

## ON THE SYNTHESIS AND THE APPLICATION OF SOME REACTIVE TRIAZINE AZODYES CONTAINING TETRAMETHYLPIPERIDINE FRAGMENT

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Received 27 January 2006  
Accepted 03 March 2006

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### ABSTRACT

The synthesis of two reactive triazine azodyes containing a tetramethylpiperidine (TMP) residue in their structure was investigated. Two applied in the practice azodyes, a yellow and a red one as basic chromophores were used. The synthesis of the dyes was controlled by thin-layer chromatography (TLC). The compounds were characterized also by UV/Vis, IR and <sup>1</sup>H-NMR spectra. The synthesised two and another eight triazine reactive dyes, three of them containing a TMP fragment and five trade products not containing a TMP fragment were investigated. Cotton fabrics were dyed and their fastness of perspiration, dry and wet treating as well as machine washing were determined. The fabrics with an intense colour and good characteristics were obtained thus presenting a possibility for extension of the applied in practice reactive dyes.

Keywords: reactive triazine azodyes, 2, 2, 6, 6-tetramethylpiperidine stabilizer.

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### INTRODUCTION

Among the triazine reactive dyes azo derivatives have an important place and are applied for dyeing of various materials. The combination of unsaturated functional group and stabilizer residue in the dye's molecule improves their light fastness [1-7], dyeing ability and possibility for application. We have previously reported the synthesis and investigation of some orange triazine reactive dyes, containing TMP fragment and unsaturated functional group, which were able to copolymerize with different monomers, thus inherently coloured polymers were obtained [6, 7]. Based on these results, it was of interest to study the synthesis of some other chromophores in order to cover the whole range of colour. This give the opportunity for extension of applied in practice reactive dyes with such kind of dyes suitable for simultaneously dyeing and stabilization of polymeric and textile materials. This was the object of the present study.

### EXPERIMENTAL

#### Materials, equipment and analyses

2-allyloxy-4-[4-(2,2,6,6-tetramethylpiperidinil)amino]-6-chloro-1,3,5-triazine was synthesized before [6]. 1,3-phenyldiamine-4-sulfonic acid (**m-PDA**) (79,52 %), 1-amino-8-naphthol-3,6-disulfonic acid (**H acid**) (75 %), N-(4-sulphophenyl)-3-methyl-5-pirazolone (**SP**) (83,57 %), aniline (90 %), sodium carbonate, sodium chloride were products of Fluka (Swiss); solvents are of p.a or analytical grade (Fluka). Procion Red H-EXL, Procion Red H-E7B, Procion Yellow H-E6G, Procion Yellow H-EXL and Procion Blue H-EXL were mixed monochlorotriazine reactive dyes [8], products of ICI (BASF), made in India. TLC analyses were made on silica gel plates (Fluka, F60<sub>254</sub>, 5x10 cm, 0,2 mm thickness, ready-to-use) using a Camag (Swiss) TLC equipment, comprising a Linomat IV device for sample application, a Scanner II and an SP429 Integrator.

pH values were controlled using a 704 pH-meter (Metrohm, Swiss).

Electronic spectra were recorded on a Hewlett Packard 8452A UV/Vis spectrophotometer; IR- on "Specord" (DDR);  $^1\text{H-NMR}$  spectra on DRX-250-Brucker equipment.

The dyeing and the colour fastness were performed in a specialized laboratory.

### Synthesis of the compounds

**Dye 1:** A solution of 1,79 g (0,0055 mol) of 2-allyloxy-4-[4-(2,2,6,6-tetramethylpiperidinil)amino]-6-chloro-1,3,5-triazine in 10 ml of acetone were added to 25 ml ice-water and to this suspension at 0-5°C a solution of 1,3 g (0,0055 mol) of **m-PDA** in 9 ml of water was added. After 2,5 h at the temperature 40-45°C and pH 7-7,5 kept by adding of 2 ml of 20 %  $\text{Na}_2\text{CO}_3$  (TLC control, silica gel and system n-propanol:ammonia-2/1, v/v), the intermediate **1.1** was isolated using 15 % NaCl, filtered off and dried at 35°C under vacuum. The intermediate was characterized by  $R_f$ , IR,  $^1\text{H-NMR}$  and Vis spectra.

0,72 g (0,0015 mol) of **1.1** were dissolved in 5 ml of water and was diazotized by adding 0,11 ml HCl and 0,1 g  $\text{NaNO}_2$  as 20 % aqueous solution. The diazo compound thus obtained after 1 h was added to an aqueous solution of 0,46 g (0,0015 mol) of **SP**, while the temperature was kept 0-5°C and pH 7-7,5 by adding 1,2 ml of 20 %  $\text{Na}_2\text{CO}_3$ . After 1 h (TLC control, silica gel and system n-propanol:ammonia-2/1, v/v), the dye **1** was isolated using 15 % NaCl, filtered off and dried at 35°C under vacuum. The dye was characterized by  $R_f$ , IR,  $^1\text{H-NMR}$  and Vis spectra.

**Dye 2:** A solution of 1,45 g (0,0045 mol) of 2-allyloxy-4-[4-(2,2,6,6-tetramethylpiperidinil)amino]-6-chloro-1,3,5-triazine in 8 ml of acetone were added to 25 ml ice-water and to this suspension at 0-5°C a solution of 1,7 g (0,0045 mol) of H acid in 8 ml water was added. After 4 h at temperature 50-55°C and pH 7-7,5 kept by 4 ml of 20 %  $\text{Na}_2\text{CO}_3$  (TLC control, silica gel and system n-buthanol:acetic acid:water - 4/1/4, v/v/v), the intermediate **2.1** was isolated using 15 % NaCl, filtered off and dried at 35°C under vacuum. The intermediate was characterized by  $R_f$ , IR,  $^1\text{H-NMR}$  and Vis spectra.

Following a standard procedure [9] diazotized aniline was obtained. The diazo compound thus obtained was added to a solution of 1,3 g (0,002 mol) of **2.1** at 0-

5°C and pH 7-7,5. After 1 h (TLC control, silica gel and system n-buthanol:acetic acid:water - 4/1/4, v/v/v), the dye **2** was isolated using 15 % NaCl, filtered off and dried at 35°C under vacuum. The dye was characterized by  $R_f$ , IR,  $^1\text{H-NMR}$  and Vis spectra.

### Chromatography

Standard solutions of the dyes were prepared with concentration  $7,5 \cdot 10^{-5} \text{ g ml}^{-1}$  in DMF. Samples (1?1) of these standard solutions were applied to plates by means of Linomat IV spotting device, equipped with a Hamilton microsyringe. The chromatograms were developed with the appropriate mobile phases, the spots were monitored under UV light (254 nm) and  $R_f$  values for each spot were measured. For quantitative analysis the chromatograms were scanned with Scanner II. The data for the area of each spot were recorded. The error was 1,5-3 % from three replicate analyses.

### Dyeing

100 % cotton fabrics were dyed according to standard procedure [10] in a specialized laboratory at 0,5, 1 and 3 % depth o.w.f. Colourimetric investigations using standard calibration curve were performed with solutions of the dyes in water (concentration  $7,5 \cdot 10^{-5} \text{ g ml}^{-1}$ ).

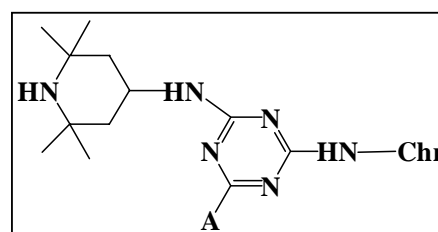
The fastness of perspiration, dry and wet friction and machine washing at 60°C were determined of the dyed with 1 % dye fabrics using the standard procedure in a specialized laboratory [10-12].

The percentage of exhaustion and fixation of the dyes were performed using the standard method.

## RESULTS AND DISCUSSION

### Synthesis of the compounds

The dyes can be presented by the following general formula I:



(I)

The meanings of **A** and **Chr** are given in Table 1.

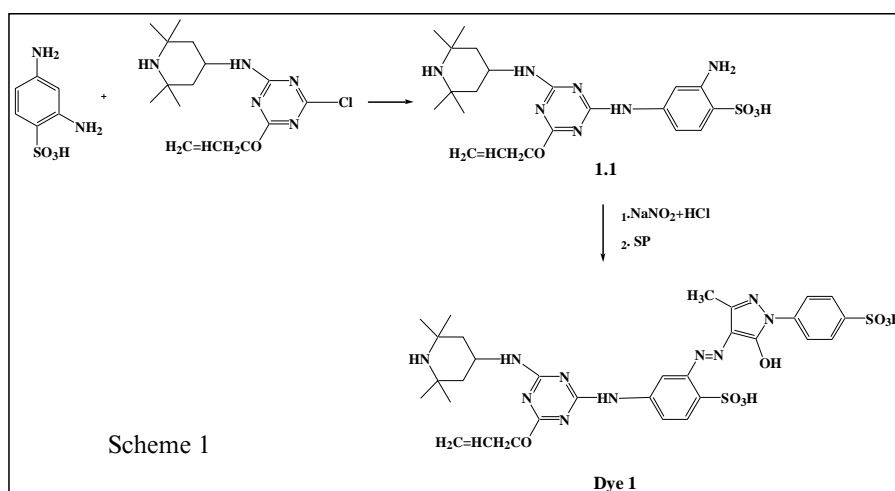
Five commercial reactive dyes were included in the present study to be determined and made a com-

Table 1. Meanings of **A** and **Chr**.

Dye №	A	Chr
1	-OCH <sub>2</sub> CH=CH <sub>2</sub>	
2	-OCH <sub>2</sub> CH=CH <sub>2</sub>	
3	-OCH <sub>2</sub> CH=CH <sub>2</sub>	
4	-Cl	
5	-NHCH <sub>2</sub> CH=CH <sub>2</sub>	

Notice: **Dyes 3, 4 and 5** were synthesized before [6]

**Dye 1:** The reaction of the 2-allyloxy-4-[4-(2,2,6,6-tetramethylpiperidinyl)amino]-6-chloro-1,3,5-triazine with *m*-PDA, was performed in water-acetone media at 40-45°C and pH 7-7,5. The process was controlled by TLC using the system *n*-propanol:ammonia-2/1,v/v. TLC control showed over 97 % conversion after 2,5 h. The product **1.1** was isolated in yield 94 %.  $R_f = 0,36$ ,  $\lambda_{max} (H_2O) = 270$  nm, IR spectra data (KBr)  $cm^{-1}$ :  $\nu_{-NH_2} = 3360$  and  $3320$ ,  $\nu_{-NH} = 3360$ ,  $\nu_{-C-H} = 2920$ ,  $\delta_{-NH} = 1560$ ,  $\delta_{-C-H} = 1430$  and  $1380$ ,  $\nu_{-C-O-C} = 1220$ ,  $\nu_{-C-N} = 1180$ ,  $\delta_{-CH=CH_2} = 1100$  and  $920$ ,  $\nu_{-SO_2} = 1040$ ;  $^1H$ -NMR spectra ( $D_2O$ , 250MHz)  $\delta$  ppm: 7.579-6.222 (m, 3H, ArH); 6.131-6.019 (m, 1H, -CH=); 5.456-5.287 (m, 2H, CH<sub>2</sub>=); 4.5-4.2 (m, 3H, -OCH<sub>2</sub>-, -NH); 2.198-



parison of the behaviour of synthesized dyes in dyeing process: Procion Red H-EXL (**Dye 6**), Procion Red H-E7B (**Dye 7**), Procion Yellow H-E6G (**Dye 8**), Procion Yellow H-EXL (**Dye 9**) and Procion Blue H-EXL (**Dye 10**), not containing a TMP fragment.

#### Synthesis of dye 1

The synthesis of the dye was performed according to the following reaction scheme 1.

First, *m*-PDA was reacted with 2-allyloxy-4-[4-(2,2,6,6-tetramethylpiperidinyl)amino]-6-chloro-1,3,5-triazine and the resulting compound **1.1** after diazotation and reaction with **SP** as a coupling component, was converted to dye **1**.

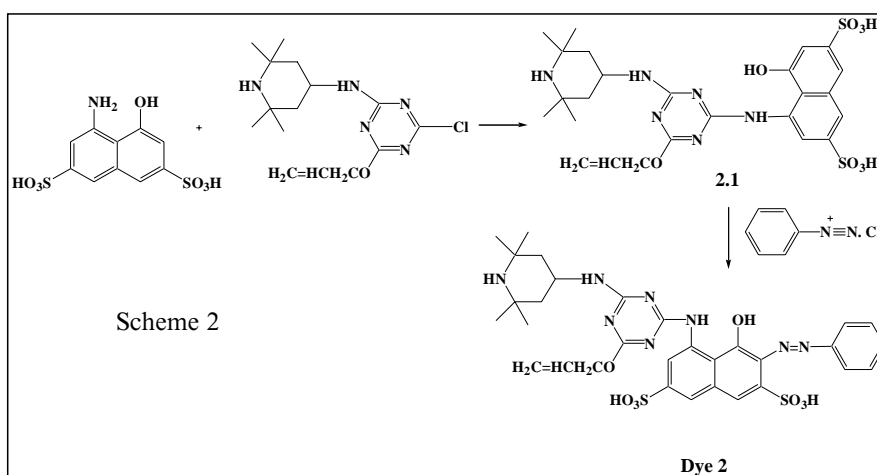
2.043 (m, 6H, 2 x -CH<sub>2</sub>-, -NH-, -CH of TMP); 1,563 (s, 6H, 2 x -CH<sub>3</sub> of TMP); 1.463 (s, 6H, 2 x -CH<sub>3</sub> of TMP).

The product **1.1** was diazotized at 0-5°C by adding HCl and NaNO<sub>2</sub>. The diazo compound thus obtained was added to a solution of **SP** in water at temperature 0-5°C and pH 7-7,5. The process was controlled by TLC using the system *n*-propanol:ammonia-2/1, v/v. After 1h the dye **1** was isolated in yield 98 %.  $R_f = 0,45$ ,  $\lambda_{max} (H_2O) = 386$  nm, IR spectra data (KBr)  $cm^{-1}$ :  $\nu_{-OH} = 3400$ ,  $\nu_{-NH} = 3360$ ,  $\nu_{-C-H} = 2940$ ,  $\delta_{-NH} = 1560$ ,  $\delta_{-C-H} = 1430$  and  $1380$ ,  $\nu_{-C-O-C} = 1210$ ,  $\nu_{-C-N} = 1170$ ,  $\delta_{-CH=CH_2} = 1100$  and  $980$ ,  $\nu_{-SO_2} = 1040$ ;  $^1H$ -NMR spectra ( $D_2O$ , 250MHz)  $\delta$  ppm: 7,902-7,756 (m, 7H, ArH);

6,1-6,048 (m, 1H, -CH=); 5,390-5,262 (m, 2H, CH<sub>2</sub>=); 4,5-4,32 (m, 3H, -OCH<sub>2</sub>-, -NH); 2,290-2,039 (m, 9H, 2 x -CH<sub>2</sub>-, -NH, -CH of TMP and -CH<sub>3</sub> of SP); 1,53 (s, 6H, 2 x -CH<sub>3</sub> of TMP); 1,42 (s, 6H, 2 x CH<sub>3</sub> of TMP).

### Synthesis of dye 2

The synthesis of the dye was performed according to the following reaction scheme II.



According to the Scheme 2, H acid was reacted with 2-allyloxy-4-[4-(2,2,6,6-tetramethylpiperidinyl)amino]-6-chloro-1,3,5-triazine and the resulting compound **2.1** after reaction with diazotized aniline, was converted to dye **2**.

**Dye 2:** The reaction of the 2-allyloxy-4-[4-(2,2,6,6-tetramethylpiperidinyl)amino]-6-chloro-1,3,5-triazine with H acid, was performed in water-acetone media at 50-55°C and pH 7-7,5. The process was controlled by TLC using the system n-buthanol:acetic acid:water - 4/1/4, v/v/v. TLC control showed over 95% conversion after 4 h. The product **2.1** was isolated in yield 94 %.  $R_f = 0,18$ ,  $\lambda_{\max}(\text{H}_2\text{O}) = 224$  nm, IR spectra data (KBr)  $\text{cm}^{-1}$ :  $\nu_{\text{OH}} = 3400$ ,  $\nu_{\text{NH}} = 3360$ ,  $\nu_{\text{C-H}} = 2940$ ,  $\delta_{\text{NH}} = 1560$ ,  $\delta_{\text{C-H}} = 1430$  and  $1380$ ,  $\nu_{\text{C-O-C}} = 1210$ ,  $\nu_{\text{C-N}} = 1170$ ,  $\delta_{\text{CH=CH}_2} = 980$ ,  $\nu_{\text{SO}_2} = 1040$ ; <sup>1</sup>H-NMR spectra (D<sub>2</sub>O, 250MHz)  $\delta$  ppm: 7,85-6,88 (m, 4H, ArH); 6,07-5,96 (m, 1H, -CH=); 5,39-5,23 (m, 2H, CH<sub>2</sub>=); 4,30-4,23 (m, 3H, -OCH<sub>2</sub>-, -NH); 2,11-1,92 (m, 6H, 2 x -CH<sub>2</sub>-, -CH, -NH of TMP); 1,42 (s, 6H, 2 x -CH<sub>3</sub> of TMP); 1,31 (s, 6H, 2 x -CH<sub>3</sub> of TMP).

The aniline was diazotized by adding HCl and NaNO<sub>2</sub> using standard procedure [9]. The diazo compound thus obtained was added to a solution of **2.1** in water at

temperature 0-5°C and pH 7-7,5. The process was controlled by TLC using the system n-buthanol:acetic acid:water - 4/1/4, v/v/v. After 1 h the dye **2** was isolated in yield 98 %.  $R_f = 0,30$ ,  $\lambda_{\max}(\text{H}_2\text{O}) = 540$  nm, IR spectra data (KBr)  $\text{cm}^{-1}$ :  $\nu_{\text{OH}} = 3400$ ,  $\nu_{\text{NH}} = 3360$ ,  $\nu_{\text{C-H}} = 2940$ ,  $\delta_{\text{NH}} = 1560$ ,  $\delta_{\text{C-H}} = 1430$  and  $1380$ ,  $\nu_{\text{C-O-C}} = 1210$ ,  $\nu_{\text{C-N}} = 1170$ ,  $\delta_{\text{CH=CH}_2} = 980$ ,  $\nu_{\text{SO}_2} = 1040$ ; <sup>1</sup>H-NMR spectra (D<sub>2</sub>O, 250MHz)  $\delta$  ppm: 7,57-7,39 (m, 8H,

ArH); 5,93-5,86 (m, 1H, -CH=); 5,24-5,12 (m, 2H, CH<sub>2</sub>=); 4,32-4,16 (m, 3H, -OCH<sub>2</sub>-, -NH); 2,04-1,99 (m, 5H, 2 x -CH<sub>2</sub>-, -CH of TMP); 1,79 (s, 1H, -NH of TMP); 1,41 (s, 6H, 2 x -CH<sub>3</sub> of TMP); 1,3 (s, 6H, 2 x -CH<sub>3</sub> of TMP).

### Spectrophotometric measurements

The absorption spectra of all dyes were recorded in water (concentration  $7,5 \cdot 10^{-5}$  g ml<sup>-1</sup>) using Hewlett Packard 8452A UV/Vis spectrophotometer. Dyes **1-5** showed only one absorption maximum, while dyes **6-8** – two absorption maxima. The dyes **9** and **10** showed only one absorption maximum as well, but they were broader than those of dyes **1-5** – for dye **9** (340-540 nm) and for dye **10** (500-680 nm). Data are given in Table 2.

### Chromatography

Using a Camag TLC equipment, comprising a Linomat IV device for sample application the dye's R<sub>f</sub> values were determined. Data are given in Table 2.

One can see from this data that dyes **6-10** are mixed dyes, where the dyes **6-8** are mix of two dyes

Table 2. Data of  $\lambda_{\max}$  (nm), A and R<sub>f</sub>.

Dye №	$\lambda_{\max}$ (nm)	A	R <sub>f</sub>
<b>1</b>	386	0,680	0.45 <sup>a</sup>
<b>2</b>	540	0,874	0.30 <sup>b</sup>
<b>3</b>	498	0,975	0.84 <sup>c</sup>
<b>4</b>	508	0,774	0.8 <sup>c</sup>
<b>5</b>	484	1,275	0.76 <sup>c</sup>
<b>6</b>	520	1,685	0,28 <sup>d</sup> and 0,53 <sup>d</sup>
	548	1,726	
<b>7</b>	518	1,303	0.16 <sup>d</sup> and 0.62 <sup>d</sup>
	542	1,313	
<b>8</b>	358	0,982	0.40 <sup>e</sup> and 0.50 <sup>e</sup>
	418	1,022	
<b>9</b>	418	1,020	0.47 <sup>e</sup> and 0.53 <sup>e</sup> and 0.63 <sup>e</sup>
<b>10</b>	624	1,784	0.47 <sup>e</sup> and 0.50 <sup>e</sup> and 0.60 <sup>e</sup>

<sup>a</sup>n-propanol:ammonia = 2/1, <sup>b</sup>n-buthanol:acetic acid:water = 4/1/4, <sup>c</sup>n-buthanol:acetic acid:water = 4/1/5, <sup>d</sup>n-buthanol:acetic acid:water = 4/2/2,5, <sup>e</sup>n-propanol:ammonia:pyridine = 2/1/1

Table 3. Colour assessment of dyed fabrics.

Dye №	Perspiration		Friction		Washing at 60°C	Percentage	
	acid	alkaline	dry	wet		Exhaustion	Fixation
<b>1</b>	4-5	4-5	5	4-5	5	56	83
<b>2</b>	3-4	3	5	5	4-5	57	82
<b>3</b>	3-4	3-4	5	5	4-5	89	93
<b>4</b>	3-4	2	5	3-4	2	83	92
<b>5</b>	4-5	4-5	5	4-5	4-5	85	92
<b>6</b>	4	3-4	4-5	4-5	3-4	-	-
<b>7</b>	3-4	3-4	5	5	4-5	-	-
<b>8</b>	4-5	4-4	5	4-5	5	-	-
<b>9</b>	3-4	2-3	3-4	4	3-4	-	-
<b>10</b>	5	3-4	5	4-5	4-5	58	87

each and dye **10** - mix of three, what corresponded of the data given in Table 3.

### Dyeing

100% cotton fabrics were dyed according to standard procedure [10] in a specialized laboratory at 0.5, 1 and 3 % depth o.w.f. Colourimetric investigations using standard calibration curve were performed with solutions of the dyes in water (concentration  $7,5 \cdot 10^{-5}$  g ml<sup>-1</sup>).

The fastness of perspiration, dry and wet friction as well as machine washing at 60°C for fabrics 1 % dyeing were determined using the standard procedure in a specialized laboratory [10-12]. Data are given in Table 3. One can see from these data that the presence of both an allyloxy group and a TMP fragment in the dye molecule led to increase of the colour fastness of the dyes.

The percentage of exhaustion and fixation of the dyes **1-5** (containing TMP fragment) and dye **10** (trade product, not containing TMP fragment) were performed using the standard method. Data are given in Table 3. One can see from these data that the percentage of exhaustion and fixation of the dyes **1, 2** and **10** are commensurable, while these of the dyes **3-5** are vastly increased.

### CONCLUSIONS

Two new triazine reactive dyes, containing allyloxy group and TMP fragment were synthesized. These and another eight dyes were investigated. Cotton fabrics were dyed with high percent of exhaustion and fixation. The obtained dyes are able to extension of applied in practice reactive dyes, because they are suitable

for simultaneously dyeing and stabilization of polymer and textile material. These reactive dyes could be used for application to polyacrylamide and polyacrylonitrile, as their influence on the process of photodegradation of the dyed samples is object of future study.

#### REFERENCES

1. V. Bojinov, T. Konstantinova, *Polim. Degrad. Stab.*, **68**, 2000, 295-298.
2. V. Bojinov, T. Konstantinova, *Dyes Pigm.*, **54**, 2002, 239-245.
3. T. Konstantinova, R. Lazarova, V. Bojinov, *Polim. Degrad. Stab.*, **82**, 2003, 115-118.
4. V. Bojinov, *J. Photochem. Photobiol. A: Chem.*, **162**, 2004, 207-212.
5. V. Bojinov, G. Ivanova, D. Simeonov, *Macromol. Chem. Phys.*, **205**, 2004, 1259-1268.
6. P. Miladinova, T. Konstantinova, *Dyes Pigm.*, **67**, 2005, 63-69.
7. P. Petrova-Miladinova, T. Konstantinova, *J. Univ. Chem. Technol. Met. (Sofia)*, **39**, 4, 2004, 405-412.
8. In The House of Representatives, 108th congress, 1st Session, HR 2642 IH, June 26, 2003.
9. U. Lehmann, (Ciba Speciality Chemicals Holding Inc., Switz), Germ. Patent EP 922, 735, C 09 B 67/22, CA, Vol. **131**, No 4, 1999.
10. Bulgarian Standard 7480-73 (ISO 105 CO6)
11. Bulgarian Standard 4668-73.
12. Bulgarian Standard 4678-73.