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Pigment Decomposition in Polymers in Applications at Elevated Temperatures

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ABSTRACT

On thermal treatment of polymers containing diarylide pigments (e.g. C.I. Pigment Yellow 13, 14, 17 and 83, C.I. Pigment Orange 13 and 34 and C.I. Pigment Red 38) above 200°C, and particularly on prolonged treatment in the higher temperature range of 240–300°C, thermal cleavage of the pigment may occur. Following extraction of the treated polymer, some degradation products could be identified as the corresponding monoazo dyes. Due to the enhanced solubility of these degraded products in various application media, the possibility of migration (bleeding and blooming) exists. Furthermore, prolonged heating in the application media at the higher temperature range leads to the release of aromatic amines, including 3,3′-dichlorobenzidine.

1 INTRODUCTION

The application fields of diarylide pigments are widely spread. The main application is the pigmentation of printing inks. Some of the diarylide pigments, with good hiding power and weather fastness, are used in coatings (coil coating, lacquers and powder coating). Due to their high color strength and apparent temperature stability, diarylide pigments are also used for the mass coloration of plastics and polymers.

Apart from C.I. Pigment Yellow 83, there are several pigments based on 3,3′-dichlorobenzidine as a bis-azo component, which have been used in

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plastics or resins above 200°C. On a chemical basis, such pigments can be divided into two classes, viz. the bisacetoacetarylide (yellow) and bisazopyrazolone (orange and red) pigments. In this investigation of the thermal stability, C.I. Pigment Yellows 13, 14, 17 and 83, C.I. Pigment Orange 13 and 34 and C.I. Pigment Red 38 were examined. All these pigments may undergo cleavage in polymers at temperatures above 200°C.

Typical applications at or above 200°C, where cleavage may occur, include the production of colored plastic articles, e.g. blow-molding and injection-molding of polyolefins, polystyrene, polyacrylates and other polymers, the production of colored films based on polyolefins or polyvinyl chloride (Luvitherm® method), and the spin-dyeing of polypropylene fibers. Applications of diarylide pigments with the highest temperature ranges are injection-molding of polypropylene (about 260°C) and the spin-dyeing of polypropylene fibers, where temperatures of 280°C may occur.

During the investigation of spin-dyed fibers, it was found that polypropylene, on pigmentation above 200°C with C.I. Pigment Yellow 83 (**1**), appears to yield products extractable with toluene, depending on the temperature of pigment incorporation. These extracts were separated by column and thin-layer chromatography. Three colored fission products which, through NMR, IR and MS analyses were identified as monoazo dyes, were isolated. Structure **4** and **8** were confirmed by synthesis.

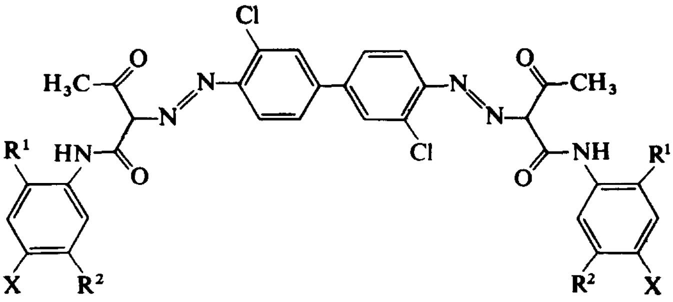
The complete cleavage of one azo group of the bisazo pigment suggested the possibility of a secondary cleavage, resulting in colorless products. Indeed, it was possible to isolate and identify, through chromatographic methods and the use of comparison products and spikes, further fission products of the original pigment.

During the extrusion of polypropylene pigmented with C.I. Pigment Yellow 83, the release of hydrocyanic acid (**5**) was recognized through its odor, and was subsequently confirmed by analytical investigation.

Until now, this pigment cleavage has gone unnoticed, since most of the fission products are similar in shade to the pigment, and coloristic deviations could not be detected. In the literature, there are only references to the resistance to heat and degradation of heat-stable diarylide pigments[1-4] which were examined merely by color strength and shade.

2 RESULTS AND DISCUSSION

Diarylide pigments based on 3,3′-dichlorobenzidine as a bisazo component are divided into two chemically distinct groups.[5] The bisacetoacetarylide yellow pigments are derived from variations of the substituents R_1, R_2 and X in the anilide part of the chemical structure shown in Fig. 1.

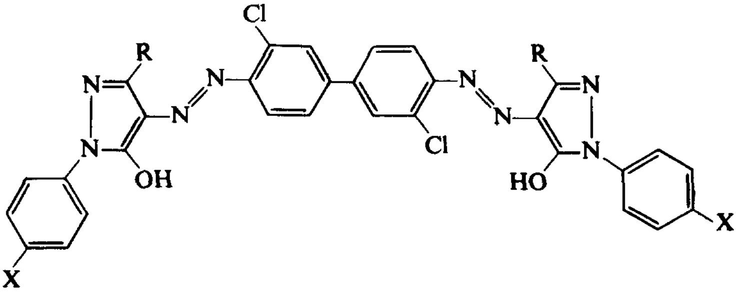


	R^1	R^2	X
C.I. Pigment Yellow 13	CH_3	H	CH_3
C.I. Pigment Yellow 14	CH_3	H	H
C.I. Pigment Yellow 17	OCH_3	H	H
C.I. Pigment Yellow 83	OCH_3	OCH_3	Cl

Fig. 1. Structures of C.I. Pigment Yellow 13, 14, 17 and 83.

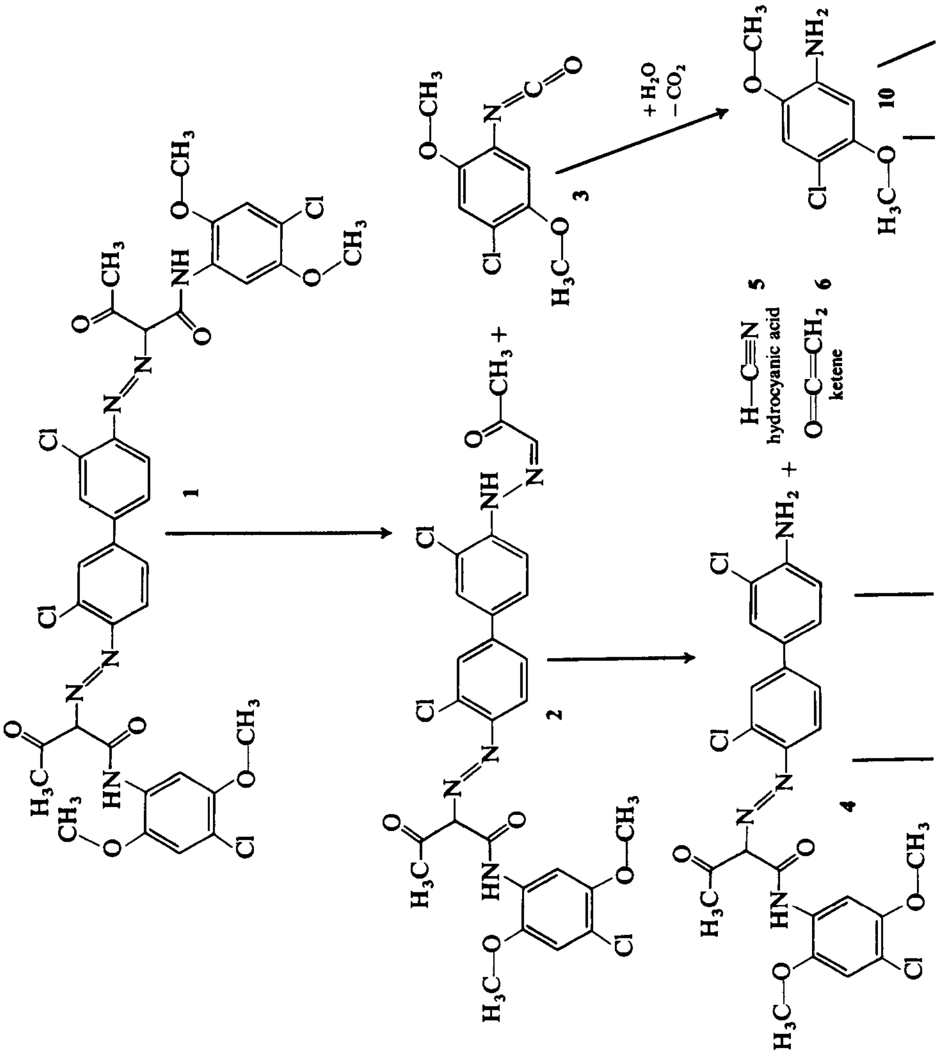
Bisazopyrazolone pigments having orange or red hues have variations in the substituents R and X in the formula shown in Fig. 2.

Superior color strength, in combination with apparent resistance to heat, are the reasons for the widespread applications of these pigments, even in polymers at temperatures between 200 and 270°C.[6] The heat resistance of these pigments in polymers was tested coloristically.[7,8] A second reference for the superior heat stability of these pigments was the differential thermal analysis of the powder pigment in the atmosphere. Analysis of C.I. Pigment Yellow 83 indicates an exothermal decomposition in this test, at temperatures starting above 340°C.



	R	X
C.I. Pigment Orange 13	CH_3	H
C.I. Pigment Orange 34	CH_3	CH_3
C.I. Pigment Red 38	$COOC_2H_5$	H

Fig. 2. Structures of C.I. Pigment Orange 13 and 34 and C.I. Pigment Red 38.


1
2
3
4
5
6
10
hydrocyanic acid
ketene
+H2O
−CO2

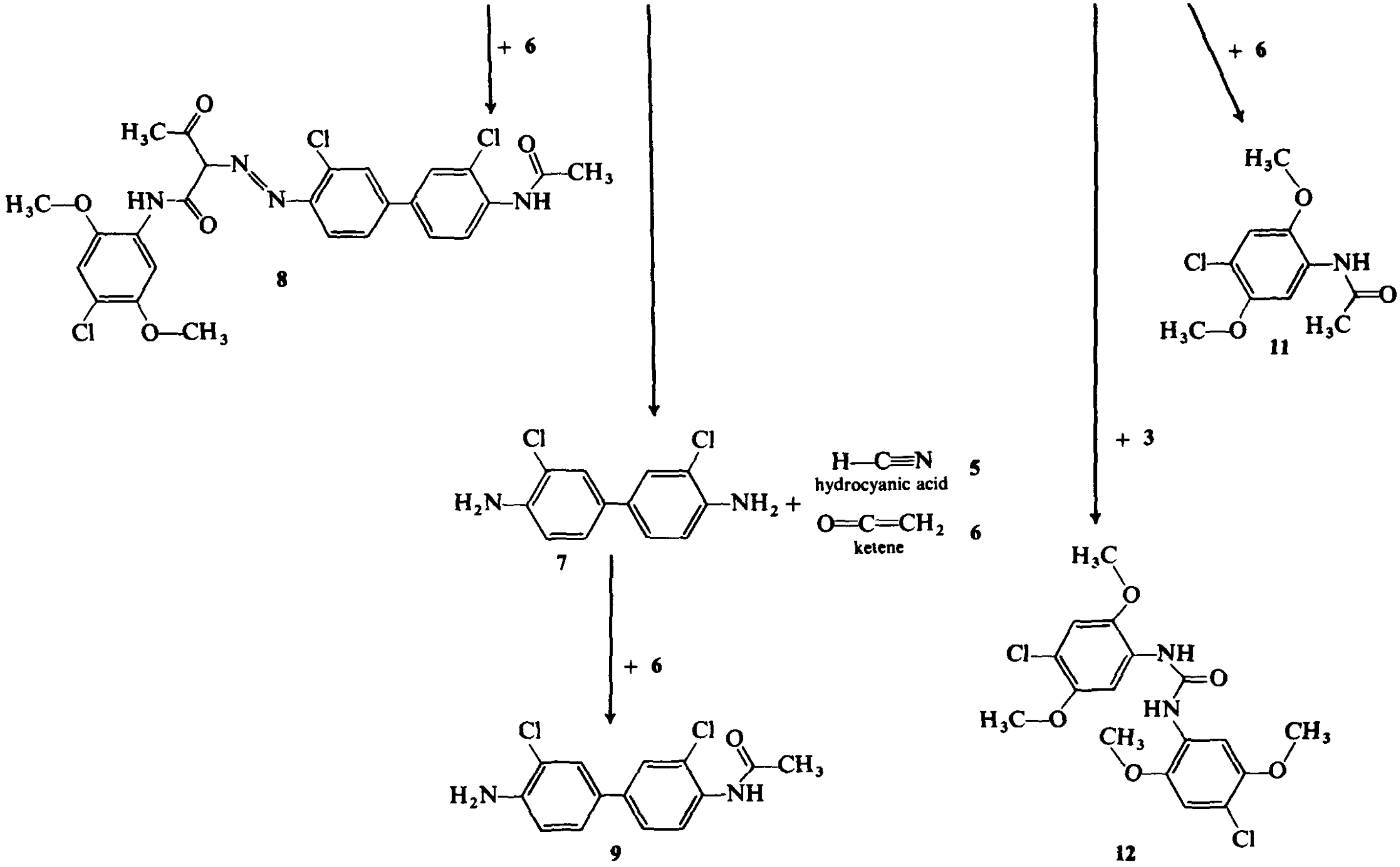


Fig. 3. Example of the thermal cleavage of bisacetoacetarylide pigment (C.I. Pigment Yellow 83).

Surprisingly, a deep yellow-colored solution was obtained when polypropylene injection-molded samples pigmented with C.I. Pigment Yellow 83, which had been treated at temperatures above 260°C, were extracted. The extraction solvent of analogous samples produced at 200°C was colorless. This result was reproduced with a higher amount of polymer and pigment. After milling the plastic, extraction with toluene, evaporation of the solvent and liquid chromatography of the residue in a silica column, at least three yellow-colored products were detected. Three fractions of the main products were pure enough for spectroscopic investigations of the chemical structures. As a result, the three compounds **2**, **4** and **8** (Fig. 3) were identified. The main products of the thermal degration are the azo dyes **2** and **4**, while product **8** is only present in trace amounts. The structures of products **4** and **8** were confirmed by synthesis and comparison of spectra (see Sections 3.4 and 3.5).

The structures of the colored fission products suggested that colorless secondary fragments, such as primary aromatic amines, must be present in the polymer. By use of HPLC analysis, comparison with precursors of the pigments, also assumed to be fission products, and spikes, a further series of fragments was identified. As shown in Fig. 3, the structures of the colorless products **7**, **9**, **10**, **11** and **12** were confirmed by synthesis or by comparison with chemicals of known structure. There is no reference in the literature describing the mechanism of this thermal degradation.

During the extrusion of polypropylene spin-dyed fibers pigmented with C.I. Pigment Yellow 83, hydrocyanic acid (**5**) was detected in the atmosphere by its odor. Air samples from the extruder port were conducted through a caustic system to absorb the hydrocyanic acid as sodium cyanide. Titration analysis of the caustic solution to measure the amount of cyanides, proved that hydrocyanic acid is one of the thermal degradation products of diarylide pigments based on Fig. 1.

Although a complete study of the kinetics of the thermal pigment degradation, and direct proof of the presence of the highly reactive products, like ketene (**6**) and the phenylisocyanate (**3**), are not available, the complete series of fission products obtained enables a mechanism for the degradation to be proposed. In a first step, beginning above 200°C, the diarylide pigments are cleaved into an azo dye (**2**) and a phenylisocyanate (**3**). The phenylisocyanate (**3**), while not detectable as such, is quickly transformed into the corresponding aromatic amine (**10**), and into traces of the symmetrical aromatic urea (**12**). At higher temperatures, when further degradation reactions occur, the acetylated aromatic amine (**11**) is also detectable. A subsequent cleavage reaction of the azo dye (**2**) into the monoazo dye (**4**) becomes dominant at temperatures around 240°C, and especially above 260°C. In this step, the original azo group is cleaved to the amine, and hydrocyanic acid is liberated. It is assumed that ketene is also liberated. As a side reaction, the acetylation of amines, resulting in the products **8**, **9** and **11**, is an indication of the validity of this assumption. The cleavage of one azo group in the bisazo pigment to an amine occurs twice, in the same manner, to yield 3,3′-dichlorobenzidine (**7**). Products **2**, **4** and **8** are quite similar in shade to the pigment, exhibiting high color strength, thus explaining why the thermal degradation was previously unnoticed.

A comparison of the thermal decomposition in polymers of C.I. Pigment Yellow 13, 14, 17 and 83 (Fig. 1), indicates that cleavage starts above 200°C. The amount of fragments increases, as a result of comparable mass temperature and dwell time, in the order C.I. Pigment Yellow 83 < 13 < 14 < 17. The solubility of the pigments increases at elevated temperatures in polymers in the same order, but the slope of the increase of thermal degradation is not very significant.

Pyrazolone pigments (Fig. 2) undergo a similar cleavage reaction into monoazo dyes, starting above 200°C. Since it was not possible to identify all possible fragments, the degradation mechanism for pyrazolone pigments cannot be presented. In contrast to the diarylide yellow pigments, pyrazolone pigments change in hue as a result of their fragmentation. Monoazo dyes isolated as fragments of C.I. Pigment Orange 13 by chromatographic methods indicate that there are at least two different ways for cleavage to occur (Fig. 4). Besides the monoazo dye **15**, which results

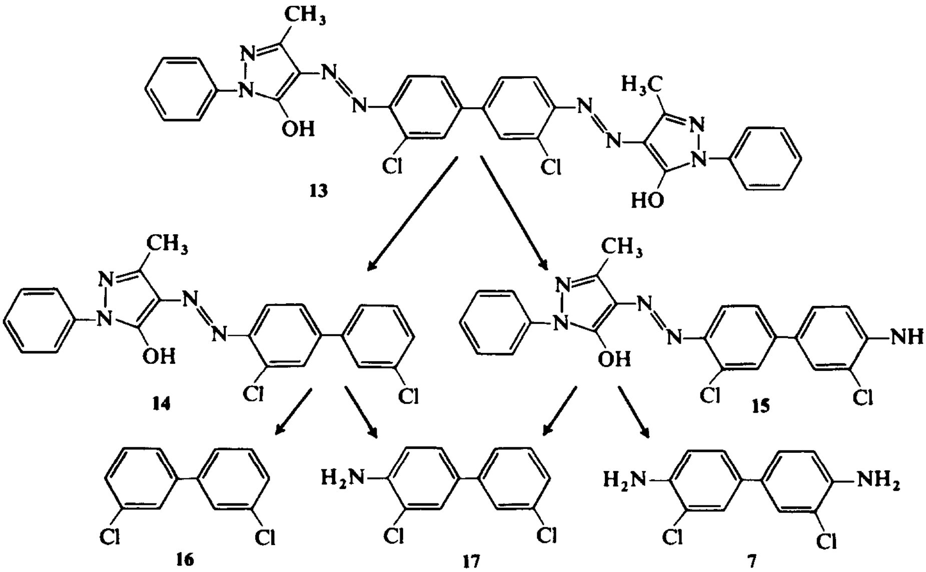


Fig. 4. Example of the thermal cleavage of bisazopyrazolone pigment (C.I. Pigment Orange 13).

from the cleavage of the azo group to the corresponding amine, an amine-free monoazo dye (**14**) is also formed as a degradation product. The amount of the dye **14** is slightly higher than that of dye **15**. In the UV-visible spectra, dye **14** shows a hypsochromic shift, resulting in a yellow hue.

Because the first step of the degradation of pyrazolone pigments leads to monoazo dye (**14**, **15**) with and without amino groups, secondary cleavage yields three biphenyl derivatives, viz. 3,3′-dichlorobenzidine (**7**), 4-amino-3,3′-dichlorobiphenyl (**17**) and 3,3′-dichlorobiphenyl (**16**), all confirmed by synthesis. Although the thermal degradation of the pyrazolone pigments also starts at 200°C, the amount of fragments, especially monoazo dyes, is much higher at 240°C compared with that obtained with diarylide yellow pigments at the same temperature. Above 260°C, pyrazolones are almost completely decomposed.

Table 1 shows the most significant results of this investigation, summarizing the amount of fission fragments in 1% spin-dyed polypropylene fiber. The concentration of the fragments in ppm (parts per million) is expressed in relation to the polymer mass.

TABLE 1
Degradation Rate

C.I. Pigment	*Spin-dyeing*		*Concentration (ppm) expressed in relation to polymer mass*			
	Temperature (°C)	*Dwell time (min)*	*3,3′-Dichlorobenzidine (**7**)*	*Aniline derivative (**10**)*	*Monoazo dye 1 (**4** or **15**)*	*Monoazo dye 2 (**2** or **14**)*
Yellow 83	200	10	n.d.	—	0·46	0·20
Yellow 83	220	10	n.d.	—	0·82	0·73
Yellow 83	240	3	0·23	32·4	1·17	12·9
Yellow 83	240	7	0·07	38·5	1·49	23·0
Yellow 83	240	10	0·11	58·5	2·56	47·4
Yellow 83	260	3	1·02	118·0	13·5	238·0
Yellow 83	260	7	2·96	143·0	20·9	234·0
Yellow 83	260	10	9·34	171·0	36·3	238·0
Yellow 83	270	10	83·60	301·0	164·0	160·0
Yellow 83	280	10	182·0			
Yellow 13	260	10	8·37		250·0	—
Yellow 14	260	10	12·3		420·0	—
Yellow 17	260	10	30·2		319·0	—
Orange 13	240	10	0·23		26·6	182
Orange 34	240	10	4·0		106·0	—
Red 38	240	10	19·8		—	—

n.d. = Not detectable.

In several other pigmented polymer systems, the rate of pigment decomposition in relation to the application temperature is quite similar. During the course of this investigation, polyethylene, polystyrene, polyvinyl chloride, polyester-based heat-curable sheet-metal prints and powder coatings were examined. Polyolefins and polystyrene have almost the same behavior. Metal prints and powder coatings are cured in a stoving/baking process, sometimes above 200°C, with a dwell time of between 10 and 30 min. Some difficulties were encountered in extracting pigment fission products and in detecting aromatic amines from cured systems. The results indicate that the thermal degradation of diarylide pigments starts between 220 and 230°C, resulting in the formation of monoazo dyes and aromatic amines. 3,3'-Dichlorobenzidine may occur in traces at 230°C after baking for about 30 min. In flexible polyvinyl chloride below 200°C, no traces of fission products are detectable under any conditions. Mass pigmented rigid polyvinyl chloride films are often manufactured in a calendering process between 230 and 250°C. PVC films pigmented with C.I. Pigment Yellow 83 showed no amines by toluene extraction. Only when the fission products are liberated from their corresponding hydrochloride salts with gaseous ammonia, can the aromatic amines be detected in a low ppm range in the extract. The analysis of PVC films containing diarylide pigments confirms also the thermal degradation of diarylide pigments leading to monoazo dyes and aromatic amines at 230 to 250°C (dwell time about 1 min). 3,3'-Dichlorobenzidine was not detected under these conditions. The fission products contain basic amino groups, which were immobilized after neutralization with hydrochloric acid present in the films. An extraction of the degraded products is only possible under these specific conditions (ammonia + solvent).

The thermal degradation of diarylide pigments as described is not a general reaction of all azo pigments. Examination of different types of azo pigments indicates that many other pigments used in the coloration of plastics are heat resistant, sometimes up to more than 300°C. It is assumed that the thermal degradation of diarylide pigments starts when the pigments begin to dissolve into the polymer. This explains the difference to the heat resistance of the powder pigments (340°C) already mentioned. Pigments containing several carbonamide and/or benzimidazolone groups are

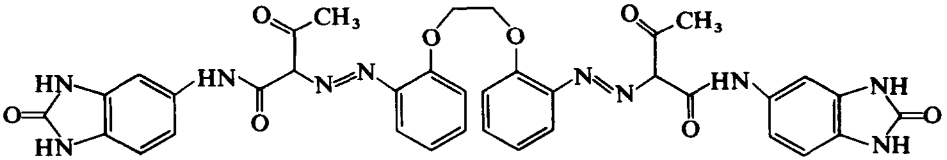


Fig. 5. Structure of C.I. Pigment Yellow 180.

completely insoluble. Pigments based on these groups, e.g. C.I. Pigment Yellow 180 (Fig. 5), are heat resistant, measured by chemical analysis (extraction and HPLC), up to 300°C.

3 EXPERIMENTAL

3.1 Spin-dyed Polypropylene fibres

For this experiment polymer samples were produced using equipment and processes typical for the industry. In each case the authors began with a polyethylene master batch (color concentrate), where the powder pigment was carefully dispersed in the polymer at 180°C. Subsequently, the highly concentrated master batch was diluted with Hostalen PPU 1780 F1 (polypropylene) in a screw extruder at 180°C, to yield a 1% pigmented polymer. This was the basic material for the production of spin-dyed fibers on a laboratory scale spinning machine, varying the extrusion temperature between 200 and 270°C and the dwell time of the polymer melt from 3 to 10 min. In this way, many of the authors' own samples were evaluated with different polymers, as well as the samples supplied by customers.

3.2 Extraction of samples

Spin-dyed fibers (50 g) were extracted in a Soxhlet extractor with 700 ml toluene (analytical grade) for 20 h. Subsequently the extract was evaporated in a vacuum to a volume of about 300 ml. After the addition of 170 ml methanol, dissolved polymers were precipitated and separated by filtration. One tenth of the solution was separated to determine the colored monoazo dyes by HPLC. The remaining 90% of the extract was concentrated by evaporation of the solvent in a vacuum. The residue was taken up in 10 ml methanol for HPLC analysis of the aromatic amines.

3.3 HPLC chromatographic analysis

The HPLC system 'Gold Universal Grad System II' (Beckman Instruments) consists of pump module 126, UV–visible detectors 166/167, automatic sampling and injection system 507, column thermostat, IBM PS2-70 computer with chromatography software package 'System Gold'. The analytical method for the detection of 3,3′-dichlorobenzidine and other aromatic amines is as follows:

—Solvent A: water double distilled; solvent B: methanol.
—Flow rate: 0·8 ml/min.
—HPLC-column: reversed-phase C-18, spherical 5 μm, 250 × 4 mm.
—Column temperature: 30°C.
—Injection volume: 20 μl.
—UV-detection: 282 nm, amines; 410 nm, monoazo dyes.
—Gradient run starting at 50% solvent A and 50% solvent B, increasing B within 40 min to 100%, after 60 min equilibration to starting conditions.

The calibration of all measured products was conducted with available or synthesized and purified products.

3.4 Synthesis of monoazo dyes for analytical comparison and HPLC calibration

In accordance to the literature[9] 3,3′-dichlorobenzidine was monoacetylated in a mixture of water–ethanol with acetic anhydride. The resulting product was confirmed by its melting point (105°C), thin-layer chromatography and spectra (NMR, IR). Subsequent diazotization with sodium nitrite in dilute hydrochloric acid yielded a diazonium salt. In a further reaction with an equimolar amount of available pigment coupling components, the corresponding acetylated monoazo fission products of all the examined pigments were obtained.

The cleavage of the acetyl group was somewhat difficult, giving satisfactory results only with a system based on butanol and 33% aqueous NaOH (25:1). The cleavage reaction was complete after 3 h at 90°C. After recrystallization from ethyl acetate, the products were characterized and identified by spectroscopic examination (MS, NMR, IR, UV–visible; see Tables 2 and 3).

3.5 Spectra

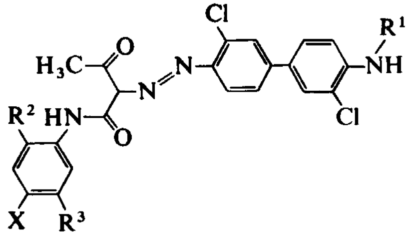
In Table 2, the synthesized monoazo fragments from C.I. Pigment Yellow 13, 14, 17 and 83 are listed, together with their spectroscopic data. Table 3 contains the corresponding data on monoazo fragments from C.I. Pigment Orange 13, 34 and C.I. Pigment Red 38.

4 CONCLUSION

All the dichlorobenzidine-based pigments examined undergo cleavage in polymers at temperatures above 200°C, yielding a mixture of monoazo dyes

TABLE 2

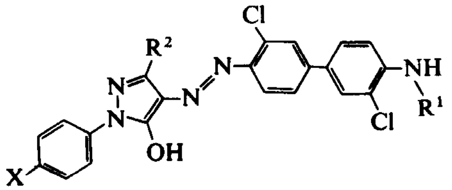
Analytical Data of Synthesized Monoazo Fragments of Diarylide Pigments



R^1	R^2	R^3	X	MS $(M^{+\cdot})$	NMR δ (ppm) $(CDCl_3)$	IR ν (cm^{-1}) (KBr)	λ_{max} (ε − mol) (nm) $(CHCl_3)$
CO—CH_3	CH_3	H	H	496	2·3 s; 2·43 s; 2·68 s; 7·0–8·7 m	1 610, 1 675	396 (40 017)
H	CH_3	H	H	454	2·40 s; 2·65 s; 6·8–8·3 m	1 610, 1 620, 1 660, 3 350	404 (36 240)
CO—CH_3	CH_3	H	CH_3	510	2·28 s; 2·33 s; 2·38 s; 2·65 s; 7·0–8·0 m	1 605, 1 675	396 (41 179)
H	CH_3	H	CH_3	468	2·30 s; 2·38 s; 2·63 s; 7·0–8·0 m	1 600, 1 620, 1 660, 3 340	404 (37 959)
CO—CH_3	OCH_3	H	H	512	2·25 s; 2·63 s; 3·95 s; 6·8–7·9 m	1 600, 1 670	399 (44 449)
H	OCH_3	H	H	470	2·63 s; 3·95 s; 6·8–7·9 m	1 600, 1 620, 1 670, 3 380	406 (39 246)
CO—CH_3	OCH_3	OCH_3	Cl	576	2·30 s; 2·63 s; 3·90 s; 7·0–8·0 m	1 600, 1 670	402 (43 134)
H	OCH_3	OCH_3	Cl	534	2·63 s; 3·90 s; 6·7–8·8 m	1 600, 1 620, 1 670, 3 360	410 (35 840)

TABLE 3

Analytical Data of Synthesized Monoazo Fragments of Pyrazolone Pigments



R_1	R_2	X	MS ($M^{+\cdot}$)	NMR δ (ppm) ($CDCl_3$)	IR ν (cm^{-1}) (KBr)	$\lambda_{max}(\varepsilon - mol)$ (nm) ($CHCl_3$)
CO—CH_3	CH_3	H	480	2·30 s; 2·43 s; 7·0–8·0 m	1 600, 1 610, 1 660, 1 710, 3 420	417 (33 068)
H	CH_3	H	438	2·43 s; 7·0–8·0 m	1 600, 1 620, 1 660, 3 360	430 (29 669)
CO—CH_3	CH_3	CH_3	493	2·28 s; 2·40 s; 7·1–8·0 m	1 600, 1 660, 3 280	416 (34 496)
H	CH_3	CH_3	451	2·35 s; 7·1–7·9 m	1 620, 1 650, 3 380	429 (30 083)
CO—CH_3	COO—C_2H_5	H	537	1·50 t; 2·28 s; 4·50 q; 7·2–8·1 m	1 600, 1 660, 1 700, 1 740	453 (31 082)

and primary aromatic amines. Prolonged heating in the application media at temperatures above 240°C leads to 3,3′-dichlorobenzidine, in a concentration of about 1 ppm in relation to the polymer article. At 280°C more than 100 ppm of 3,3′-dichlorobenzidine, a proven animal carcinogen, was found.

In order to avoid the possibility of health hazards, those pigment producers who are members of ETAD (Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry), have advised against the use of diarylide pigments for general applications in polymers involving the use of temperatures above 200°C.

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