 V. V. Rode, P. N. Gribkova, Ja. S. Vygodskii, S. V. Vinogradova and V. V. Koršak, Vysokomol. Soed., A 10 (11) (1968) 2550.
6 E. R. Krasnov, V. P. Aksänova and S. N. Har'kov, Vysokomol. Soed. A 11 (9) (1969) 1930.
7 E. R. Krasnov, V. M. Savinov, L. B. Sokolov, V. I. Logunova, V. I. Belyakov and G. A. Poljakova, Vysokomol. Soed., 8 (3) (1966) 380.
8 G. S. Kolesnikov, O. Ya. Fedotova and G. S. Matvelašvili, Vysokomol. Soed., A 14 (3) (1972) 608.
9 RZH 14H283, 1976.

Zusammenfassung — Die DT- und TG- Analyse von acht Derivaten von 1,4-bis-(5'-Hydroxy-7'-sulpho-2'naphthyl)-benzoldiamid zeigte, dass diese Verbindungen mit einem Maximum im Temperaturbereich 280-330°C einen eindeutigen exothermen Effekt aufweisen. Derivate mit 4-Nitroanilin-2-sulfonsäure zeigen eine explosionsartige Zersetzung im

Temperaturintervall 255-265°C und 285-290°C, was sich in den TG-Kurven in einer großen Stufe wiederspiegelt.

Die Thermoanalyse von Bisazopigmenten ermöglicht eine Ermittlung ihrer Anwendbarkeit für höhere Temperaturen.