

## A NEW APPROACH FOR THE MODIFICATION OF PAPER SURFACE PROPERTIES BY POLYOXOMETALATES

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### SUMMARY

A new approach for the chemical modification of the surface of paper based on the application of colloidal mixtures containing cationic starch and polyoxometalates on uncoated base paper is presented. Polyoxometalates with the Keggin-type structure and physical properties similar to those presented by coating pigments, namely  $H_3PW_{12}O_{40} \cdot 23H_2O$ ,  $H_4SiW_{12}O_{40} \cdot 24H_2O$ , and  $K_7PW_{11}O_{39} \cdot 9H_2O$ , have been used in order to improve the quality of inkjet printing. The analysis of the different samples by FTIR-ATR spectroscopy showed the presence of the polyoxometalates (and the cationic starch) on the top surface of the paper. In addition, the determination of surface energy parameters, namely the polar component ( $\sigma_s^p$ ) and the dispersive component ( $\sigma_s^d$ ) of the surface energy, by contact angle measurements revealed that, for the new samples, the polar component was much higher than that of the uncoated base paper. The quality of inkjet printing, evaluated by parameters such as the gamut area and the optical density, was considerably improved by these surface treatments.

**Keywords:** cationic starch, inkjet printing, paper functionalization, polyoxometalates.

### INTRODUCTION

The treatment of the paper surface in order to control surface properties relevant to printing, such as surface energy, smoothness, porosity, and chemical properties, has been thoroughly explored. The modification of the paper surface properties should lead to a good paper-ink interaction (in inkjet or offset) in order to fix the ink colorants on the paper surface (without spreading) and to allow rapid absorption or evaporation of the ink vehicle. Therefore, a good affinity between the dyes (or pigments) used as colorants and the chemical compounds used in the paper surface treatment is desirable.

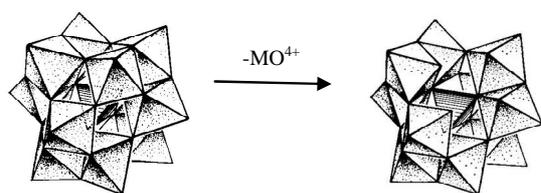
Two general approaches for the treatment of the paper surface are usually considered: surface sizing and coating. Surface sizing is usually performed by the application of an aqueous suspension of cationic starch alone or combined with a synthetic polymer (eg: poly(styrene-co-acrylate)) [1,2]. The coating processes use a different type of chemical formulation which includes a pigment (with kaolin, calcium carbonate, titanium dioxide, aluminum oxide, and silica the most common ones used), a binder (eg: polyvinyl alcohol), a co-binder (eg: carboxymethyl cellulose), a thickener (eg: carboxymethyl cellulose) and a dispersant (cationic polymer additive) [3-5].

Besides the classical uses of paper, such as printing and food packing, there is a large range of applications that can be envisaged for modified papers or new paper-based materials, depending on the type of chemical functionalization achieved at the paper surface. For instance, new catalytic or antibacterial functions may be designed if suitable substances, possessing specific properties, are efficiently immobilized at the paper surface, without losses of the strength and structural properties of the paper matrix.

In the present study, the use of polyoxometalates, never tested before for the modification of the paper surface, is addressed. Polyoxometalates (or polyoxoanions) are metal-oxygen cluster anions with the general formulae  $[M_xO_y]^{m-}$  or  $[X_zM_xO_y]^{n-}$ , where  $z \leq x$ , and M stands for Mo, W, or V, and X is a variable element. They present unique structural and electronic properties which make them appealing

in several fields, ranging from molecular architecture and catalysis to materials science [6-9]. In particular, polyoxometalates with the Keggin structure,  $\alpha\text{-[XM}_{12}\text{O}_{40}]^{p-}$  (Fig. 1), where X stands for *P* or *Si*, and M stands for *Mo* or *W* are well known to form inorganic/organic hybrid associations with protonated organic species derived from *N*-containing heterocycles, protonated amines, and with quaternary ammonium groups, among others [10-13]. This characteristic may be used to explore new ways of paper functionalization regarding inkjet printing. The removal of one  $\text{MO}^{4+}$  group from the Keggin anion gives rise to the corresponding monolacunary species,  $\alpha\text{-[XM}_{11}\text{O}_{40}]^{(p+4)-}$  (Fig. 1).

A new methodology consisting in the application of a colloidal suspension containing cationic starch and a polyoxoanion at the paper surface, is presented. Polyoxometalate compounds ( $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 23\text{H}_2\text{O}$ ,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ , and  $\text{K}_7\text{PW}_{11}\text{O}_{39}\cdot 9\text{H}_2\text{O}$ ) with properties similar to those of coating pigments, such as high reflectance in all the visible wavelength range, brightness, solubility (or good mixing) in water were chosen with the objective of increasing the quality of inkjet printing.



**Figure 1.** Polyhedral representation of the structure of the polyoxometalates  $\alpha\text{-[XM}_{12}\text{O}_{40}]^{p-}$  and  $\alpha\text{-[XM}_{11}\text{O}_{39}]^{(p+4)-}$  (X = P, Si; M = Mo, W)

## EXPERIMENTAL

### Materials

A commercial calendered uncoated paper ( $80\text{g/m}^2$ ) produced with a *Eucalyptus globulus* Kraft pulp was used as the base paper for the surface treatments. Cationic starch solid (with a nitrogen content of 0.37%) and  $\alpha$ -amylase solution were supplied by the industry. Cationic starch suspensions having solids content of 10%, 12% and 14 wt % (and without polyoxometalate) were analysed using a Rheometer Rheostress (Haake), with the objective of selecting the one with the most suitable viscosity for further experiments. For the improvement of inkjet printing quality, the polyoxometalate compounds considered were  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 23\text{H}_2\text{O}$ ,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ , and  $\text{K}_7\text{PW}_{11}\text{O}_{39}\cdot 9\text{H}_2\text{O}$ . The former two were supplied by Sigma-Aldrich and the latter was prepared as described in [14].

### Preparation of the cationic starch/polyoxometalate mixtures for the paper surface treatment

Water (at  $60\text{ }^\circ\text{C}$ , 37 mL) was added to 10 g of cationic starch. After heating the mixture to  $65\text{ }^\circ\text{C}$  with vigorous stirring, more 20 mL of hot water ( $60\text{ }^\circ\text{C}$ ) was added and the heating was extended to  $70\text{ }^\circ\text{C}$ . Then, 3.3  $\mu\text{L}$  of  $\alpha$ -amylase was added and the mixture was heated again up to about  $80\text{ }^\circ\text{C}$  and left at this temperature for 5 min. The starch enzymatic conversion was stopped by the addition of 1.7 mL of a  $\text{ZnSO}_4$  solution (30 g/L). The colloidal suspension obtained was heated up to  $90\text{-}92\text{ }^\circ\text{C}$ , and left stirring at this temperature during 15 min [15]. After, it was cooled to  $50\text{ }^\circ\text{C}$ , 2.5 g of solid polyoxometalate compound was added in small portions and the resultant suspension left stirring for about 10 min. The cationic starch content was finally adjusted to  $12.0 \pm 0.1$  wt % by the addition of hot water. The suspension was maintained near  $50\text{ }^\circ\text{C}$  before its application on the paper surface.

### Treatment of the paper surface

The surface formulations were applied in both sides of the paper surface using a Mathis laboratory coating device, following the procedure reported elsewhere [16]. The surface-treated samples were no further calendered. Four treated paper samples were obtained (Table 1).

The pick-up of the surface treatment was obtained according to the ISO 536 standard. The values were in the range of  $2.5\text{-}3\text{ g/m}^2$  (Table 1).

**Table 1. General characteristics of the mixtures used for the treatment of the paper surface and paper samples obtained**

Paper samples	Mixtures used in the surface treatment		Average pick-up (g/m <sup>2</sup> ) <sup>(a)</sup>
	relative amounts (w/w) of solid compounds	pH (T~50 °C)	
1	100% Cationic starch	5.9	2.73
2	80% cationic starch/ 20% H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	2.3	2.92
3	80% cationic starch/ 20% H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	2.1	2.51
4	80% cationic starch/ 20% K <sub>7</sub> PW <sub>11</sub> O <sub>39</sub>	6.0	2.88

(a) The pick-up was obtained as the average of two replicates which did not differ more than 0.5 g/m<sup>2</sup>.

### *Evaluation of the paper surface properties*

The FTIR spectra were obtained by using a Mattson 7000-FTIR spectrometer equipped with an ATR cell from PIKE Technologies. The spectra were registered with a resolution of 4 cm<sup>-1</sup>, 256 scans and a signal gain of 10, in the range 300-4000 cm<sup>-1</sup>. The crystal used in the ATR cell was diamond with a refractive index of 2.4. An incident radiation at 45° was applied.

The contact angles of the paper samples with four distinct liquids (water, formamide, ethylene glycol, and propylene glycol) were measured with a DataPhysics OCA20 using the sessile drop method, in order to determine the surface energy ( $\sigma_s$ ) of each paper sample, and the corresponding polar ( $\sigma_s^p$ ) and dispersive components ( $\sigma_s^d$ ) by the Owens and Wendt method [17].

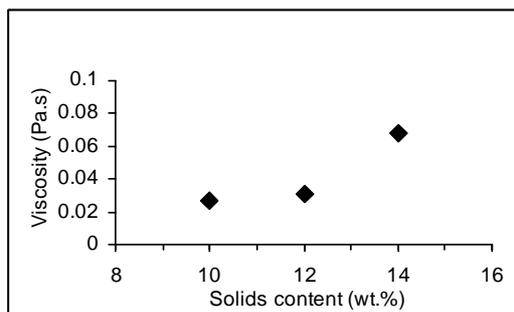
Inkjet printing quality was evaluated by measuring the optical density (cyan, magenta, yellow and black), gamut area, print-through and some line and dot quality parameters in a specified mask printed with a HP Deskjet F370-target IJ12 (plain paper type and normal print quality) on the paper samples.

Both the optical density, gamut area, and print-through were assessed by using the spectrophotometer AVAMOUSE. In addition, line width, dot diameter, and intercolor bleed (a measure of the mixture between two adjacent colours) were evaluated. The determination of these parameters was performed in the QEA portable digital microscope equipped with the personal image analysis system (PIAS).

## RESULTS AND DISCUSSION

### *Treatment of the paper surface with cationic starch and polyoxometalates*

A preliminary study of the viscosity of the cationic starch suspension was made at three different amounts of solids content (10%, 12% and 14 wt %). As shown in Fig. 2, the hot suspensions (50 °C) of cationic starch with solids contents of 10 wt % and 12 wt % have not very different viscosities. At the solids content of 14 wt % a great increase of the viscosity to values near 70 mPa.s is observed. Given the reference value for some industrial applications (around 35 mPa.s), suspensions having 12 wt % of cationic starch were used in all subsequent experiments [15].



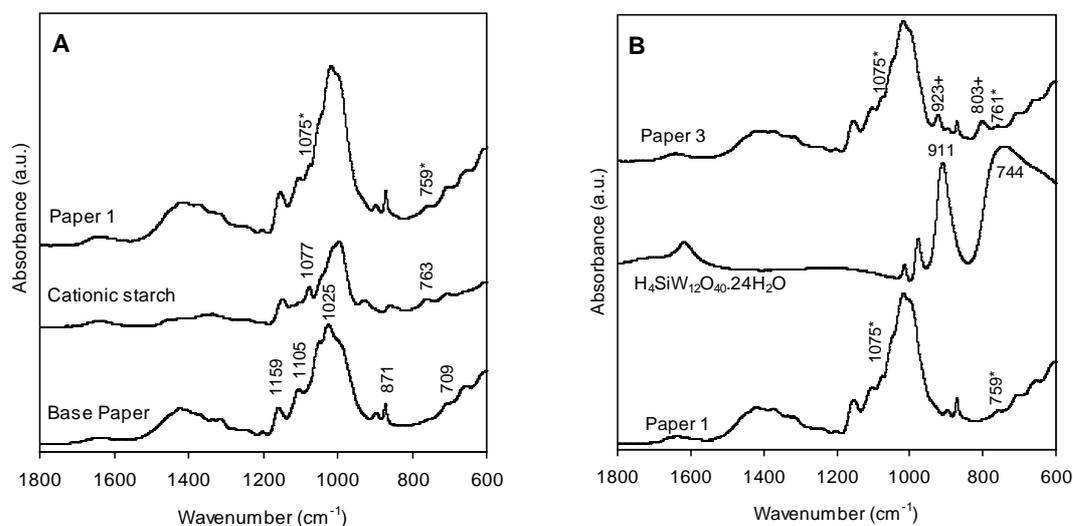
**Figure 2. Viscosity at the maximum shear rate (600 s<sup>-1</sup>) of the cationic starch suspensions (50°C) vs. solids content**

Due to the high solubility of  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 23\text{H}_2\text{O}$  and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$  in water, even at low temperature, and to their strong acid behaviour [6], there is a significant decrease of the pH from about 6 to 2-2.5 after the addition of those compounds to the cationic starch suspension (Table 1). The compound  $\text{K}_7\text{PW}_{11}\text{O}_{39}\cdot 9\text{H}_2\text{O}$  is also quite soluble in water, but, as expected, its addition to the starch suspension does not alter the pH of the suspension (near 6.0).

It should be noted that the cationic starch used to prepare the colloidal suspension has a very low content of epoxypropyltrimethylammonium groups ( $[\text{C}_3\text{H}_6\text{ON}(\text{CH}_3)_3]^+$ ) (based on the nitrogen analysis it was determined that per each 100 monomer units, 96 are glucose and the other four are substituted by the cationic groups). Considering the relative amounts of cationic starch and polyoxometalate solids used in each formulation for the treatment of the paper surface, 80/20 w/w, respectively (Table 1), the molar ratio between the epoxypropyltrimethylammonium groups and the polyoxoanions is estimated to be between 3 and 3.5.

### Characterization of the new paper samples by FTIR-ATR

Infrared spectra of the surface of the base paper and of the four new paper samples (Table 1), and of the cationic starch and polyoxometalates used in the treatment of the paper surface, were obtained. Some representative spectra are shown in Fig. 3. The infrared spectrum of the base paper (Fig. 3 A) shows several bands due to calcium carbonate, cellulose, and hemicelluloses [16]. The infrared spectrum of the paper treated with cationic starch (paper 1) shows two bands at 1075 and 759  $\text{cm}^{-1}$  (Fig. 3 A), not observed at the surface of the base paper, which are due to the presence of the cationic starch. These two bands are attributed to the C1-H bending and C-C stretching, respectively [18].



**Figure 3. FTIR-ATR spectra of (A) base paper, cationic starch, and paper 1 (treated with cationic starch) and (B) paper 1,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ , and paper 3 (treated with cationic starch and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ )**

The FTIR-ATR spectrum of the surface of the paper 3, obtained after treatment with the formulation containing  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$  and cationic starch is shown in Fig. 3 B. The infrared spectrum of  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$  presents four main bands at 1015, 977, 911 and 744  $\text{cm}^{-1}$  corresponding to  $\nu_{\text{as}}(\text{Si-O})$ ,  $\nu_{\text{as}}(\text{W-O})$ ,  $\nu_{\text{as}}(\text{W-O}_b\text{-W})$  and  $\nu_{\text{as}}(\text{W-O}_c\text{-W})$  [19]. For the paper treated with the mixture having 80/20 (w/w) of cationic starch and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ , respectively, two new bands not observed at the surface of the paper treated only with cationic starch appear at 923 and 803  $\text{cm}^{-1}$ , which are due to the  $\nu_{\text{as}}(\text{W-O}_b\text{-W})$  and  $\nu_{\text{as}}(\text{W-O}_c\text{-W})$  stretching vibrations, respectively. The latter band is shifted to higher wavenumber by about 60  $\text{cm}^{-1}$  in comparison to the analogous band observed in the spectrum of  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 24\text{H}_2\text{O}$ . This behaviour should be caused mainly by the presence of the epoxypropylammonium groups, but also by the macromolecular structure of starch [19]. Similar

considerations can be made for the analysis of the FTIR-ATR spectra of the paper samples 2 and 4.

### Surface Energy Parameters

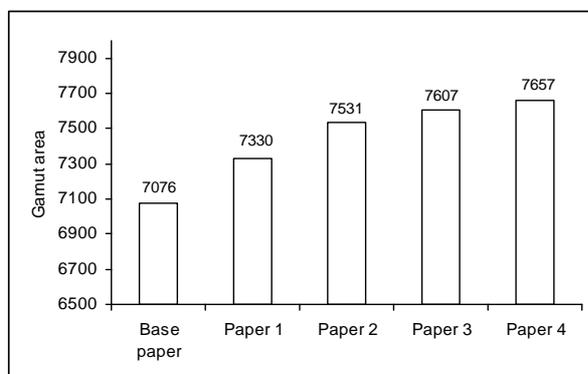
The contact angles of the five papers with water as well as the surface energy parameters computed by using the Owens and Wendt model [17] are presented in Table 2. The paper that exhibits the highest water contact angle is the base paper (102°) revealing a hydrophobic character. For all the paper samples treated with cationic starch and polyoxometalates, and for that treated only with cationic starch, the water contact angles are in the range of 30-50°, *i.e.*, are significantly lower. These results are not unexpected because the cationic starch molecules are polar (hydrophilic) and the polyoxoanions species typically have very low hydration energy [6]. The paper sample that presented the lowest water contact angle (30°) was that obtained by the treatment with the mixture containing 80/20 (w/w) of cationic starch and  $K_7PW_{11}O_{39} \cdot 9H_2O$ , respectively (paper 4). The slightly different water contact angles observed for the treated paper samples reflect the different chemical affinity of the paper surfaces to the water molecules which should depend mostly on the type and charge of the polyoxoanions used for the surface treatment, and on the counter-cations provided at the surface ( $H^+$ ,  $K^+$ ). Regarding the surface energy parameters, all the paper samples obtained after the surface treatment present  $\sigma_s^p$  values significantly higher (and  $\sigma_s^d$  values significantly lower) in comparison to the base paper which is in agreement with the smaller contact angles with water.

**Table 2. Water contact angles and surface energy parameters determined for the paper samples**

Paper samples	Water contact angle (°)	Surface energy, $\sigma_s$ (mN/m)	Polar component, $\sigma_s^p$ (mN/m)	Dispersive component, $\sigma_s^d$ (mN/m)	Correlation ( $R^2$ )
Base paper	101.7±2.2	47.4	0.1	47.3	0.660
1	38.2 ± 1.8	73.8	72.7	1.1	0.992
2	49.7 ± 2.3	59.6	56.9	2.7	0.991
3	42.2 ± 3.9	73.7	73.2	0.48	0.994
4	29.7 ± 2.4	87.4	87.2	0.21	0.988

### Printability

The gamut area results obtained for the different paper samples are presented in Fig. 4. As can be seen, the paper samples obtained by the surface treatment exhibit gamut areas significantly higher than that of the base paper, which is an indication of better colour reproducibility. Furthermore, the polyoxometalates have a positive impact in the gamut area, since the corresponding values obtained for the papers 2, 3 and 4 are higher than that of paper 1.



**Figure 4. Gamut areas for the different paper samples**

The values of the optical density (Table 3) are higher for the treated paper samples, with a few exceptions. For the black and magenta inks all the treated papers present slightly higher values in comparison with the base paper. As for the cyan and yellow, there is no clear tendency. However, it

can be concluded that paper 2, 3 and 4 exhibit a better behaviour regarding the cyan, magenta and yellow (dyes) whereas paper 1 is the best regarding the black optical density.

**Table 3. Optical density for distinct colours**

Paper samples	cyan	magenta	yellow	black 0
Base paper	0.935	0.91	0.968	1.376
1	0.897	0.922	0.958	1.482
2	0.951	0.924	1.029	1.459
3	0.976	0.948	1.005	1.425
4	0.914	0.939	0.980	1.462

The results presented in table 4 reveal that the surface treatment has a clear positive influence in reducing both the print-through and intercolor bleed (the values for these parameters should be as low as possible, for better inkjet printing quality). A slight increase of the dot diameter, on the other hand, confirms a better retention of the inks at the surface. However, the role of the polyoxometalates is not evident. The values of the black line width may be considered similar to all samples.

According to all the inkjet printing quality parameters that were evaluated, paper sample 4 has a slightly better performance, considering its higher gamut area, higher optical density, lower intercolor bleed and low print-through. Paper samples 2 and 3 have also a good performance, being, for some parameters, better than paper 1, treated only with cationic starch. In general, the addition to the cationic starch of specific polyoxometalates for the paper surface treatment, improve printing quality.

**Table 4. Print-through, line and dot printing quality parameters**

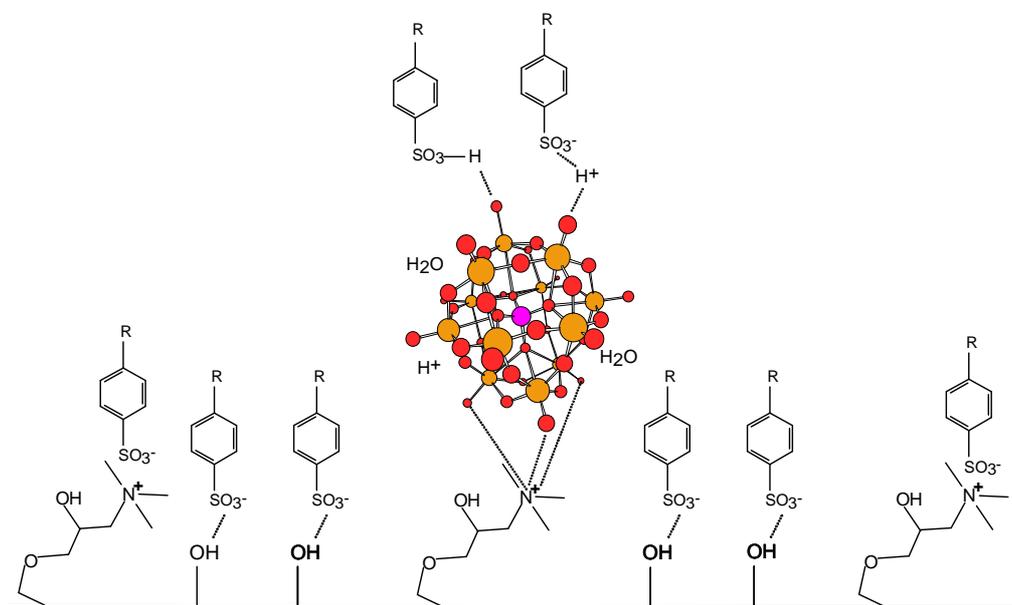
Paper samples	Print-through [0.0.0]	Line width, (black, $\mu\text{m}$ )	Intercolor bleed	Dot diameter (black, $\mu\text{m}$ )	Dot diameter (magenta, $\mu\text{m}$ )
Base paper	1.31	474	50.1	507	409
1	0.53	465	37.4	527	419
2	0.70	480	39.4	529	413
3	0.42	519	43.3	551	426
4	0.64	480	36.4	528	416

### ***Relation between printability and chemical and surface properties of the new paper samples***

Based on the alterations of the surface energy observed after the treatment of the base paper surface with cationic starch and polyoxometalates and on the presence of infrared bands at the paper surface due to both cationic starch and polyoxoanion species it is proposed that those two types of compounds are retained mostly at the paper top surface. Regarding cationic starch, this is in agreement with recent studies by ToF-SIMS [20] and FTIR-ATR [16] for papers having high internal sizing degree. On the other hand, polyoxoanions of Keggin-type should be held at the paper surface, mainly by electrostatic bonding with the epoxypropyltrimethylammonium groups of substituted starch forming ionic pairs (Fig. 5), as observed in related cases [11,13].

In inkjet, typically colorants are azo dyes having in their molecular structure sulfonic or carboxylic acid groups attached to an aromatic backbone. Other functional groups and substructures such as hydroxyl, amino, and nitrogen-containing heterocycles may be present as well [21]. Due to the high acidity of the sulfonic acid groups (and carboxylic acids in less extent), the corresponding dyes are predominantly anionic at the pH of the ink formulation (6.5-9). Therefore, the existence of cationic groups ( $[\text{C}_3\text{H}_6\text{ON}(\text{CH}_3)_3]^+$ ) at the paper surface, provide regions of high interaction with the sulfonic groups (anionic) of the inks. On the other hand, the polyoxoanions, located close to the quaternary ammonium groups of modified starch are not directly attracted to the anionic dyes structures. However, when the polyoxoanions are immobilized at the paper surface the counter-cations of the compounds used for the surface treatment are also available. For the heteropolyacid compounds used in the surface treatment of paper samples 2 and 3, there is also a concomitant release of protons to the

medium (3 and 4 protons for the  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  and  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  anions, respectively) due to their strong acidity (Table 1). These protons should be close to the polyoxoanions structure, being attracted by the polyoxoanion and simultaneously attracting the sulfonic acid groups, the latter of which can be protonated (Fig. 5). These interactions may contribute to the better ink dye retention at the paper surface in comparison to the use of cationic starch alone.



**Figure 5. Schematic representation of the main chemical interactions which may occur at the paper surface functionalized with cationic starch (the cationic groups are the  $[\text{C}_3\text{H}_6\text{ON}(\text{CH}_3)_3]^+$ ) and heteropolyacids in the process of the ink dyes immobilization (the dyes are represented as an aromatic structure linked to a sulfonic group)**

The results obtained with cationic starch and  $\text{K}_7\text{PW}_{11}\text{O}_{39}\cdot 9\text{H}_2\text{O}$  (paper 4) are pleasantly surprising since a high gamut area was achieved, although the optical density (namely of cyan and yellow) was not as high as that of papers 2 and 3. In this case, potassium cations together with the polyoxoanions are released to the paper surface. It is unlikely that potassium ions have the same affinity to the anionic dyes as the protons, although present in higher number (seven cations per one anion). However, paper sample 4 proved to have the most polar surface of all paper samples (the polar component was about 13% higher than that of paper 1, treated only with cationic starch) which can facilitate the retention of some colorants.

## CONCLUSIONS

In the present work a new methodology for the functionalization of paper surface, aiming a better printability, was developed. This methodology is based on the use of colloidal suspensions containing cationic starch and polyoxometalates for the treatment of the paper surface. Several new paper samples were obtained, and characterized by FTIR-ATR spectroscopy and contact angle measurements. The results of these studies showed that, for the new samples, the polyoxometalates (and cationic starch) are present on the paper surface and increase the polar component of the surface energy significantly, in comparison to the base paper.

The new paper samples were evaluated with regards to inkjet printing quality. In general, the gamut area and the optical density increased in comparison to the base paper, while the print-through and intercolor bleed decreased. For the paper samples treated with mixtures of cationic starch and polyoxometalates ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  and  $\text{K}_7\text{PW}_{11}\text{O}_{39}$ ), better results of gamut area and optical density of cyan, magenta and yellow when compared to those of paper treated only with cationic starch were obtained. It is proposed that the polyoxoanions and the corresponding counter-cations, by

increasing of the electrostatic interactions with the anionic dyes (including, in the cases of paper samples 2 and 3, the protonation of the ionized sulfonic or carboxylic acid groups present in the structure of ink dyes) provide a better retention of the colorants at the paper surface.

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