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THERMAL ANALYSIS OF DIAZO PIGMENTS
II. Derivatives of 1,4-bis-(8'-hydroxy-3',6'-disulpho-1'-naphthyl)-benzene-diamide

G. Simeonov, A. Draganov and D. Ructschev

Sofia Technological University, 1156 Sofia, Bulgaria

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Abstract

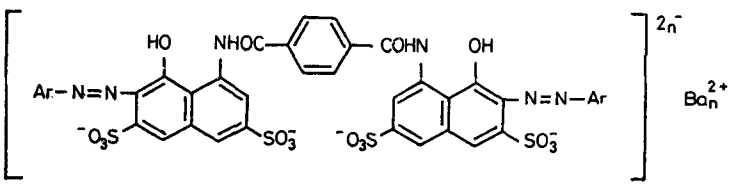
The differential-thermal and thermogravimetric analysis of eight derivatives of 1,4-bis-(8'-hydroxy-3',6'-disulpho-1'-naphthyl)-benzenediamide showed that these compounds have a marked exothermic effect, with maxima in the temperature range 290–340°C. The 4-nitroaniline derivative was found to undergo a blast-like decomposition in the temperature interval 285–295°C, reflected by large steps in the TG curves.

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

Keywords: diazo pigments

Introduction

The present paper reports an analysis of the processes of thermal degradation of diazo pigments, derivatives of 1,4-bis-(8'-hydroxy-5',6'-disulpho-1'-naphthyl)-benzenediamide, with the following general structural formula:



in which Ar denotes residues of aromatic amines used as diazo components.

Products with such a structure have been obtained by Draganov and Simeonov through multi-stage synthesis [1].

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Table 1 Quantity of the volatile pyrolysis products (in %) at different temperatures

Pigments	Diazocomponent	Volatile pyrolysis products /°C									
		50	100	150	200	250	300	350	400	450	500
k	2-aminobenzoic acid	0	2.5	6.7	8.8	11.2	16.3	20.6	24.5	32.4	35.4
l	4-nitroaniline	0	3.4	8.4	11.3	12.8	54.1	57.8	60.0	63.0	65.0
m	4-toluidine	0	3.5	8.4	12.3	12.8	16.8	18.8	22.7	29.6	34.6
n	4-nitroaniline-2-sulphonic acid	0	2.5	5.4	6.7	7.7	9.3	22.6	26.6	30.5	32.5
o	aniline	0	3.7	8.9	12.2	14.0	17.8	21.5	26.2	31.8	39.3
p	2.5-dichloroaniline	0	2.0	8.5	13.7	15.7	17.7	23.8	31.0	38.7	44.3
q	2-aminonaphthyl-4.8-disulphonic acid	0	0.0	2.1	5.4	8.6	10.7	22.6	30.1	36.5	48.4
r	1-aminonaphthyl-5-sulphonic acid	0	0.0	1.2	1.9	3.4	8.2	11.6	17.4	32.9	40.6

The thermal stabilities of organic compounds containing amide groups have been studied by a number of authors [2–4]. The pyrolysis of azo pigments containing amide groups has not been studied well. It is known that the data on the thermal stability of pigments are of extreme importance for staining plastic articles, rubber, textile fibres, etc. Derivatographic analysis has been used to characterize the compounds synthesized, because it gives abundant information on the thermal stabilities of the substance.

The compounds studied form a continuation of our earlier studies on the thermal analysis of diazo pigments, derivatives of 1,4-bis-(5'-hydroxy-7'-sulpho-2'-naphthyl)-benzenediamide [5]. The first part of the paper contains literature data on the thermochemical destruction of compounds with similar structure. The results on the thermal analyses of diazo pigments, derivatives of 1,4-bis-(5'-hydroxy-7'-sulpho-2'-naphthyl)-benzenediamide, have demonstrated that the thermal stabilities of these compounds is determined by the azo and amide groups in them. The aim of the present studies is to verify the possibility of selection of diazo pigments for staining polymers in a mass, by determining their thermal properties.

Experimental

The pigments studied were obtained by coupling the azo component 1,4-bis-(8'-hydroxy-3',6'-disulpho-1'-naphthyl)-benzenediamide with diazonium of aromatic amines, using the method described by Draganov and Simeonov [1]. The thermal stabilities of the synthesized pigments were tested by recording their DTA and TG curves. Thermal analysis was performed with a QD-102 derivatograph (MOM), under the following conditions: heating rate 10 deg·min^{-1}, uncontrolled air air medium, final temperature 500°C, inert substance – Al_2O_3, quantity of sample – about 1 g.

Results and discussion

Table 1 shows the diazo components (Ar in the formula) and the amounts of the volatile pyrolysis products. Figures 1–8 depict the DTA, DTG and TG curves of the compounds studied, and reveal that they have some common thermochemical reactions.

Similarly to the azo pigments obtained with 1,4-bis-(5'-hydroxy-7'-sulpho-2'-naphthyl)-benzenediamide, in this group of azo pigments there were also three characteristic transformation intervals. The interval 20–200°C is characterized by endothermal processes with maximum rate at 115–120°C. The maxi-

mum endothermal effect in the DTA curve is at 140–150°C. The mass loss at the maximum rate ranges between 3% and 6%, reaching 13.7% at the end of the interval (20–200°C). For pigment *r* (Fig. 8), the endothermal processes occur with maximum at 115°C, without appreciable mass loss, the loss at the end of the interval being only 1%. This suggests high thermal stability. If the azo pig-

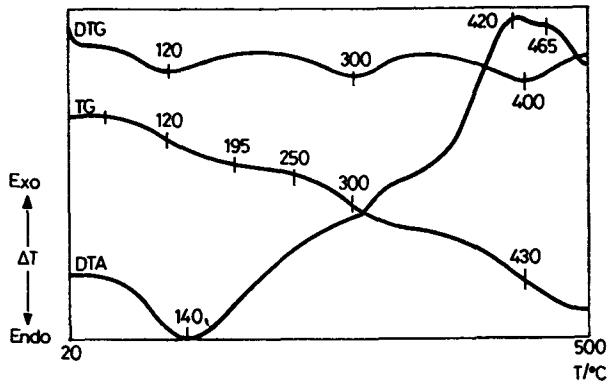

Fig. 1 DTA, DTG and TG curves of pigment (*k*)

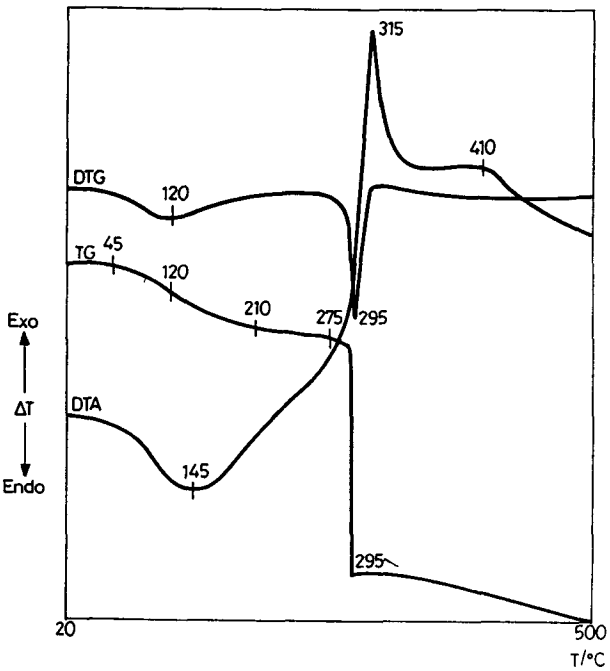

Fig. 2 DTA, DTG and TG curves of pigment (*l*)

ment samples are heated to 200°C and examined under a microscope, it is seen that the particles are pulverized, but this is not accompanied by changes in colour or staining capacity. The visible spectral curves recorded before and after heating of the samples to 200°C do not differ. The compounds do not change in the interval 200–250°C. Between 250 and 350°C there are processes accompanied by sharp changes in the mass of the specimen. These changes are particularly abrupt in the TG curve for pigments *l* and *n* (Figs 2 and 4). These pigments contain nitrogen groups in their molecule. Such thermal reactions are also observed in pigments obtained with the same diazo components and 1,4-bis-(5'-hydroxy-7'-sulpho-2'-naphthyl)-benzenediamide [2]. These results prove the assumption that breaking of the azo bonds in the molecule results in the formation of nitro compounds which boil at much lower temperatures than 250°C, and are instantly evaporated or burned, these processes being registered as a leap in the TG curve. This step is considerably less pronounced in the TG curves of the compounds containing salt-forming groups in the molecules of the diazo components. The thermochemical processes in the range 250–350°C are accompanied by an exothermal effect, with a maximum in the interval 290–340°C in the DTA curve. This effect is most pronounced for pigments *l* and *n* (Figs 2 and 4). When the compounds studied are heated to temperatures above 350°C, the decrease in mass of the samples is relatively more uniform.

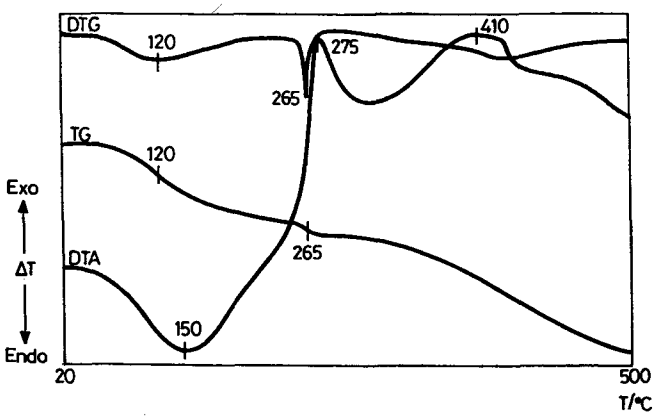

Fig. 3 DTA, DTG and TG curves of pigment (*m*)

Comparison of the TG curves of all products shows that the least stable compound is pigment *l* (Fig. 2), obtained with the diazonium salt of 4-nitroaniline, which is destroyed explosively at 285–295°C. With the pigment obtained with the diazonium salt of 4-nitroaniline and 1,4-bis-(5'-hydroxy-7'-sulpho-2'-naphthyl)-benzenediamide, this process takes place at 255–265°C [2]. Up to

300°C, pigment *l* releases 57.1% volatile pyrolysis products. Pigment *r* is most stable, releasing only 8.2% volatile pyrolysis products up to 300°C (Table 1).

The group of compounds studied differs in structure from those discussed in [2] by the binding site of the amide groups and by the greater number of sulpho groups on the naphthalene nuclei. The pigments synthesized with identical diazonium salts undergo similar thermochemical reactions.

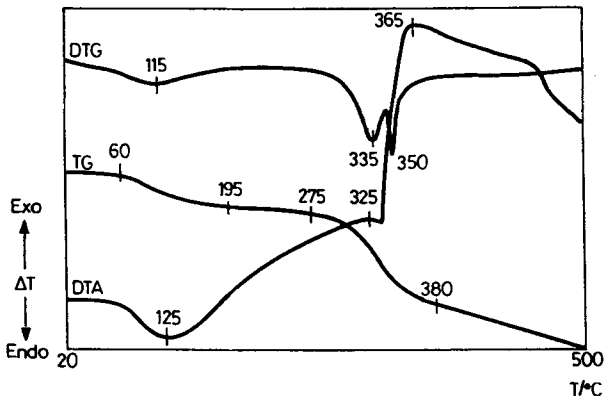

Fig. 4 DTA, DTG and TG curves of pigment (*n*)

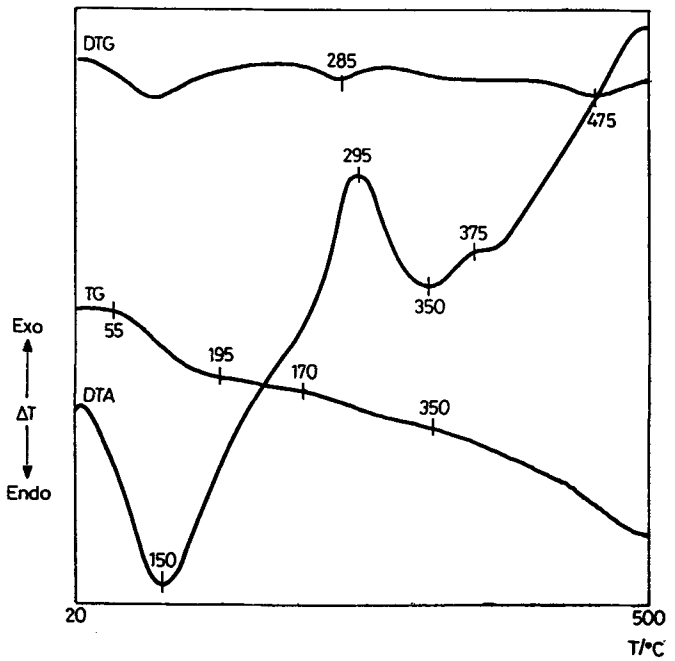

Fig. 5 DTA, DTG and TG curves of pigment (*o*)

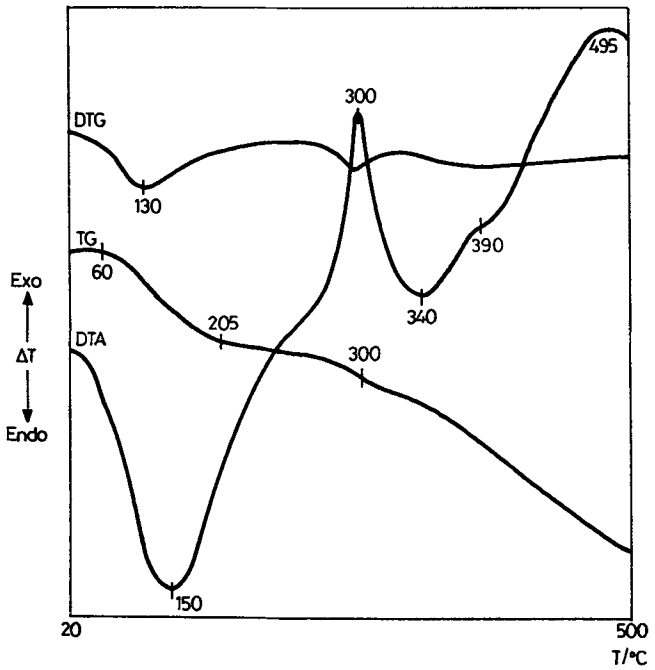

Fig. 6 DTA, DTG and TG curves of pigment (*p*)

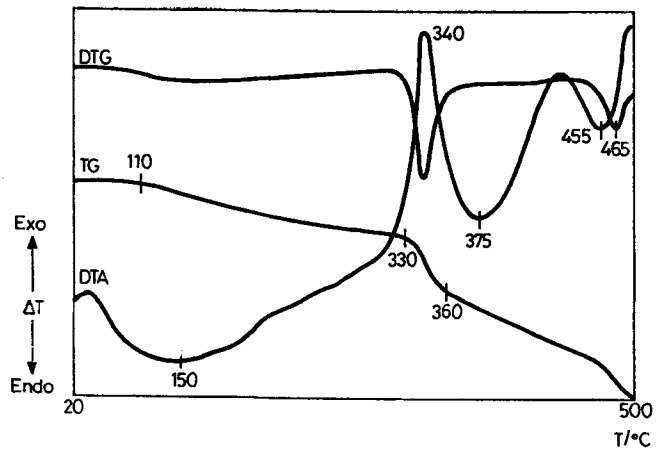

Fig. 7 DTA, DTG and TG curves of pigment (*q*)

The differential-thermal and thermogravimetric tests carried out on these diazo pigments, derivatives of 1,4-bis-(8'-hydroxy-3',6'-disulpho-1'-

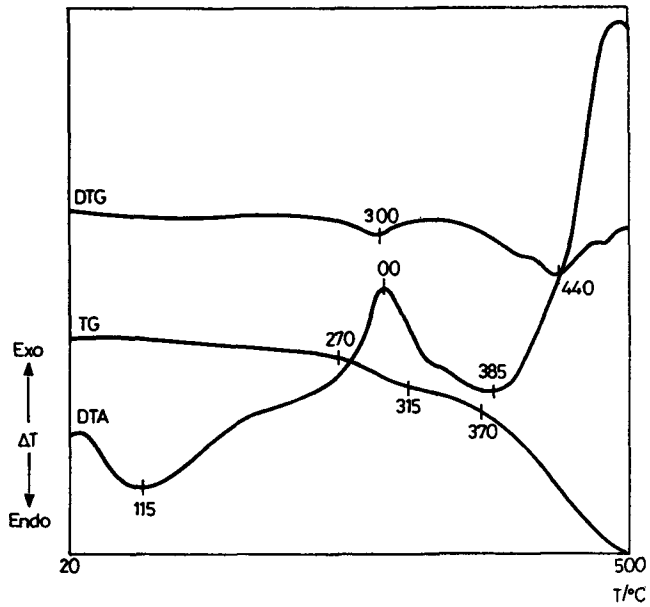

Fig. 8 DTA, DTG and TG curves of pigment (*r*)

naphthyl)-benzenediamide, show that they can be used for the mass dyeing of polymer fibres, for which a thermal stability of up to 250°C is required.

Conclusions

1. The DTA curves of these azo pigments, derivatives of 1,4-bis-(8'-hydroxy-3',6'-disulpho-1'-naphthyl)-benzenediamide, have a marked exothermal effect, with a maximum in the temperature range 290–340°C.

2. The thermogravimetric curves show that the derivative with 1-amino-α-naphthyl-5-sulphonic acid is most stable up to 300°C, giving 8.2% volatile pyrolysis products, while the derivative with 4-nitroaniline releases 57.1% volatile substances.

3. The pigment obtained with 4-nitroaniline disintegrates explosively in the temperature range 285–295°C, whereby a high threshold is observed in the TG curve.

4. The pigments synthesized with the same diazonium salts and 1,4-bis-(8'-hydroxy-3',6'-disulpho-1'-naphthyl)-benzenediamide or 1,4-bis-(5'-hydroxy-7'-sulpho-2'-naphthyl)-benzenediamide undergo similar thermochemical reactions.

5. The thermal analysis of pigments with similar structures allows a choice from among them as to which would be suitable for the mass dyeing of polymer materials.

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Zusammenfassung — DTA und DTG von acht Derivaten von 1,4-Bis-(8'-hydroxy-3',6'-disulfo-1'-naphthyl)-benzoldiamin zeigen, daß diese Verbindungen über einen ausgeprägten exothermen Effekt mit einem Maximum im Temperaturintervall 290–340°C verfügen. Das 4-Nitroanilinderivat unterliegt im Temperaturintervall 285–295°C einer explosionsartigen Zersetzung, was sich in großen Stufen in den TG-Kurven wiederspiegelt.
Die thermische Analyse von Diazopigmenten erlaubt einen Schluß auf deren Anwendbarkeit bei höheren Temperaturen.