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NOVELL 2-CHLORO-PARAPHENILENE-DIAMINE AND 2,4,5-TRICHLORO-ANILINE DERIVATIVES AS ORGANIC PIGMENTS. SYNTHESES AND PROPERTIES

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Această lucrare descrie sinteza a 6 noi pigmenţi azo de dispersie pentru produse din poliesteri armati cu fibre de sticla. Pigmenţii au fost obţinuţi prin reacţii de cuplare plecând de la 2-cloro-parafenilen-diamină şi 2,4,5-tricloro-anilină, folosind drept componente de cuplare: 2,4-acetoacet-xilidină, 2,5–dimetoxi-4-cloro-acetoacetanilidă, acid chromotropic şi β-naftol. Structura pigmenţilor a fost confirmată prin spectre IR şi UV-Vis, iar calităţile tinctoriale prin vopsirea unor plăci din poliesteri armaţi cu fibră de sticlă. Noii coloranţi sintetizaţi au prezentat o bună rezistenţă la acţiunea apei şi la lumină, ceea ce îi recomandă pentru noi aplicaţii.

This paper describes the synthesis of 6 new dispersion pigments produced from fiberglass reinforced polyester. The pigments were obtained by coupling reactions starting from the amines: 2-chloro-paraphenylene-diamine, 2,4,5-trichloro-aniline using 2,4-acetoacet-xylidine, 2,5-dimethoxy-4-chloro-acetoacetanilide, chromotropic acid and β-naphthol as coupling components. Pigments structures were confirmed by IR and UV-VIS spectra and their tinctorial properties were tested by painting glass fiber reinforced polyester tiles. The pigments showed good resistance to water and light, making them suitable for new applications.

Keywords: azo pigments, 2-chloro-paraphenylene-diamine, 2,4,5-trichloro-aniline, IR and UV-Vis spectra, painting of glass fiber reinforced polyester tiles

1. Introduction

Pigments are intensely colored and water and organic solvents insoluble. They could be embedded in several materials (plastic, rubber, linoleum etc.) or applied (from a suspension) on the surface of a natural or synthetic support, using a brush or by spraying or dipping. The first in reinforced polyester procedures, the manual lamination or contact formation procedure is the most common due to simplicity, low investments and yield of unique products at low prices, of small or

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medium series. Coloring can be made in the resin mass or only at the product surface.

Fiberglass reinforced resin products (F.R.R.P.) combine the properties of plastic masses with the hardness of resins which are reinforced with fiberglass fabrics. Fiberglass fabrics that are used have adaptable hardness and they cast to the type of synthesized final product. Polyesteric resins for fiberglass have diverse characteristics in respect with their uses: protection against fire or environmental agents (corrosion, temperature changes, solar radiation etc.), producing food recipients used in food industry.

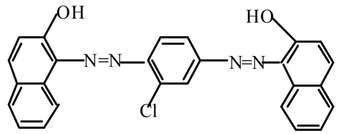
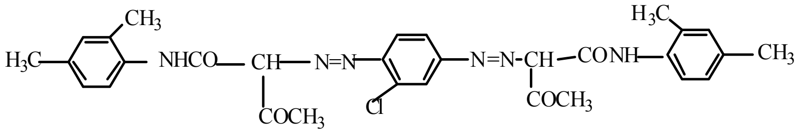
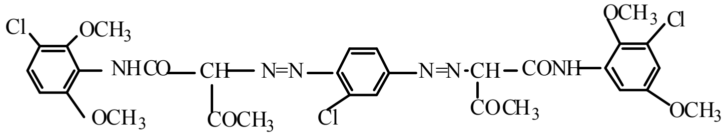
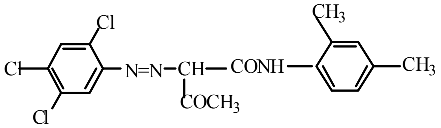
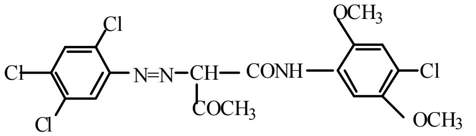
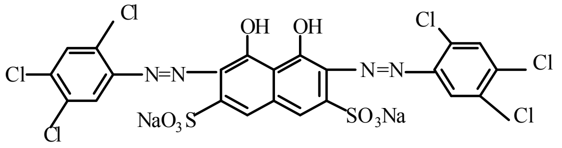
Naphtol azo derivatives can be used as pigments for coloring F.R.R.P. [1]. They are mainly red colored. Their structure includes the carboxyl group of 2-hydroxy-3-naphtoic acid modified as aryl-amide. The first pigments from this class were patented in 1931 and they were commercialized much more lately. However, due to the high costs they were not used. Other classes of red pigments appeared later on the market.

The common monoazo pigments are red. They are suitable for typographic inks and viscose fibers [2]. Many of them are light proof and resistant enough to trichloroethylene in order to enable them to be used in textile inks. However, due to their low solvent resistance, they are not usable in baked enamels. Nonetheless, they are used for coloring plastic masses and rubber, as they can penetrate in those materials. Pigments containing a sulphonyl group within the diazo component have excellent tinctorial properties. Among those pigments Red CI5 (C.I.12490) is the eldest, being introduced on the market as Permanent Carmine FB [3].

In the present work are described the syntheses of six new pigments for coloring F.R.R.P. denominated P1 –P6. The pigments synthesis was performed starting from two amines: 2-chloro-paraphenylene-diamine, 2,4,5-trichloro-aniline, which were diazotized and coupled with 5 coupling components: 2,4-acetoacet-xylidine, 2,5–dimethoxy-4-chloro-acetoacetanilide, chromotropic acid, 1-phenyl-2-methyl-5-pirrazolone, and β-naphtol. The structure of the six pigments is shown in Table 1.

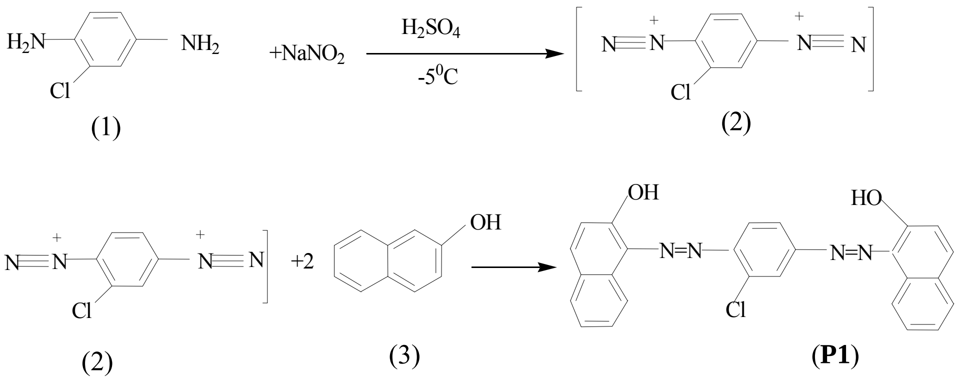
Table 1

Structures of the synthesized pigments

P1	
P2	
P3	
P4	
P5	
P6	

2. Experimental

Pigments syntheses were made according to the similar recipes described in literature [4] for analogous pigments. Scheme 1 illustrates the synthesis of pigment P1.



Scheme 1

a) Diazotization of 2-chloro-para-phenylenediamine (**1**)

Two solutions were prepared in two Erlenmeyer flasks as follows:

S1: 22.9g (0.2 moles) 2-chloro-paraphenylenediamine dissolved in 100mL 94% sulphuric acid, and

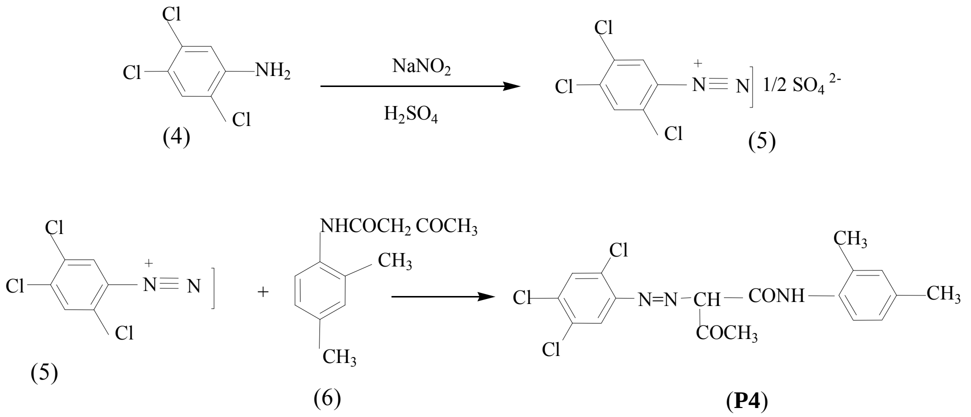
S2: 10g $NaNO_2$ dissolved at 5°C in 50mL 94% sulphuric acid.

The two solutions were cooled at -5 ÷ -10°C. S2 was poured onto S1. The temperature was raised at 0°C during about 3 hours. The nitric acid excess was removed with urea or thiourea.

b) Coupling of 2-chloro-paraphenylenediamine with β-naphtol [5]

28.8g (0.02 moles) β-naphtol was dissolved in a solution formed from 260mL water and 36g NaOH. The diazonium salt solution obtained at point *a)* and 20 g of 40% NaOH were added successively onto this at a temperature under 5°C, to keep a basic pH during the entire experiment. 100 g NaCl were added after heating at 60°C for 3h. The pigment was then precipitated by cooling, and it was dried at 70°C. 41.5g of pigment (P1) were obtained (91% yield).

The reaction scheme illustrating the synthesis of pigment P4 is shown in Scheme 2.



Scheme 2

c) Diazotation of 2,4,5- trichloroaniline

This reaction was realised as described in references [5, 6]. 7 g (0.101 moles) of anhydrous $NaNO_2$ were added in portions to 60 mL (1.5moles, 110 g) H_2SO_4 94% at a temperature below 10°C. After 30 minutes, the solution was heated at 70°C, and then it was cooled on a water bath at 10-12°C. 16.2g of dry, fine powdered 2,4,5-trichloroaniline were then added during 2 - 3 h, under stirring, without exceeding 15°C. The reaction mass was stirred for two hours at 15°C. 200mL of acetic acid were added under stirring and the mixture was poured onto 300g ice and 100g water.

d) Coupling of 2,4,5- trichloro-aniline with 2,4-acetoacet-xylidine

20.5g (0.11mole) 2,4-acetoacet-xylidine was dissolved in a solution prepared from 4.2g NaOH in 160mL H_2O ($pH \geq 9$). The temperature should not exceed 5°C. The diazonium salt solution was added alternatively to the reaction and to a solution formed from 150g H_2O, 100g ice and 100g NaOH 15%. The reaction mixture was kept 12 hours at room temperature. The final pH had to be 7. The obtained pigment was filtered and dried at 60°C. 37.5g pigment (P4) were obtained (93.8% yield).

The syntheses of pigments P2, P3 were performed similarly as for pigment P1, while those for pigments P5, P6 were made as described for pigment P4. In Table 2 are given the specific reaction conditions for all synthesized pigments.

The pigment purifications were made by 2 - 3 successive recrystallizations from 1:1 ethanol-methanol mixtures. Pigment purity was evaluated from the melting point with a Bőetius apparatus. The synthesized colorants purity was tested by thin layer chromatography on a silica support, and eluting with dimethylformamide. The structures of those colorants were confirmed by IR spectra, recorded on a Perkin Elmer apparatus in KBr pills (Merck). UV-Vis spectroscopy analysis for the obtained pigments was performed using a GBS Cintra 101 spectrophotometer, using quartz cuves with an optical path of 10 mm. In order to determine the pigments extinction coefficients, sample of each pigment were weighed and dissolved in spectrally pure acetone (Merck) to form solutions of variable concentrations, and their spectra were recorded on a Jasco V670 spectrometer.

Pigments P1- P6 were applied on fiberglass reinforced polyester tiles with a 2x2cm^2 dimension, after the following procedure. The working table was prepared by cleaning, unction with wax and polishing. 1g of azo organic pigment was introduced into 49g of Nestrapol H 450 unsatured polyesteric resin heated in a crystallizer, and then the mixture was grinded for 30 minutes to obtain a homogenous colored paste. 3g of catalyst (methylethylketone peroxide (MEKP)-3% in ethanol) and 2g of accelerator (diethylamine - 2% in ethanol) were introduced in the polyesteric resin solution. The mixture was stirred thoroughly and the first resin layer was applied, followed by the fiberglass fabric, then another resin layer was applied and pressed with a roller. The above described procedure was repeated three times. The tile was left over night to terminate the reaction and then it was dried.

Similarly, 3, 5, and 7g of pigment representing, respectively, 3, 5, and 7% of the application suspension, were incorporated into the glass fiber tiles. The tiles coloring and the variation of the color intensity with the pigment concentration were examined.

For the determination of the tiles painting water resistance, the probe was introduced in a water bath, were it was kept for 72 hours. In order to determine the painting resistance to solar light, the probe was kept in solar light at a temperature of 27-28 ^{0}C, for 72 hours. Then the probes color modifications were observed with respect to the initial probes.

3. Results and discussion

Two categories of pigments were synthesized. The first category is represented by three new pigments obtained by diazotizing of 2-chloro-para-phenylenediamine, followed by coupling the diazonium salt with different coupling components: β-naphtol, 2,4-acetoacet-xylidine, 2,5-dimethoxy-4-chloro-acetoacetanilide. The second category is represented by three new pigments starting from a monoamine, 2,4,5-trichloro-aniline, which was diazotized to a diazonium salt and then coupled with: 2,4-acetoacet-xylidine, 2,5-dimethoxy-4-chloro-acetoacetanilide and chromotropic acid. The reaction scheme illustrating the synthesis was presented in the experimental part. Table 2 contains details about the specific preparation conditions in the synthesis of these two classes of pigments.

Table 2

Specific coupling components and conditions for the synthesis of pigments P1-P6

Pigment	Diazotized amine	Coupling component [g]	Reaction time [hours]	pH	Yield [%]
P1	2-chloro-para-phenylenediamine	β-naphtol (28.8)	0.5	6	91.5
P2	2-chloro-para-phenylenediamine	2,4-acetoacet-xylidine (21)	12	7	92.1
P3	2-chloro-para-phenylenediamine	2,5-dimethoxy-4-chloro-acetoacetanilide (42)	12	7	76.64
P4	2,4,5-trichloro-aniline	2,4-acetoacet-xylidine (20.5)	3	6	93.8
P5	2,4,5-trichloro-aniline	2,5-dimethoxy-4-chloro-acetoacetanilide (27.15)	12	7	90.1
P6	2,4,5-trichloro-aniline	Chromotropic acid (10.0)	12	7	90.6

The structures of these pigments were confirmed using IR and UV-Vis spectra. Spectral analysis results are given in Table 3. From the analysis of Table 3 data it could be observed that IR spectra are in accord with the literature data [9], the characteristic functional groups of these pigments being present. $C_{asymmetric}$ –N and $C_{aliphatic}$ –N bond vibrations are identifiable in the spectrum by 2960 cm^{-1} (ν_{as}) , 2175 cm^{-1} ($\nu_{symmetric}$) , 1380 cm^{-1} (δ), 1045 cm^{-1} (ρ) bands, respectively, 2920 cm^{-1} ($\nu_{asymmetric}$), 2850 cm^{-1} ($\nu_{symmetric}$) and 78 cm^{-1} (ρ) bands; the OH groups by 3560-3600 cm^{-1} and 1105 cm^{-1} ($\nu_{C\text{-}O\ asymmetric}$) bands, and the azo group by the weak band from 1570 cm^{-1} [10, 14].

Pigments P1 - P6 were tested to determine the light resistance. Each pigment was applied on fiberglass reinforced polyester tiles following the above presented procedure. A uniform coloring was observed in the application solution for all the tiles and also the growth of the color intensity with the pigment concentration increase. In Fig. 1 is shown this dependence for pigment P2.

Table 3

Spectrometric analysis in IR and UV-VIS

Pigment	Functional group	Frequence (cm^{-1})	λ_{max} in UV (nm)	λ_{max} in VIS (nm)	Colour
P1	N=N OCH_3 Cl OH	1570 2964.7 693 1105	327.9; 270.3	500; 540.5; 400	Magenta
P2	N=N OCH_3 Cl NH	1570 2964.7 693 3070	322.5; 218.7	424	Cream
P3	N=N OCH_3 Cl NH	1570 2964.7 693 3070	338; 277.7	505; 370; 434.8	Dark yellow
P4	N=N OH Cl	1570 1105 693	206.2; 222.2; 295.7	512.8; 540.4; 625; 400	Yellow
P5	N=N OCH_3 Cl OH	1570 2964.7 693 3560	332; 343.9	540.5; 512.8; 496.7	Light yellow
P6	N=N C=O Cl CH_3 NH SO_3Na	1570 1710 693 2964.7 2960 680.5	285.7; 312.5; 243.9	540.5; 512.8; 413.2	Violet red

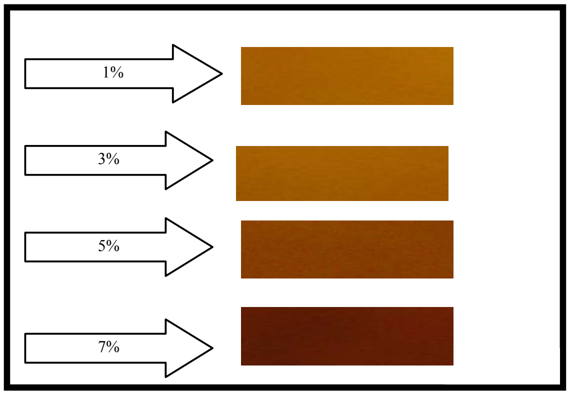


Fig. 1. Variation of the fiberglass reinforced polyester tiles color with the concentration of the pigment P2 in the application solution

Fiberglass reinforced polyester tiles painting resistance to water and sun light was determined. In Fig. 2 it is shown the behavior of the pigment P6 colored tile (in concentration of 5%) after sunlight exposal for 72 hours, according to previously presented procedure. No color modification for the sample was observed with respect to the initial probe. Similar results were obtained for water exposal. No modification of the sample with respect to the initial probe was noticed also in this case. Pigments were uniformly dispersed in the resin forming a homogenous paste and leading to uniform paintings.

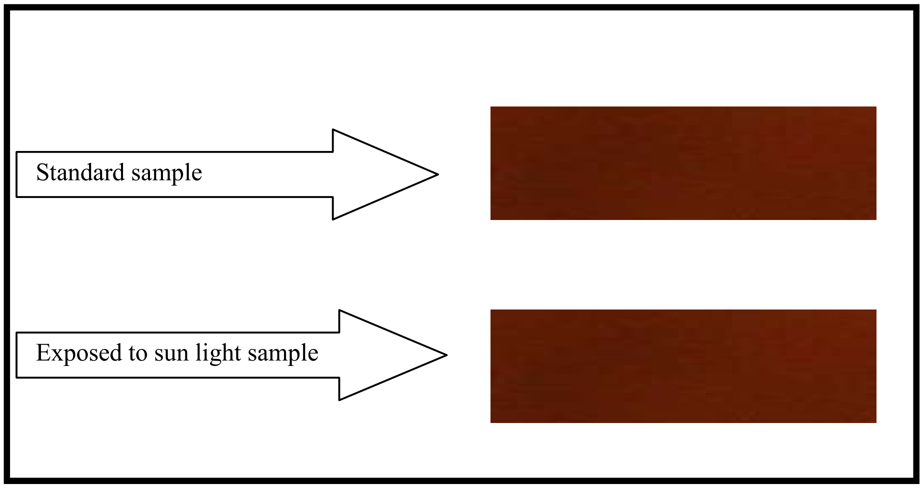


Fig. 2. Light behavior of fiberglass reinforced polyester tiles containing the pigment P6 (in concentration of 5% in the application suspension)

4. Conclusions

The related experiments involved the synthesis of six new pigments for polyester fibers. Their structure was tested using IR and UV-Vis spectra. Their tinctorial properties were tested by painting several fiberglass reinforced polyester tiles. The painting method consisted in the manual application of the pigment dispersed in a resin which contained the catalyst and the accelerator. The procedure is remarkable for its technological simplicity and for the low costs. Light and water resistant paintings were obtained.

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