# Analysis of the Behaviour of PAN Functionalized with Basic Compounds, During Dyeing Process with Acid Dyes

**VASILICA POPESCU[1]*, IRINA CRINA ANCA SANDU[2, 3], GABRIEL POPESCU[4]**

[1] Gheorghe Asachi Technical University, Faculty of Textiles, Leather Engineering and Industrial Management, 29 Mangeron Blv.,TEX 1 Building, 700050, Iasi, Romania

[2] Universidade de Évora, Laboratório HERCULES, Palácio do Vimioso, Largo Marques de Marialva, 8, 7000-809, Évora, Portugal

[3] Romanian Inventors Forum, 3 Sf. P.Movila Str., L11, III/3, 700089, Iasi, Romania

[4] Gheorghe Asachi Technical University, Faculty of Mechanical Engineering, 43 Blvd. Mangeron, Iasi- 700050, Romania

*Romanian acrylic fibers (PAN) were functionalized with substances that have different basicities: NaOH ($pK_b$ = 0.2), Chitosan (CS with $pK_b$ = 7.8) and hydroxyl amine (HA with $pK_b$ = 8.02). All the chemical changes that occur on the acrylic support during functionaliazation were evaluated with FTIR analysis and colorimetric method. Dyeings with non-specific dyes (acid dyes) using different concentrations, durations, and pHs were performed. The influence exerted on the K / S values was studied function of the reagents type used in functionalization. Comparing the tinctorial behaviors of the acrylic functionalized substrates were deducted the ideas as HA and HA+NaOH cause the chemical changes that most favor the dyeing with acid dyes. Durability of the functionalization effects has been demonstrated by good values for the resistances to wet treatments. The color differences ($\Delta E^*$, $\Delta L^*$, $\Delta a^*$ $\Delta b^*$, $\Delta C^*$ and $\Delta H^*$) indicate that any functionalized PAN sample is dyed more intensely than the witness, having brightness smaller and shades slightly different than of the witness.*

*Keywords: functionalized PAN, chitosan, hydroxyl amine, acid dye, dyeing*

Any acrylic fiber can be dyed with cationic dyes due to the electrostatic attraction between the dye's cation and the anion attached onto acrylic polymer [1-9]. Anionicity of the acrylic fiber comes from the synthesis mode: either from the initiator used to obtain the PAN polymer, either from a comonomer. Melana, the Romanian acrylic fiber is based on a ternary polymer (85% acrylonitrile, 10% vinyl acetate, and 5% $\alpha$-methyl styrene) obtained by the reaction of radical polymerization initiated in the redox system: potassium persulphate-sodium metabisulphite [10-16]. Most acrylic fibres contain a mixture of groups of strong acid and weak acid [1, 17]. However, it is necessary that the fiber to have a character of sufficient acid for that connections between acrylic fiber with dye to be stable [1, 17]. Anionicity of the fiber influences the resistance to light fastness; the stronger the attraction exerted by the centres of fiber dyeing, the dyeing resistances are better; such $-SO_3^{2-}$ groups results in a better light resistance than the $COO^-$, derived from weak acids.

The fields of use for PAN fiber are as follow: fabric and outerwear knitwear, technical articles, furs, carpets etc. Some properties as a pleasant touch, a good thermal insulation capacity, a low specific weight, confer special qualities to PAN which allow its use for winter clothing.

The current trend of diversification of the synthetic fibers, generally and acrylic fibers in particular, are the chemical changes and/or physical properties of traditional polymers, and less on the synthesis of new classes of polymers for fibers [16, 18-21].

In this article the chemical modifications of PAN fibers were conducted with substances with character basic (HA, CS), and the mixture of each amine with NaOH. Acquisition of new functional groups makes it possible the dyeing of PAN fiber with acid dyes, in a deeply and uniformly manner.

## Experimental part

### *Materials*

The basic substances used for PAN functionalization were: NaOH, hidroxyl amine (purchased from Merck) and chitosan highly viscous (from Fluka Company). The acid dyes used in dyeing processes were obtained from Alibaba and Benzema companies. The names of these dyes and their main characteristics are shown in table 1. Oxalic acid was used to create the acid environment required to dye with acid dyes; this acid was obtained from Merck. For washing these samples after functionalization and after dyeing we used Lavaton DSU from Bezema Company.For functionalization, the PAN samples were treated with 2.5% reagent at 100°C for 30 min, 1:150 liquor ratio (table 2). After functionalization stage the samples were intensely washed with de-ionized water (at 40°C) and then with cold water at room temperature. All the treatments / functionalizations were carried out on Mathies Policolor machine.

Functionalized samples were subjected to dyeing with four acid dyes, whose structures were shown in table 1. The dyeing with acid dyes was made according to the following steps: protonation in the first 10 min ($pH = 1.5 \div 4$ made with oxalic acid) and dyeing using the recipes: 1 g/L, 4 g/L or 10 g/L dye concentrations, T = 98°C, for one hour using a liquid ratio of M = 1:75 but without to add an electrolyte. After dyeing, the samples were washed with 1 g/L Lavaton DSU, M = 1:75, t = 30 min, T = 90°C. Finally,

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* email: vpopescu65@yahoo.com

**Table 1**
CHEMICAL STRUCTURES AND MAIN CHARACTERISTICS OF ACID DYES

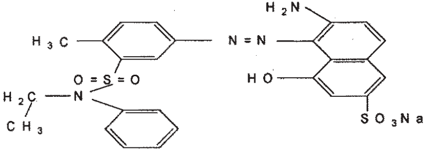
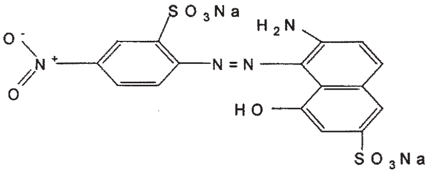
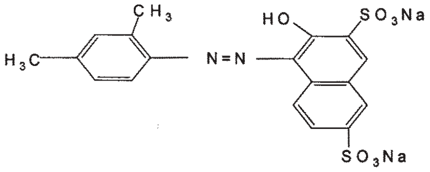
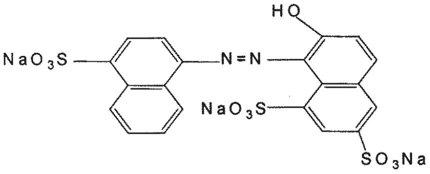
| Chemical structure | Abbreviation | Acid group no. | Molecular weight (g) | Coupling component |
|---|---|---|---|---|
|  **C.I Acid Red 118 (C.I. 26410)** | **AR118** | 1 | 540.619 | ϒ Acid |
|  **C.I Acid Violet 1 (C.I. 17025)** | **AV1** | 2 | 512.37 | ϒ Acid |
|  **C.I Acid Red 26 (C.I. 16150)** | **AR26** | 2 | 480.42 | R Acid |
|  **C.I Acid red 18 (C.I. 16255)** | **AR18** | 3 | 604.47 | G Acid |

**Table 2**
WORKING CONDITIONS

| **Sample code** | **Reagent for functionalization** |
|---|---|
| F1 | 2.5% NaOH |
| F2 | 2.5% CS |
| F3 | 2.5% HA |
| F4 | 2.5% CS + 2.5% NaOH |
| F5 | 2.5% HA +2.5% NaOH |

they were hot then cold rinsed and dried into air. All dyeings and final treatments were performed on Mathies Policolor machine.

*Methods of Analysis*

*FT-IR – analysis* was performed on a Spectrophotometer FTIR IRAffinity-1 Shimadzu (Japan), but the spectra registration was realized with 250 scans in the 4000–600 $cm^{-1}$ range. The overlapping spectra were performed using KnowItAll software from BioRad Company.

*Colour strength* (K/S) was measured by the light reflectance technique using Kubelka-Munk equation (1) [22-40] on a Datacolor Spectrophotometer Sprectroflash SF300.

$$\frac{K}{S}=\frac{(1-R)^2}{2R} \qquad (1)$$

where:

K/S = colour strength;

R = reflectance of the dyed sample [%].

*Fastness properties:* Fastnesses testing for functionalized and dyed were made according to ISO standard AO5-CO6 in 1999 using grey scale related (grey and grey change Stain Scales) to assess the change in colour of samples after a wash, respectively the degree of soiling/dye staining accompanying samples, undyed.

*Colour differences:* the total colour difference (ΔE*) were estimated by ΔL*, ΔC*, Δa*, Δb* and ΔH* values. The significance of these variables [41] is: ΔL* = the difference in colour between the examined sample and witness, i.e. the distance between the respective positions in CIELAB space; ΔL*=difference in brightness; ΔC* = saturation difference; Δa* is the difference on the red-green coordinate, Δb* is the difference on the blue-yellow coordinate; ΔH* = hue difference.

## Results and discussions

*Mechanism*

PAN Functionalization with NaOH determines the conversion of acetate groups into a new functional group, type OH (by saponification reaction) and the nitrile group into a COOH group (via amide group through the hydrolysis reaction) (table 3).

HA acts on both the acetate group (from the vinyl acetate, comonomer in PAN) as well as on the CN group (from the acrylonitrile comonomer). At the level of acetate group takes place a N-acylation reaction with formation of a OH group. At the nitrile group takes place a reaction of amylosis (table 3) when we obtained amidoxime.

The NaOH+HA mixture generates a hydroxamic acid group (O=C-NH-OH) by a N-acylation reaction; initially, the CN group was transformed in COOH, so was created the possibility as HA to act as a nucleophile agent [42].

The solution of CS (which gives a *p*H weak acid to the reaction environment because of the acetic acid used in the dissolution of CS) does not convert the acetate and nitrile groups from PAN, but gives only electrovalent connections with anionic groups (sulfonic) located at the ends of the macromolecular chains of these acrylic polymers [43-48].

Instead, the mixture CS+ NaOH acts as a pronounced basic medium that gives COOH groups through the conversion of CN groups in the first phase; in a second stage takes place the CS addition at COOH group, with formation of a monosubstituted amide (table 3). The acetate groups are converted by NaOH in OH groups, by saponification reactions.

**Table 3**

NEW FUNCTIONAL GROUPS OBTAINED BY CONVERTING OF ACETATE GROUPS AND NITRILE [42-49]

| Code sample | Reagent | Transformation of OCOCH3 group in: | Transformation of CN group in: | Final acid group at the end of the chain |
|---|---|---|---|---|
| F1 | NaOH | -OH<br>*by saponification reaction* | -CO-NH₂ or<br>-COOH<br>*by alkaline hydrolysis* | -SO₃Na |
| F2 | CS | -OCOCH₃ | CN | -SO₃⁻NH₃⁺-CS |
| F3 | HA | -OH<br>*by N-acylation reaction* | C=N–OH<br>\|<br>NH₂<br>Amidoxime (as amidine monosubstituted)<br>*by amylosis reaction* | -SO₃Na |
| F4 | CS + NaOH | -OH<br>*by saponification reaction* | \|<br>C =O<br>\|<br>NH<br>\|<br>CS<br>amide monosubstituted<br>*by N-acylation reaction* | -SO₃Na |
| F5 | HA + NaOH | -OH<br>*by saponification reaction* | C=O<br>\|<br>NH<br>\|<br>OH<br>Hydroxamic acid<br>(as amide monosubstituted)<br>*by N-acylation reaction* | -SO₃Na |

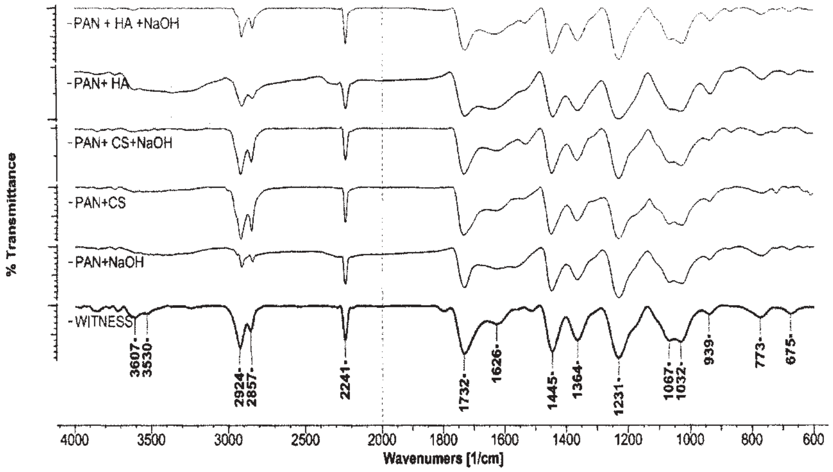


Fig. 1. FTIR spectra for untreated PAN (witness) and functionalized samples

*FTIR*

The FTIR analysis indicates the presence of the acetate group at 1732 cm$^{-1}$ and the CN group at 2241 cm$^{-1}$ [42].

As the table 3 indicates, the reagents used for the PAN functionalization have led to significant chemical changes; the formation of the OH group by the conversion of the acetate group has generated the modification of the absorption bands from 3385 cm$^{-1}$ (OH stretching (s)), 1069 cm$^{-1}$ (C-OH stretching (s)), and near 1400 cm$^{-1}$(for O-H in-plane deformation (m)) [42, 50-52].

Reducing of the peak height assigned for CN group (2241 cm$^{-1}$) is visible in figure 1. This confirms the conversion of CN groups (in a certain percentage, not total) in new groups, such as COOH, amidoximes, amides or hydroxamic acid (table 3) [42, 50-52].

The treatment of PAN with CS solution lead only to the formation of electrovalent links between acid groups from the end of the macromolecular chain of PAN and the -$NH_3^+$ groups from CS solution (obtained during the protanation of $NH_2$ groups from CS). This is confirmed by the changes occurring in the spectrum of PAN+CS sample, namely: in the 3692-3156 cm$^{-1}$ field (OH primary group in CS) and increasing peaks in the 2917-2850 cm$^{-1}$ field (CH stretching overlap (increase as proof of attachment CS) with -$NH_3^+$ deformation vibration). Also, are observed the specific absorption bands for -$NH_3^+$ asymmetric deformation (at 1626 cm$^{-1}$) and -$NH_3^+$ symmetric deformation (at 1537 cm$^{-1}$).

By functionalization of PAN with CS+NaOH, at the level of CN group it is forming a monosubstituted amide; the presence confirmation of this amide is given by the peaks from 1630 cm$^{-1}$ (for C=O stretching vibration), 1535 cm$^{-1}$ (assigned for combination of N-H deformation and C-N stretching vibrations); the peak at 3220 cm$^{-1}$ (assigned to N-H stretching vibration) appears also [43].

The PAN treatments with NaOH, HA or HA+NaOH also led to a specific polymeric chain degradation of PAN, i.e. a decrease in the number of C-C links; this can be seen in figure 1 where the peaks heights in the field 2924-2866 cm$^{-1}$ are lower than for untreated PAN.

NaOH converts the CN groups in COOH groups (via amidic groups), fact confirmed by the height of the peaks at 1732 cm$^{-1}$ (assigned to C=O stretching (s) and 1233 cm$^{-1}$ for C-O stretching vibration (s)); instead, the bigger height of the peaks at 1630 cm$^{-1}$ (C-O stretching (s), 1565 cm$^{-1}$ (N-H out of plane (m)) confirm the presence of amidic groups [42, 43, 53].

The presence of amidoxime in PAN functionalized with HA is confirmed by the absorption bands from 1645 cm$^{-1}$ (C=N stretching, (m)), 3650-3150 cm$^{-1}$ (N-H and O-H stretchings, (s)) and near 937 cm$^{-1}$ (N-O stretching, (w)) [42, 50-52].

In the sample functionalized with NaOH + HA appeared hydroxamic acid groups; the presence of these groups was confirmed by the absorption bands from 1670-1600 cm$^{-1}$ for combination of C-N and C=O stretching (m-s), 1534 cm$^{-1}$ for N-H deformation and C-N stretching (m), and near 937 cm$^{-1}$ for N-O stretching (w) [42, 43, 50-52].

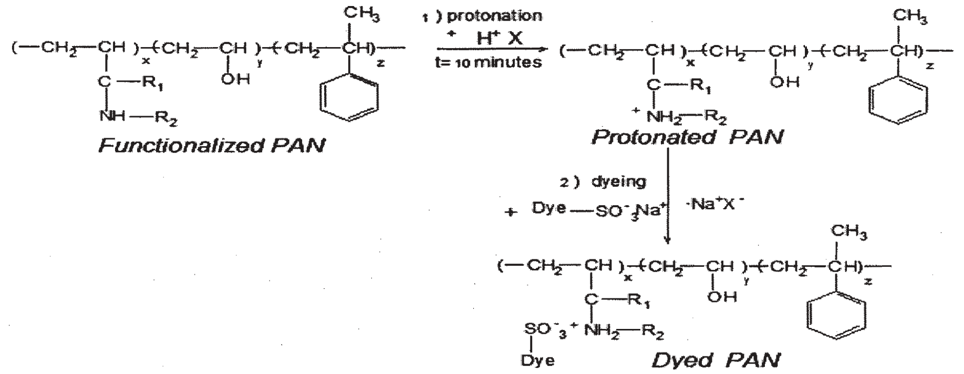


Fig. 2. Scheme for the protonation of functionalized PAN and for dyeing of protonated PAN ($R_1$ is =O (in amides or hydroxamic acid); =N-OH (in amidoximes); $R_2$ is H (in amides and amidoximes); OH (in hydroxamic acid); pyranozic ring from chitosan; X it is HCOO-COO$^-$)

*Tinctorial answer to changes caused by amine ± NaOH*

In the classic version, PAN fibre can be dyed with cationic dyes, but this system presents the risk of unlevelness in dyeing because the two partners have opposite electric charges, and the speed of reaction is extremely high [1, 17]. In order to avoid this disadvantage a rigorous inspection of the dyeing process is made or the acrylic fibre is chemically modified to be dyed with anionic dyes. In this last manner was done in this paper, when after functionalizations with amines ±NaOH, the acrylic fibre is dyed with acid dyes. Chemical and physical changes generated by functionalizations have as tinctorial answer a uniform and profound dyeing. Thus, for the acrylic fibre modified by functionalizing, the capacity of dyeing was studied with four acid dyes: Acid Red 118 **(**abbreviated as AR118**),** Acid Purple 1 **(**abbreviated as AV1), Acid Red 26 **(**abbreviated as AR26) and Acid Red 18 **(**abbreviated as AR18). These dyes are monoazo type and contain 1-3 sulphonyl groups in addition to other substitutes (OH, $NH_2$ or $CH_3$) attached to the coupling component, of naphthalene type (table 1). The sites of dyeing with acid dyes of acrylic fibre modified by functionalization with amines, are even the amino groups, newly formed (table 3) by conversion of CN from acrylonitrile comonomer. In acidic environment realized with oxalic acid, these groups become protonated and the chemical reaction that underlies dyeing can be written according with figure 2.

The ability to dye depends on how easily can be protonated the acrylic fiber functionalized, in the acidic environment of the dyeing. The protonation ability of -C(NH-$R_2$)–$R_1$ groups existing in the functionalized fibers depends on the particularities to the respective group and the interactions with the nitrogen atom, basic center. Therefore, the protonation ability depends on the strength of the effects exerted by $R_1$ and $R_2$ substitutes. On the nitrogen aminic are exerting two types of actions (fig. 3):

a) the repugnant electron actions manifested by the +Es electrophile effects of the $R_2$ substitutes; these effects increase the electron density at the N atom, giving it character basic.

b) The attractive electron actions manifested by the -Es effects of the $R_1$ substitutes; these effects attract the free electrons from the nitrogen atom.

In case of the hydroxamic acids groups (fig 3a), with how these simultaneous and contradictory effects have intensities approximatively equal, with both the electrons not participated from the aminic nitrogen atom remain disposable to accept a proton, when come in contact with the acid from dye bath.

In case of amidoximic groups (fig. 3b), the effects inside $R_1$ are annihilated reciprocal because of C=N group has an effect -$E_S$ approximatively equal with +$E_S$ effect exercised by OH group. In this case the doublet of not participated electrons from the N atom (from $NH_2$ group) is available to accept and to bind a proton through a coordinative link [54]. Therefore, the acrylic fibers containing amidoximic groups respectively hydroxamic acid groups will protonise easily and will establish a significant number of ionic links, with the anions of the dyes used in dyeing process.

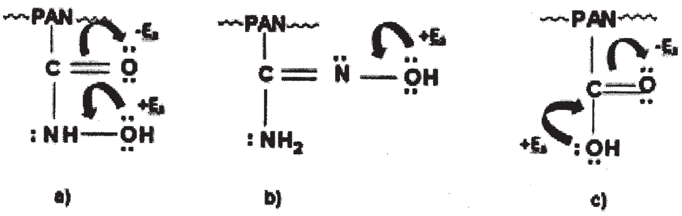


Fig. 3. Effects exercised by substituents from functional groups: a)hydroxamic acid; b) amidoxime; c) carboxylic acid

In case of all chemically modified acrylic fibres by functionalizations (having amides, amidoximes/amidines groups), the affinity towards acid dyes can be explained not only by means of an electrostatic loading in strongly acidic environment (*p*H < 3) but also by their ability determine (at *p*H> 3), with groups corresponding from dye molecule, H-links and other polar forces. Also, existing methylene groups from PAN fibre (attached to styrene or existing in unprocessed acetate group of vinyl acetate comonomer) also contribute to the binding of the dye to fibre by nonpolar forces established with hydrophobic portions of the dye.

*Influence of treatment with amines concerning colour strength values*

The functionalizations influence the colour strength K/S acquired after dyeing with acid dyes, not only by nature and basicity amines used in these treatments but by concentration (fig. 4) and duration of each treatment (fig. 5).

In the figure 4, it is noticed that increase concentration of agents from functionalizations determine an increase of K/S values as a greater numbers of CN groups from PAN is converted in acid or amide/amidine groups (table 3). HA as a nucleophilic agent, with small molecular weight and medium basicity, determines the most pronounced conversions in the acrylic fibre (by making amidoximes); the conversions are reflected by the highest K/S values.

Another factor that influences the values of K/S is the structure of the dye used in dyeing. Thus, the higher affinity of monosulphonic dye (AR118) compared to the polysulphonic dyes (AV1, AR26 and AR18 – table 1) can be explained as follows: a monosulphonic dye has a well determined position into the fibre in sense of the electrostatic attraction between the anionic dye and amino group (from fibre) it does not prevent the alignment of dye molecule (in relation to fiber macromolecule) or the establishment of secondary links. In the case of disulphonic dyes (AV1 and AR26) and trisulphonic dye (AR18) the behaviour is different: they are simultaneously

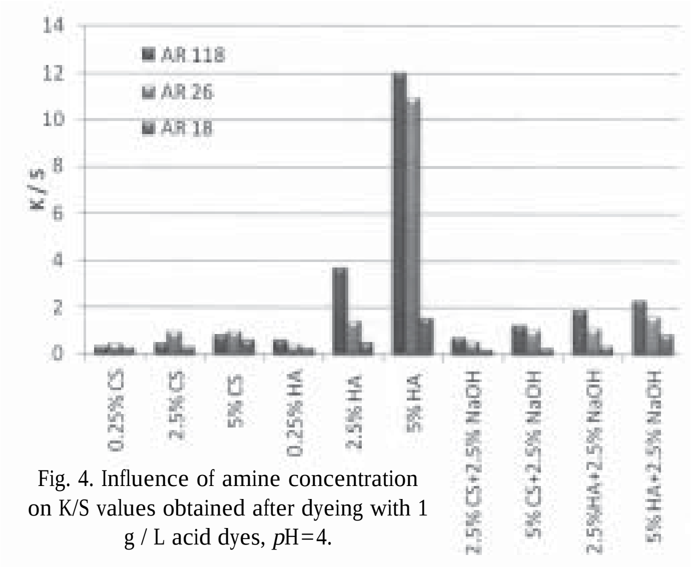


Fig. 4. Influence of amine concentration on K/S values obtained after dyeing with 1 g / L acid dyes, *p*H=4.

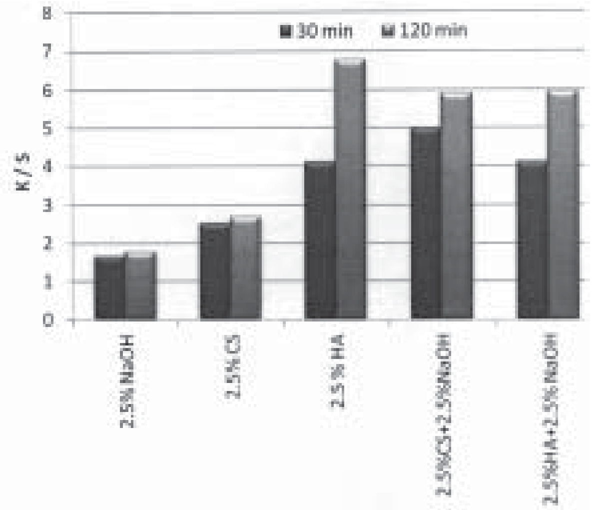


Fig. 5. Influence of functionalization duration on K/S values made by dyeing with 10 g/L AV1 (at *p*H=4)

attracted (because of those 2 or 3 sulphonic groups) by two protonated amino groups, from two different macromolecules. Because of this, the dye molecule oscillates between the two macromolecular chains and cannot occupy an adjacent position to the macromolecules and hence cannot determine secondary bindings.

Whatever the acid dye used for dyeing, the colour strength K/S increases together with the increase of duration of functionalization (fig. 5).

*Influence of dyeing parameters (dyes concentration and pH) on K/S values*

The experimental results indicate that the values of K/S depend on dye concentration (fig. 6) and *p*H used in dyeing bath (table 4).

In figure 6 it is noticed the following fact: as the basicity of amine used in the functionalization decreased, the K/S values after dyeing with acid dye AV1 increased, at *p*H = 4. Another important factor that controls the passage of dyes from the dyeing bath into acrylic fibres modified by functionalization is pH. For those four acid dyes (table 4) were tested the effects of some *p*H values (*p*H = 1.5, 2.0, 3.0 and 4.0), made with oxalic acid.

At low *p*H in the absence of electrolyte, all acid dyes show high K/S values, irrespective of their sulphonic group content. In neutral solution, on the other hand, multi-sulphonics dyes generally show much lower K/S values than monosulphonics dye. In table 4 the highest values for K/S are achieved at *p*H = 1.5 in all cases, except of AV1 when the optimal *p*H is 4. This fact demonstrates that AV1 has the highest affinity for acrylic fibre modified by functionalization. This fact demonstrates that AV1 has the greater affinity for acrylic fibre modified by amination then the other dyes studied in this paper. AV1 has a nitro group in the composition that can determines the forming the dye-fibre links (inclusive polar links) in a greater number. The dyeing at *p*H = 4 leads to levelling dyeings because the presence of two acidic groups (sulfonic acid type) favours desorption of the dye. In addition, through the disturbance to the ratio crystalline/amorphous during functionalizations are facilitated both diffusion, migration and the levelling of dyeing.

**Table 4**

THE K/S VALUES OBTAINED AFTER DYEING WITH 1g/L ACID DYE AT A TEMPERATURE OF 100°C, FOR 60 MINUTES

| **Acid Dyes (no. acid groups)** | **pH Dyeing** | **Reagents used in functionalization treatments** | | | | |
|---|---|---|---|---|---|---|
| | | **2.5% NaOH** | **2.5% CS** | **2.5% CS + 2.5% NaOH** | **2.5% HA** | **2.5% HA + 2.5% NaOH** |
| AR118 (1 acid groups) | 1.5 | 1.945 | 2.30 | 2.10 | 20.80 | 21.70 |
| | 2 | 1.768 | 1.760 | 2.090 | 14.17 | 19.01 |
| | 3 | 1.000 | 0.981 | 1.350 | 4.450 | 5.100 |
| | 4 | 0.987 | 0.453 | 0.668 | 3.700 | 1.853 |
| AR26 (2 acid groups) | 1.5 | 1.588 | 2.110 | 1.423 | 30.30 | 26.00 |
| | 2 | 1.264 | 1.026 | 0.593 | 25.30 | 9.660 |
| | 3 | 0.954 | 0.968 | 0.586 | 3.600 | 2.100 |
| | 4 | 0.857 | 0.956 | 0.549 | 1.413 | 1.088 |
| AV1 (2 acid groups) | 1.5 | 0.897 | 1.026 | 0.611 | 1.790 | 2.150 |
| | 2 | 0.943 | 1.346 | 0.648 | 2.380 | 2.370 |
| | 3 | 0.991 | 1.968 | 0.656 | 3.770 | 2.440 |
| | 4 | 1.019 | 2.540 | 2.720 | 5.795 | 2.850 |
| AR18 (3 acid groups) | 1.5 | 0.489 | 0.350 | 0.212 | 2.210 | 1.125 |
| | 2 | 0.453 | 0.332 | 0.192 | 2.200 | 0.773 |
| | 3 | 0.394 | 0.316 | 0.157 | 1.443 | 0.587 |
| | 4 | 0.354 | 0.285 | 0.188 | 0.494 | 0.338 |

In cases of AR118, AR26 and AR18 dyes, at *p*H = 1.5, takes place the protonation of a greater number of amino groups from the chemically modified acrylic fibres, which intensifies the electrostatic interactions with the anions of dyes (sulphonic-groups) from the dyeing bath. In the case of dyeing at the *p*H < 3 more and more amino groups (inside of amide, peptide -CO-NH- or amidine - acquired by functionalization with amine ± NaOH) are combined with a proton from acid and in this case the quantity of attached dye increases but a certain degradation of fibre appears. The affinities of these dyes are small which justifies getting the values K/S higher at *p*H = 1.5 than at

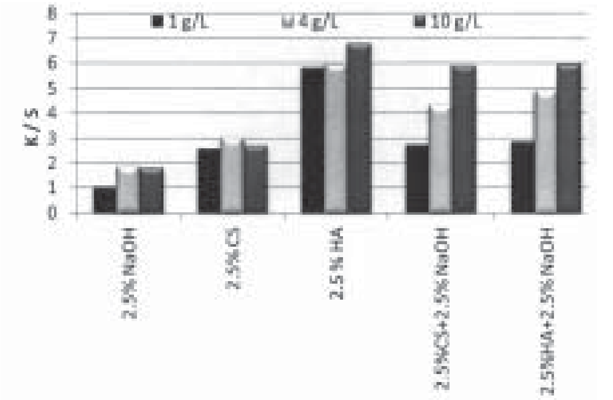


Fig. 6. Influence of AV1 concentration on the K/S values after 120 min of functionalization

**Table 5**
THE VALUES OF FASTNESS TO WASHING

| Acid Dye Code | Reagents used in functionalization treatments | | | | |
|---|---|---|---|---|---|
| | 2.5% NaOH | 2.5% CS | 2.5% CS + 2.5% NaOH | 2.5% HA | 2.5% HA + 2.5% NaOH |
| AR118 | 5/5/5 | 5/5/5 | 5/5/5 | 4-5/5/4-5 | 4-5/5/4-5 |
| AR26 | 4-5/5/4-5 | 4-5/5/4-5 | 4-5/5/4-5 | 4-5/5/4-5 | 4-5/5/4-5 |
| AV1 | 5/5/5 | 5/5/5 | 5/5/5 | 5/5/5 | 5/5/5 |
| AR18 | 5/5/5 | 5/5/5 | 5/5/5 | 5/5/5 | 5/5/5 |

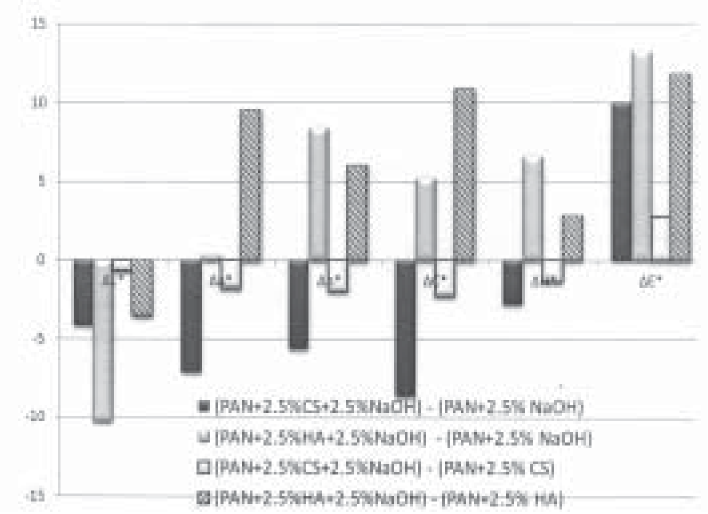


Fig. 7. Colour differences (expressed as ΔL*, Δa*, Δb*, ΔC*, ΔH* and ΔE*) after functionalization of PAN (30 min) and dyeing with 10 g/L AV1 at *p*H = 4

*p*H = 4. The small affinity justifies the high desorption capacity and therefore the good diffusion and migration of these dyes.

In conclusion all dyes used, indifferent of the number of sulphonic groups, dye in a uniform manner.

In Table 4, it is noted that HA and HA+NaOH lead to the highest K/S values. These affirmations can be explained both on the basicity of compounds formed after protonation and on the structure of the dyes.

Shall be deducted that agents HA respective HA+NaOH, used in functionalization, determine the biggest values for K/S, because the groups acquired under their action (amidoximic and hydroxamic acid type) can be protonated most easily. In these two situations there are the possibilities of formation of H bonds with each of the dyes studied, because amidoximic groups and the corresponding hydroxamic acid hold one -OH group. This -OH group may be involved in the intermolecular hydrogen bonds with one of N atoms component of azo group from each acid dye. Polar bonds can be realized also, with polar groups from acid dyes, especial in AR118 and AV1.

Comparing the values of K/S in table 4, according to the structure of the dyes can be deducted the followings:

- the dyes used in dyeing processes differ in the number of sulphonic groups; the dyes having 1-2 sulphonic groups lead at the higher K/S values on all acrylic fibres functionalized;
- AR118 and AV1-dyes have similar structure, with the same coupling component (gamma acid). Both dyes can form ionic bonds and polar with any protonated support. Additionally, AR118 can establish hydrophobic interactions due the alkylic groups attached at the diazo component.

In conclusion, for each acid dyes used, the variation of K/S is the tinctorial answer for chemical changes suffered by the PAN, for the protonation ability, for the dye-fibre interactions and not least the particularities of dye used (planarity, molecular volume, nature of the substitutes and their positions).

The qualitative appreciations between affinity-diffusion have been made in this paper. It is considered that the diffusion takes place in jumps by alternating adsorption and desorption but the affinity brakes the desorption. Therefore, a low affinity (AR18, AR26, and AR118) determines a big coefficient of diffusion and vice versa. The coefficient of diffusion determines the value of the migration capacity of which depends on levelling dyeing. In this paper, good uniformity of dyeing (acclaimed visual) can be explained based on both affinity and a significant refinement of the structure of functionalized PAN fibres. Refinement is proven by values far higher for hygroscopicity of the treated samples than for the standard samples.

### *The fastness to washing*

Chemical modifications made in PAN and implicit the durability of these transformations is proven by the ease with which the dyeing with acid dyes is made respectively by the values of fastness to washing (resistance to wet treatments). The dyeings made with four acid dyes (at *p*H=4 for AV1 and at *p*H=1.5 at the other dyes) have excellent fastness to washing and are presented in Table 5 as three digits indicating the changing in colour after washing / the staining of PAN / the staining of wool.

It is known that if the sulphonic groups' number grows, the dye molecule obtains substantivity for water. That explains why AR118 dye has better results than AR26 (table 5). Comparing the acid dyes with the same number of sulphonic groups it is noticed that AV26 has a slightly weaker resistance than AV1, this is explained by affinity and a lower molecular weight for AV26 compared to AV1.

In case of all acid dyes used in this paper, the component of the naphtalenic coupling includes the OH and/or $NH_2$ substitutes, attached in ortho position to azo bond. So, it is possible forming of H bindings between these groups and nitrogen atoms from â position of azo groups. Consequently, acid-base balance of the OH, $NH_2$ groups is shifted to *p*H < 2 or *p*H > 11. This is very important because the dissociation of OH groups, respectively the protonation of $NH_2$ groups can cause unwanted changes in colour or will split naphthalenic proton in a *p*H range unusual for washing.

### *Colour differences*

Colour differences were determined using a spectrophotometer Spectroflash type Datacolor SF 300 and were indicated in figure 7.

Demonstration of chemical changes realized by functionalizations can be done with the aid values as characterizing uniform colour space. For this fact, some samples were treated for 30 min and then dyed with 10 g/L AV1 (at 98°C, 60 min, *p*H = 4, liquid ratio M = 1: 75), parameters L, a, b, C, H were determined.

To determine the values of ΔL*, Δa*, Δb* ΔC*, ΔH* and ΔE* for samples functionalized and dyed we proceeded to choose the appropriate witness (fig. 7), thus:

-to determine the effect produced by each amine used at functionalization: we compared samples dyed with 10/L AV1 subsequently to treatment with 2.5% amine + 2.5 % NaOH, respectively to 2.5% NaOH (as witness);

-to determine the effect on the colour generated by NaOH used in treatment we compared samples treated with 2.5 % amine + 2.5% NaOH respectively with 2.5 % amine (as witness).

In figure 7 it is noticed that all systems used for treatment, in order to modify the chemical structure of acrylic fibre were effective and after dyeing they produced brightness values $\Delta L^* < 0$, that are darker than the selected witnesses. As it is known in uniform colour space $L^*$ $a^*$ $b^*$ (CIELAB), negative values for $\Delta a^*$ and $\Delta b^*$ of all samples indicate the greenish tint blue except samples that were functionalized with HA ± NaOH these have shades of red and yellow-green, brown. $\Delta E^*$ indicates the difference of colour; this has its highest values in case of functionalization with HA followed by case HA + NaOH.

## Conclusions

The acrylic fibres are physically and chemically modified by functionalizations. The groups obtained by modifying of CN groups from PAN fibre may be protonated in the acidic environment of the dyeing. Many types of interactions between the protonated fiber and the dye were observed: ionic bonds, polar and hydrophobic sometimes. The values of K/S obtained after dyeing depend on the modifications from fibres through the functionalization, by the ability of protonation and the structure and dyes affinity. The levelling of dyeing is the result to the interdependences of the kinetic and thermodynamic factors. Comparing the tinctorial behaviors of the acrylic functionalized substrates were deducted that HA and HA+NaOH cause significant chemical modifications; these modifications led to the obtaining of the biggest K/S values, in the dyeing processes with acid dyes. Durability of the functionalization effects has been demonstrated by good values for the resistances to washing. The fact that any functionalized PAN sample is dyed more intensely than the witness is shown by the color differences. The highest values for $\Delta E^*$ were obtained in the case of functionalization with HA, followed by case HA+NaOH.

## References

1.GRINDEA, M., FORST, T., HANGANU, A., Tehnologia vopsirii si imprimarii textilelor, Ed. Tehnica, Bucuresti, 1983, p. 435.

2.DINU, M., Industria usoarã, Textile, Tricotaje, Confecþii Textile, **26,** no. 3, 1975, p. 124.

3.POPESCU, V., BUTNARU, R., POPESCU, G., Revista Românã de Textile-Pielãrie, **4,** 2000, p. 89.

4.DINU, M., GRINDEA, M., Buletinul I.P.I, Tomul XVIII (XXII), fasc. **1-2**, 1972.

5.POPESCU, V., BUTNARU, R., POPESCU, G., Revista Românã de Textile-Pielãrie, **1**, 2001, p.85.

6.POPESCU, V., BUTNARU, R., POPESCU, G., Revista Românã de Textile-Pielãrie, **4,** 2001, p.85.

7.POPESCU, V., BUTNARU, R., POPESCU, G., Revista Românã de Textile-Pielãrie, **3-4, 2**002, p.71.

8.GRINDEA M., DINU, M., Mat. Plast., **11,** no. 5, 1974, p. 237.

9.BUTNARU, R., POPESCU, V., Dialog Textil**, 7-8**, 1996**,** p. 20**.**

10.DINU, M., Buletinul IPI, Tom XVIII (XXII), fasc. **3-4,** 1972, p.155.

11.AVARVAREI, E., Mat. Plast., **12** no. 2, 1975, p. 83.

12.GRINDEA, M., DINU, M., Buletin IPI, Tom XIX(XXIII), fasc.**1-4**, 1973, p. 25

13.POPESCU, V., Buletin Institut Politehnic, IAªI**,** Tom LV (LIX), fasc. **2**, 2009, p. 59.

14.DINU, M., GRINDEA, M., Mat. Plast., **11**, no. 1, 1974, p. 35.

15.GRIGORIU, A., Mat. Plast., **12,** no. 1, 1975, p. 41.

16. POPESCU, V., MANEA, L.R., SANDU, I. G., CHIRCULESCU, A. I., SANDU, I., Rev. Chim. (Bucharest), **64,** no. 3, 2013, p. 281

17. MARIE, M. M., American Dyestuff Reporter, **9**, 1993, p. 86.

18.POPESCU, V., RADU C. D., MANEA. L. R., Industria Textila, **61**, no. 1, 2010, p. 23.

19.BUTNARU, R., POPESCU, V., Industria Textilã, **47**, no. 4, 1996, p. 235.

20.SÎRBU, A., Dialog Textil, **9,** 1996, p.12.

21.BECKMANN, C., Textil Month, **9**, 1986, p. 7.

22. SCHANDA, J., Colorimetry. Understanding the CIE System, Wiley Interscience, 2007.

23.SANDU, I., SANDU, I.C.A., SANDU, I.G., Colorimetry in Art, Ed. Corson, Iasi, 2002.

24.PUSCAS, E.L., RADU, D.C., Introducere in cunoasterea si masurarea culorii, Ed. Dosoftei, Iasi, 1997, p.154.

25.RADU, C. D., Colour measurement, Ed. Rotaprint, Iasi, 2004, p.61.

26.RADU, C.-D., BERCU, E., SANDU, I., FOIA, L.G., Mat. Plast., **51**, no.1, 2014, p. 104.

27.PUSCAS, E.L., Colour theory and measurement, Ed. Rotaprint, Iasi, 1983, p.167.

28.WARDMAN, R.H., An update on numerical problems in colour physics, Rev. Prog. Coloration, **24**, 1994, p. 55.

29.ATODIRESEI G.V., SANDU, I.G., TULBURE, E.A., VASILACHE, V., BUTNARU, R., Rev. Chim. (Bucharest), **64**, no. 2, 2013, p. 165.

30.BERCU, E., DIACONESCU, R.M., RADU, C.D., POPESCU, V., European J. of Sci. and Theology, **8**, 2012, p. 235.

31.BERCU, E., SANDU, I., RADU, C.D., VASILACHE, V., TOMA, V., Mat. Plast., **50**, no. 3, 2013, p. 215.

32.BERCU, E., SANDU, I., RADU, C.D., VASILACHE, V., TOMA, V., ALDEA, H.A., Mat. Plast., **49**, no. 4, 2012, p. 270.

33.SANDU, I.C.A., LUCA, C., SANDU, I., Rev. Chim. (Bucharest), **51**, no. 7, 2000, p. 532.

34.SANDU I., LUCA C., SANDU I.C.A., CIOCAN, A., SULITANU, N., Rev. Chim. (Bucharest), **52**, no. 9, 2001, p. 485.

35.SANDU, I.C.A., LUCA, C., SANDU, I., POHONTU, M., Rev. Chim. (Bucharest), **52**, no. 7-8, 2001, p. 409.

36.SCARLET, R., MANEA, L.R., SANDU, I., MARTINOVA, L., CRAMARIUC, O., SANDU, I.G., Rev. Chim. (Bucharest), **63**, no. 7, 2012, p. 688.

37.SCARLET, R., MANEA, L.R., SANDU, I., CRAMARIUC, B., SANDU, A.V., Rev. Chim. (Bucharest), **63**, no. 8, 2012, p. 777.

38.POPESCU, V., SANDU, I. G., VASLUIANU, E., SANDU, I. CAMPAGNE, C., Rev. Chim. (Bucharest), **65**, no. 12, 2014, p. 1439.

39.POPESCU, V., SANDU, I., Rev. Chim. (Bucharest), **65**, no. 7, 2014, p. 811.

40.POPESCU, V., SANDU, I., MURESAN, E. I., ISTRATE, B., LISA, G., Rev. Chim. (Bucharest), **65**, no. 6, 2014, p. 676.

41.ZARUBICA, A. R., MILJKOVIC, M.B., PURENOVIÆ, M.M., TOMIÆ, V. B., - Facta Universitatis, Series: Physics, Chemistry and Technology**,** **3**, no 2, 2005, p. 205.

42.POPESCU, V., MURESAN, E.I., Ind. Eng. Chem. Res., **52**, 2013, p. 13252.

43.POPESCU, V., SANDU, I., POPESCU, G., POPA, A., RADU, C.D., Rev. Chim. (Bucharest), **66**, no. 11, 2015, p. 1768.

44.POPESCU, V., RADU, D.C., New achievements concerning the chitosan utilization in the tinctorial processes, The 13th International Salon of Research, Innovation and Technological transfer "Inventica" Iaºi, Romania, June 4th-6th, 2009, p. 583.

45.POPESCU, V., RADU, C.D., MANEA, L.R., AMARIEI, N., Efectele modificarilor generate de anumite pretratamente chimice efectuate pe polimeri acrilici , 1st International Conference Technical Textiles Multidisciplinary Domain, Bucharest, Romania, 22-23 May, 2008, p. 134

46.MANEA, L.R., POPESCU, V., RADU, C. D., BRANISTEANU, D. E., Chitosan effects o tinctorial capacity of acrylic fibers, The 5th International Conference Of Textile Research Division TRD-NRC, Textile Processing: Cairo, Egypt, 6-8, April, 5 (IX), 2008, p. 458.

47.POPESCU, V., RADU, C. D., MANEA, L.R., BRANISTEANU, D. E., New possibilities for acrylic fibers dyeing**,** The 8th Joint International Conference CLOTECH 2008, "Inovative materials & Technologies in Made- up textile articles and footwear", Lodz, Poland, 12-13 June, 2008, p. 79.
48.RADU, C. D., POPESCU, V., MANEA, L.R., Chitosan- pretreatment reagent for acrylics dyeing, The 8th AUTEX Conference AUTEX, Città Studi in Biella– Italy, 24–26 June, 2008.
49. REDA, M.E.L-S., NAHED, S.E.A., Coloration Technology, **121**, 2005, p.139.
50.AVRAM, M., MATEESCU, GH., Infrared spectroscopy. Applications in Organic Chemistry, Ed. Tehnica, Bucuresti, 1988.
51.COATES, J., Interpretation of Infrared Spectra, A Practical Approach, in Encyclopedia of Analytical Chemistry (R.A. Meyers Ed.), John Wiley & Sons Ltd, Chichester, 2000, p. 10815–10837.
52.MILLER, J., BARTICK, E., Appl. Spectrosc., **55**, 2001, p.729.
53.POPESCU, V.**,** Urea treatment of acrylic fibers in case of dyeing with anionic dyes,2nd International Conference "Metrology in Textile Engineering", Lodz Technical University, Poland, Nov. 20-25, 2000, p. 117.
54. CLAYDEN, J., GREEVES, N. N., WARREN, S., WOTHERS, P., Organic Chemistry, Oxford University Press, 2001.

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