WOOD RESEARCH
60 (2): 2015
263-272

OPTICAL STABILITY OF OFFICE PAPERS TREATED WITH COCAMIDOPROPYL BETAINE

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ABSTRACT

This paper presents the examination of effects of amphoteric surface active chemical cocamidopropyl betaine (CAPB) on the optical properties of various office paper brands (Navigator, Fabriano, Rcopy, Pioneer, IQ and Plano Premium). In order to analyse the effects of cocamidopropyl betaine on the office papers' optical stability, two types of sample treatments were performed: Soaking and disintegration. Likewise, for the purpose of better optical stability evaluation, the same analysis was done with distilled water. All paper samples were exposed before and after treatment to visible and ultraviolet electromagnetic radiation. The influence of ultraviolet radiation on all treated office papers was examined through reflectance spectra using X-rite Spectrophotometer. The gained results showed that cocamidopropyl betaine affected optical properties of all analysed office papers, independently of the type of treatment, compared to non-treated originals. It was evident that the degree of surfactant solution effect on the optical stability was conditioned by paper composition.

KEYWORDS: Office paper, disintegration, soaking, cocamidopropyl betaine, paper ageing.

INTRODUCTION

Office papers are used on a daily basis and not only for photocopying purposes but also for writing and printing of documents used for archiving. Due to their widespread use, papers properties have to meet certain requirements, such as adequate water resistance, dimensional and optical stability. These properties are achieved by adding appropriate substances in the course of paper production. Except for cellulose fibres, which can be either virgin or recovered by their origin, there are many other organic and inorganic components that are added to the paper network structure, such as fillers, adhesives, pigments, binders, etc. According to the paper type, these materials are added in larger or smaller quantities, thus making office papers available on the market different based on their chemical composition (Neimo 1999). Paper products are an important part of everyday life (households, offices and industry). Nowadays, there is an increasing demand for quality production of writing paper as well as printing paper. The main priority in that process is to achieve physical and chemical properties that ensure best printing or writing quality.

Paper optical properties are extremely important in graphic industry because they contribute, more than any other factor, to the overall paper appearance and appeal (Thompson 2004). As a result of paper ageing, optical properties are significantly changed (Jääskeläinen and Liitiä 2007). Electromagnetic radiation, which is absorbed by a molecule, may lead to a chemical reaction. Pure cellulose absorbs visible light only to a small extent (380 – 550 nm), while absorption in the near UV spectral region (300 – 380 nm) is more distinct. It is precisely due to that, that most of the damage in cellulose during the exposure to electromagnetic radiation is induced in that spectral range (Kolar et al. 2005). The optical properties of paper are very sensitive to its structure. In high quality papers, such as printing paper, different fillers and coatings, of a few microns in size, are used for improving products' appearances. The chemical bonds between cellulose fibres, fillers or coating particles and the used sizing agents, comprise the three-dimensional paper structure and determine paper surface porosity and roughness. Accelerated ageing causes the occurrance of chemical and physical changes in organic materials during deterioration (Neimo 1999).

Surfactant also plays an important role in the optical properties. A surfactant is a molecule with two distinct regions – a water soluble polar head and a non-polar hydrocarbon tail which is sparingly soluble in water. They are classified based on their ionic properties in water: Non-ionic (no charge), anionic (negative charge), cationic (positive charge) and amphoteric (either positive or negative charge) (Zhao et al. 2004).

Surfactants encompass many chemical types and are used depending on their charasteristics. They have an important role in the deinking of recycled paper during flotation, washing and enzymatic process. When a surfactant is introduced into the pulp, the hydrophobic end associates with the ink, oil and dirt, while the hydrophilic end remains in the water. This action removes and captures dirt particles and prevents their re-deposition (Ferguson 1992).

Cocamidopropyl betaine (CAPB) is an amphoteric detergent, which can exist in solution in either cationic or anionic form, depending on the pH (it can have a negative or a positive hydrophilic part). The synthesis of CAPB (HERA Substance Team 2005, Hunter and Fowler 1998) is indicated in Fig. 1. Coconut oil, or fatty acids hydrolysed from coconut oil, react in contact with dimethylaminopropylamine (DMAPA) in an aqueous solution forming dimethylaminopropyl cocamide, a tertiary amine, also referred to as amidoamine. This material then reacts with sodium monochloroacetate (SMCA) forming CAPB and sodium chloride.

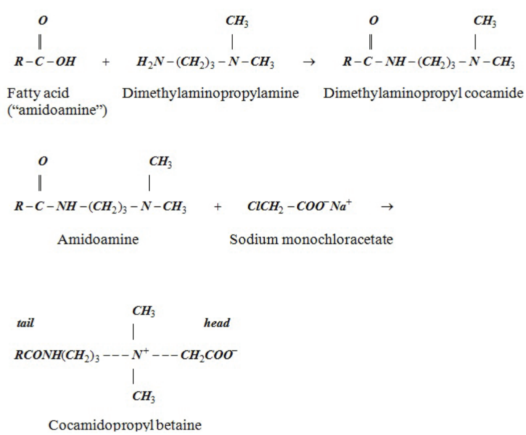

Fig. 1: CAPB synthesis path.

The knowledge about the behaviour of that surfactant in the paper industry is quite limited, except of its primary use in the cosmetic industry. Our previous paper described that, during the accelerated ageing, CAPB affects optical stability of paper better than other selected surfactants (Plazonic et al. 2009). In addition to that, this surfactant has an acceptable price on the market and it is environmentally friendly (Ahrens 2008, HERA Substance Team 2005). Thus, the aim of this paper is to present the analysis of the effect of CAPB on optical properties of several office paper brands available on the Croatian market (Navigator, Fabriano, Rcopy, Pioneer, IQ and Plano Premium).

MATERIAL AND METHODS

Six different office papers (Navigator, Rcopy, Fabriano, Pioneer, IQ and Plano Premium) with the grammage of 80 g m^{-2} were analysed. Each office paper used in the analysis was cut to pieces of approximately 1 g.

The impact of CAPB solution on all used office papers was monitored in the course of 10 minutes of soaking and 2 minutes of disintegration time. After the process of disintegration in a 500 mL CAPB solution (1.0 %), filtration was performed with a handmade Büchner funnel for handsheets (with appropriate vacuum device), forming new samples (Fig. 2.). After new handsheets were formed, the water used for processing was filtered by Büchner funnel, enabling the calculation of the mass loss after disintegration (Eq. 1). The same procedure was performed for each sample.

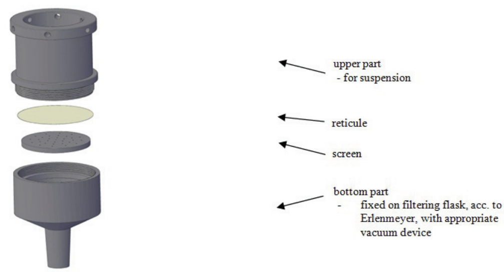

Fig. 2: Handmade laboratory Büchner funnel handsheet former.

The samples were dried naturally for two days at a 25°C where upon the electric lamp, which emits visible and ultraviolet electromagnetic radiation, was used for achieving accelerated aging. Examined samples were exposed to radiation in 60 minutes long intervals. For the purpose of better determination of the CAPB effects on the optical properties of office paper, the same experiment was performed under the same conditions using distilled water. In order to achieve better quality evaluation, the reflectance spectra of non-treated samples, called original samples, were measured as well.

Determination of mass loss after disintegration

The loss of mass after disintegration was calculated according to the following Eq. (1):

$$m_{loss} = \frac{m_{filter\ paper\ after\ filtration} - m_{filter\ paper\ before\ filtration}}{m_{office\ paper\ sample}} \cdot 100 \qquad (\%) \qquad (1)$$

Spectrophotometric measurement

Paper reflectance measurements were processed using X-rite Spectrophotometer, Digital Swatch book in the wavelength interval from 410 to 700 nm, for every 10 nm. The measurements were supported by Color Shop 2.0 software and the results were calculated by Data Analysis and Technical Graphics Origin 6.0. The diffuse reflection was the basis for the evaluation of papers' optical properties. The method for measuring reflectance employed d/0^0 geometry, Illuminant D65, with the instrument set to measure CIEY, 2^0 standard observer. During the spectrophotometric measurements, the relative humidity of the atmosphere was approximately 60 % and the temperature was around 21°C.

The brightness (R_{457}) method was developed in order to monitor the pulp bleaching. The goal of almost all bleaching operations is the removal of coloured chromophores, which are largely lignin-based (lignin absorbs blue region of spectrum). In general, that can be accomplished using oxidative lignin-degradation or lignin-retaining processes. The largest change of reflectance during the pulp bleaching occurs in relation to short wavelengths (from 400 to 500 nm). Although the complete spectral properties of paper could be positively determined, the optical properties of paper product were characterised by papermaker's brightness. With the introduction of modern spectrophotometers, it was convenient to use reflectance at 460 nm (Lee et al. 1989). The results obtained for the reflectance at a wavelength of 457 and 460 nm were practically the same.

Effective agents for increasing the whiteness impression of paper products are fluorescent whitening agent (FWA). FWAs are organic materials which absorb UV electromagnetic radiation and emit blue fluorescence. The standard illuminant D65 (black body radiation at 6500K) corresponds to outdoor illumination with relatively high proportion of UV radiation. As it is evident from Fig. 3, the reflectance values became low in the UV part of the spectrum, where the energy was absorbed, while in the visible blue part (420-500 nm), the fluorescence emission exceeded the total radiance (R>1).

Reflectance values (R) were measured in relation to all samples before ageing ($R_{non\ aged}$) and after the accelerated ageing (R_{aged}) of the following i) original office papers, ii) office papers soaked in distilled water and CAPB and iii) handsheets formed after the office paper disintegration in distilled water and CAPB. The results of reflectance measurements (Fig. 3) are presented as ΔR according to the following equation (2):

$$\Delta R = R_{non\ aged} - R_{aged} \tag{2}$$

As optical properties are strongly related to the chemical composition of the paper structure, some analytical analysis of papers were also performed.

Volumetric determination of $CaCO_3$

Alkalimetric titration was performed for all selected original papers. For that purpose, a sample with the weight of 1 g was prepared in an Erlenmeyer flask with 25 mL of distilled water. The volume of 20 mL of standardized 0.1 molL^{-1} HCl solution was piped into the flask and heated up to the boiling point. It was boiled for approximately 1 minute. The cooled flask content was then titrated with standardized NaOH solution of 0.1 mol.L^{-1}, with phenolphthalein as indicator. Determination of calcium carbonate amount in each sample was based on the reaction of calcium carbonate in the paper with added HCl solution:

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)} \tag{3}$$

Acid residue which has not reacted with calcium carbonate was then titrated with NaOH solution, whereby neutralization reaction was achieved:

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} \qquad (4)$$

Measuring the volume of NaOH for neutralization, calcium carbonate mass fraction was calculated indirectly according to the following Eq. (4):

$$w(CaCO_3) = \frac{(c_{HCl} \cdot v_{HCl} - c_{NaOH} \cdot v_{NaOH}) \cdot 0.05}{m} \cdot 100 \quad (\%) \qquad (5)$$

where: c_{HCl} and c_{NaOH} –concentrations of HCl and NaOH solutions, in mol L^{-1};
V_{HCl} and V_{NaOH} – volumes of HCl and NaOH solutions, in L;
m –a mass of sample for titration, in g;
0.05 –recalculation factor.

Determination of paper ash content

Office paper with weight of 1 g was ignited in laboratory furnace at 920°C. The same procedure was performed in relation to all used original photocopy papers and chemically treated samples. Ash content was calculated according to the following Eq. (5):

$$w(ash) = \frac{m_{ash}}{m_{dryed\ sample}} \times 100 \quad (\%) \qquad (6)$$

RESULTS AND DISCUSSION

The results of determination of ash and $CaCO_3$ content in all used original office papers are shown in Tab. 1.

Tab. 1:. Ash and $CaCO_3$ content in all used original photocopy papers.

Original non-treated office paper	Content (%)		
	Ash	Calcium carbonate	Calcium oxide
Navigator	13.13	23.81	101.54
Rcopy	11.18	20.99	105.11
Fabriano	13.69	24.58	100.52
Pioneer	12.67	22.59	99.81
IQ	9.99	17.90	100.35
Plano preminum	11.55	17.45	84.58

In relation to office papers with higher ash amounts (Navigator, Fabriano, Pioneer), volumetric titrations showed high quantities of $CaCO_3$. On the other hand, papers with lower ash amounts (Rcopy, IQ,Plano Premium) had lower $CaCO_3$ quantities. In order to establish other inorganic components (except for $CaCO_3$) in papers, all original office papers were burned at 920°C. When that was performed, $CaCO_3$ filler decomposed to CaO and CO_2 according to the following reaction:

$$CaCO_{3(s)} \xrightarrow{900^{\circ}C} CaO_{(s)} + CO_{2(g)} \qquad (7)$$

The quantities of CaO in the ash were directly associated with $CaCO_3$ amounts in papers. From the reaction ensues the following Eq. 7:

$$m_{CaO} = \frac{m_{CaCO_3} \cdot M_{CaO}}{M_{CaCO_3}} \tag{8}$$

On the basis of obtained results for CaO masses, CaO amounts in the ash content were calculated using the following equation:

$$w_{CaO} = \frac{m_{CaO}}{m_{ash}} \cdot 100 \quad (\%) \tag{9}$$

Burned original office papers with calcium oxide share over 100 %, contain also calcium oxide as an inorganic filler. Only Plano Premium office paper contains some other inorganic substances in addition to the calcium carbonate and calcium oxide, but they were not examined in this research.

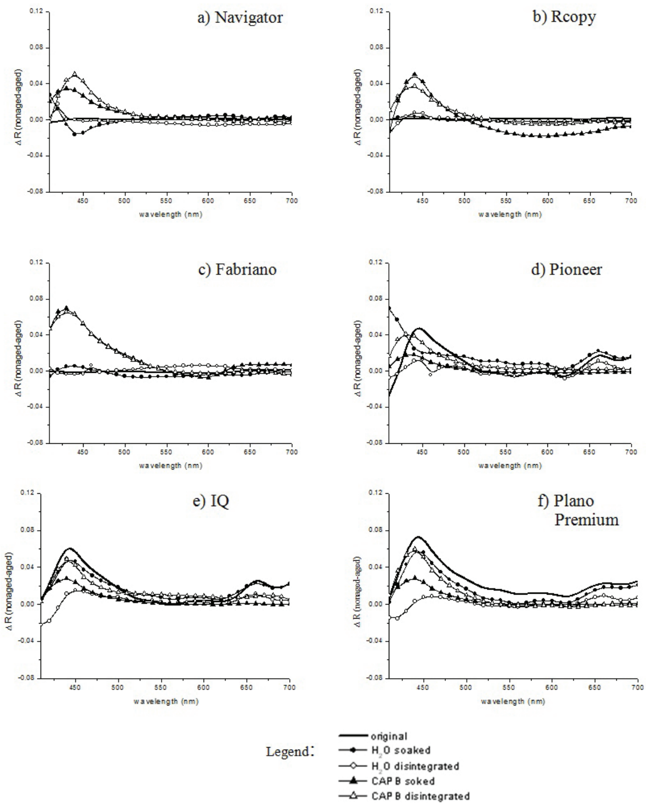

Fig. 3: The impact of distilled water and CAPB on office papers reflectance values.

Since paper is a complex structure consisting mainly of a network of fibres, filler pigment particles and air, light is not reflected only on paper surface. Within the surface layer, that is, in the paper structure, light also interacts with fibres and pigments. Calcium carbonate and clay, as the main fillers in paper production, have different light absorption coefficients. In general, clay pigments have a relatively high absorption coefficient in the visible part of electromagnetic spectrum, while $CaCO_3$-pigments can have varying light absorption (Thompson 2004).

After performing accelerated ageing with an electric lamp, the reflectance values of original Navigator, Rcopy and Fabriano papers (Fig. 3a-c) were not changed, thus the ΔR calculated according to the afore mentioned formula (1) was approximately zero for all measured spectra wavelength. Among all used office papers, the original papers proved to be optically high-quality papers because of their stability under the influence of the electromagnetic radiation. The three original papers displayed relatively high quantities of $CaCO_3$ in comparison to the gained ash amount, which was the reason for their appearance as optically high-quality papers. Namely, $CaCO_3$ displays higher light reflectance than other fillers (lower absorption coefficient) (Alava and Niskanen 2006). Both treatments (soaking and disintegration) in distilled water displayed minor changes in reflectance values of treated papers. The reflectance changes were within the interval of measurement error ($\Delta R \approx 0$). On the other hand, for samples treated with CAPB the reflectance values were notably lower after the ageing process. The influence of the near UV electromagnetic radiation on the afore mentioned paper samples led automatically to positive ΔR, according to the Eq. 1, especially in the blue part of spectra at wavelength varying from 410 to 500 nm. Those changes were within the interval 5-7 %.

Accelerated ageing had the strongest impact at wavelengths varying from 410 to 500 nm (Fig. 3d-e) with reflectance values of original Pioneer ($\Delta R_{max} \approx 5$ %) and IQ paper ($\Delta R_{max} \approx$ 6 %). Changes in reflectance values for Plano Premium paper (Fig. 3f) were evident in relation to all measured wavelength intervals (from 410 to 500 nm $\Delta R_{max} \approx 7$ %, from 510-700 nm $\Delta R_{max} \approx 2$-3 %). Positive ΔR highlighted the impact of ultraviolet radiation on the reflectance value, especially in relation to short wavelengths, which indicated lower optical quality of those original papers when compared to Navigator, Rcopy and Fabriano original papers (Fig. 3a-c). IQ and Plano Premium (Fig. 3e-f) original papers used in the research contain relatively small quantity of $CaCO_3$ in comparison to the obtained ash amount (Tab. 1), which manifested them as optically lower quality papers. It could be assumed that those papers contain clay, accompanied by $CaCO_3$, which, in general, has a relatively high light absorption (Pauler 2001). Improvements in sample stabilisation were observed after the treatment in distilled water and CAPB solution. Better optical stabilisation for Pioneer, IQ and Plano Premium samples were achieved during the disintegration in distilled water compared to the one in CAPB. If we observe the impact of distilled water on Pioneer and IQ papers as it has on Plano Premium paper (Fig. 3d-f), it could be concluded that the type of treatment has an important role on the reflectance value changes. It was interesting to observe that water treatment changed the surface characteristics of those papers; soaking resulted in smaller changes but disintegration in more significant ones. The accelerated ageing of dried soaked samples in distilled water resulted in increasing reflectance values in comparison to the original; that was the reason why the ΔR was not so positive (ΔR_{max} $\approx$ 2-6 % in all samples). The ageing of dried handsheets formed after the disintegration in distilled water resulted in additional increases of reflectance values ($\Delta R_{max} \approx$ 1-2 % in all samples), when compared to the original and to the samples soaked in distilled water. When compared to samples treated with water, obtained results of reflectance for aged handsheets formed after the disintegration in CAPB were completely different. In fact, aged handsheets formed from Pioneer, IQ and Plano Premium (Fig. 3d-f) papers after the disintegration in CAPB solution, displayed higher optical stability than original samples. However, they displayed significantly lower stability than soaked original samples of those papers.

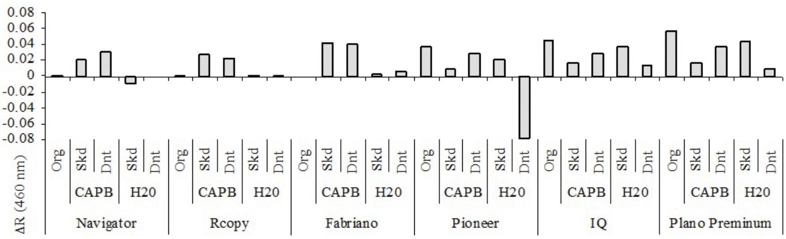

Fig. 4: ΔR (460 nm) of office papers (Org.-original, Skd.-soaked, Dnt.-disintegrated).

The most significant changes of reflectance were observed in the wavelength area of blue part of spectra. Due to that appearance, it is customary to observe the changes in brightness, ΔR_{460}, (Fig. 4.). The best optical properties characteristics were perceived in relation to Navigator and the worst ones in relation to Plano Premium original office papers.

After the disintegration in distilled water as well as in CAPB solution, it was possible to determine the mass loss during the handsheet forming (Tab. 2.).

Tab. 2: Mass loss and the relative change of mass loss after the disintegration in distilled water and CAPB.

Office paper	Mass loss after disintegration (%)		$\Delta m_{rel} = \frac{m_{CAPB} - m_{H_2O}}{m_{H_2O}} \times 100$ (%)
	H_2O	CAPB	
Navigator	12.95	12.19	- 5.87
Rcopy	8.90	11.25	26.40
Fabriano	10.11	14.96	47.97
Pioneer	7.70	11.18	45.19
IQ	5.85	12.03	105.64
Plano preminum	5.95	9.70	63.03

The presented results show that the mass losses were significantly higher in papers with smaller quantities of calcium carbonate disintegrated in CAPB, compared to the mass loss in handsheets formed after the disintegration in distilled water.

Basic components of paper pulp are fibres, fillers and binders. Binders are added into the paper structure or into the surface layer of paper. Nowadays, the most frequently used binder is starch. Starch is used as an adhesive to connect vessel segments and the loose fibres at the sheet surface, to enhance paper strength and stiffness, and to improve dimensional stability and printability. In a customary sheet of copy paper, for example, the starch content may be as high as 8 %. In all office papers used in this research, the starch was detected by Lugol's solution. The purpose of starch is to improve the surface of paper through mechanical and optical properties. During the penetration of water and CAPB solution into the paper, hygroscopic wood fibres swell with water intake. It is well known how water penetration into the pore space between the fibres and then into the fibres causes changes of the porous fibre network. After being soaked in water, the surface, facial layers of paper samples, are distorted. In relation to all used office papers, soaking in water did not result in any significant changes regarding optical stability (especially in relation to Navigator, Rcopy and Fabriano). On the other hand, soaking in CAPB displayed higher optical stability only in relation to office papers with a smaller share of calcium carbonate (Pioneer, IQ and Plano Premium); the CAPB destabilizes optical properties of papers with higher share of calcium carbonate (especially in the blue part of spectra). Taking that into account, the chemical treatment for those papers is redundant. Amphoteric CAPB molecules obviously merge with starch polymer molecules on paper surface.

The fibres, organic and inorganic components, get released from the paper network structure during the disintegration of original paper. It was interesting observe that the mass loss was significantly higher in CAPB solution than in distilled water. That can be explained by chemical bondage of amphoteric CAPB molecules with polymer starch molecules in the paper. In such a manner, fillers are released from paper network structure strengthened by binders. If this assumption is correct, that would explain the different reflectance values of handsheets formed after the disintegration in distilled water and of one handsheet formed after the disintegration in CAPB solution. The handsheets' structures are different in terms of paper transmittance, pores space among fibres, retained organic and inorganic components disposition in comparison to the original paper; all that has an adverse impact on the visible and ultraviolet electromagnetic radiation influence. Considering all the results, it could be concluded that CAPB solution is not the best choice of surfactant for office paper disintegration.

CONCLUSIONS

Cocamidopropyl betaine solution as a used surface active agent, had impact on optical properties of all analysed office papers, to a higher or smaller degree, in both types of treatments (soaking or disintegration). It was evident that the degree of surfactant solution effect on the optical properties was connected to paper composition. The best aging resistance was obtained in papers with a high quantity of calcium carbonate and small quantity of ash (Navigator, Rcopy, Fabriano); those could be recommended for archival applications. However, for those papers, CAPB was not the best choice of surfactant for disintegration. The other three office papers (Pioneer, IQ, Plano Premium) with a high quantity of ash and some other fillers apart from calcium carbonate (very likely clay, koalin) were optically not high-quality papers. In relation to those papers, treatment with cocamidopropyl betaine (soaking and disintegration) enhanced the reflectance value, particularly in a blue part of spectra.

Since chemical composition of analysed office papers (fibres' origin, addition of necessary chemical additives as fillers, pigments, dyes, optical bleaching substances, etc…) is a manufacturers secret, it is difficult to establish with which component in the paper structure the cocamidopropyl betaine actually interacts.

In order to obtain a more stable paper structure under the influence of the near UV and visible electromagnetic radiation, the stabilisation through the unchanged reflection spectra ($\Delta R \approx 0$) was examined. If $CaCO_3$ in the paper would have an optimal share, the paper would show good stability in the applied experimental conditions. There would be no need for any additional chemical treatment. However, if the clay (or some others impurities) is a part of the paper structure, additional chemical treatment is necessary for improving paper stability. The best results in the course of research were achieved in samples made using IQ and Plano Premium paper soaked in CAPB or disintegrated in H_2O.

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