

# Properties of Cellulose Sheets Modified with Potassium-Humate and Copper (II)-Sulfate

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*Abstract. Throughout our research we have made potassium-humate from brown coal of Dudar. With potassium-humate and copper(II)-sulfate we made test sheets of linter cellulose fibers. The surface energy, surface wettability, CIE Lab color-coordinates changing, bending resistance and tensile strength of the produced test sheets has been examined. There was no big difference in the different samples during surface energy and wettability testing. Examination of mechanical properties suggests that potassium-humate content increases bending resistance of the test sheets. The bending resistance of samples increased by 32%, 100% and 336% compared to the control test sheets while adding potassium-humate.*

*Keywords: Potassium-humate, cellulose, copper(II)-sulfate, mechanical properties, surface free energy, surface wettability*

## Introduction

The humic acids – humic acid, fulvic acid and himatomelanic acid belong here – are natural substances with overwhelmingly vegetal origin [1]. The fossil forms of the humic matters formed in the geologic ages and under the geologic effects in other former recent forms buried by stratifications. The compounds that formed them also can be found in different quantities (depending of the circumstances) in mineral coals [2]. Their extraction happens with the most modern technologies from vegetal sediments (eg. peat).

The humic acids are complex polymers built up from aromatic heterocyclic and isocyclic rings attached to each other with covalent bond directly. The side chains attaching to the backbone chain have acid character (fenol-OH, alcoholic-OH, carbonic-OH and carboxylic-OH) or basic character (imino and amino character) [3] [4]. There is a genetic context between soil humic acids and coal humic acids, their chemistry construction stands very close to each other. The latter ones are very important in terms of soil enrichment and cultivation, their usage will be intensify in the field of bio cultivation [5]. Besides their role in soil, the humic acids are biologically active substances on all areas of science, they may get role even in the fields of medicine and veterinary medicine.

Alkali humates – water-soluble salts of the humic acids – are produced from brown coal, lignite and peat with the help of alkaline extraction. The extraction results in potassium-humate if potassium hydroxide is used as extractant and sodium-humate if sodium hydroxide. The brown coal of Dudar (Hungary) has high potential in humate production since it has remarkably high humic acid content [6] [7] [8]. These kind of alkali-humates are connected with metals well. The aromatic carboxil- and hydroxyl groups found in humate can make a metastable complex with metals and other cations [9] [10] [11].

In the course of paper-making cellulose fibres are treated with aluminium sulphate, which increases the strength of paper and destroys the harmful microorganisms [12]. In our study we prepared a handsheets with the addition of copper(II)-sulphate instead of aluminium-sulphate, which dissolves in water and has acidic pH similarly to aluminium-phosphate. The antibacterial characteristics of copper(II)-sulphate is better contrary to aluminium-sulphate. Alkali humate is well bonded to metals and positive ions. Immobilization of copper on cellulose fibres can provide antimicrobial characteristics to the cellulose sheet as reported by Llorens et al. (2012), Booshehri et al. (2015), whilst humate can presumably increase the adsorbed copper onto the fibres [10] and offer gas absorption properties[15].

In the course of our research, potassium-humate was added to make test sheets containing copper ions with different content of potassium-humate (weight/weight %). Our aim was to examine the effect of CuSO<sub>4</sub> and potassium-humate prior the microbial and gas absorption tests to see how these additives changes the mechanical, colour, surface properties and air resistance of the cellulose sheet.

## 1. Materials and Methods

### 1.1 Materials

Brown coal from Dudar were supplied by Agroterm Kft. (Hungary),

KOH (Mw=56.11 g/mol, 2.13 g/ml)(Molar Chemicals Kft., Hungary,)

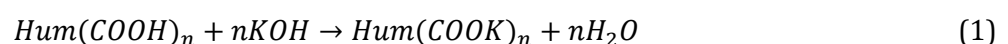
CuSO<sub>4</sub> (M=249.68 g/mol, 2.28 g/ml) (Molar Chemicals Kft., Hungary)

Cellulose (primer linter cellulose)

### 1.2 Methods

#### 1.2.1 The production of alkali humate

The production of alkali humate was based on patent no. HU 209 134. According to the patent we mixed 100 g dudar coal with 50 ml 5M KOH solution, mixed it for 3 hours with a magnetic stirrer. The mixture was then elutriated at room temperature for one night and fractioned the next day with a centrifuge for 10 minutes at 2400rpm. The treatment of coal with a solution of KOH gives soluble potassium-humate (PH) (1):



### 1.2.2 The preparation of test sheets

Cellulose fibers were cured for 40 minutes in order to achieve adequate fibrillation in a Dutch mill. The drainability of the fibers were measured according to MSZ EN ISO 5267-1: 1999 as 48 SR°.

Preparation of alkali humate test sheets was made based on HU 207 682 Patent no, with changes. To the cellulose fibers (moving on a magnet stirrer), CuSO<sub>4</sub> was added until the suspension had a pH of 4.5. After standing at room temperature for one day, the potassium-humate solution was added. It was stirring for 20 minutes at 200 rpm. Different proportions of potassium-humate mixtures were prepared from the suspension of the fiber, and test sheets were prepared on Erst Haage D-45476 type sheet forming.

The composition of the handsheets are listed in Table 1.

Content (weight rate)	
Test sheet 1	Control 1: 0.1
Test sheet 2	Copper-cellulose : potassium-humate 1:0.25
Test sheet 3	Copper-cellulose : potassium-humate 1:0.5
Test sheet 4	Copper-cellulose : potassium-humate
Test sheet 5	Copper-cellulose

Table 1: Different test sheets compositions

Before each test, the samples were conditioned at 23°C and 50% RH for at least 24 h.

### 1.2.3 Colour difference of test sheets

Test sheets were evaluated using an X-Rite 500 spectrodensitometer from X-Rite, USA. The values presented here are the b\* values, a\* values, L\* values and ΔE values.

b\* values correspond to the blue-yellow colour axis, a\* values correspond to the red-green colour axis and the L\* values correspond to the lightness axis in the CIELAB colour space (higher b\* value indicating a more yellow). CIELAB colour difference (ΔE) of the test sheets were calculated using the following equation:

$$\Delta E = \sqrt{(L_i^* - L^*)^2 + (a_i^* - a^*)^2 + (b_i^* - b^*)^2} \quad (2)$$

L<sub>i</sub>\*: L values of test sheet

L\*: L reference values

a<sub>i</sub>\*: a values of test sheet

a\*: a reference values

b<sub>i</sub>\*: b values of test sheet

b\*: b reference values

#### 1.2.4 Surface wettability and Surface free energy

For contact angle measurements PG-X Goniometer was used, 10 measurements were performed with a measuring drop of 5 µl, and the contact angle was measured at 0.031 sec after the release of the droplet. Test liquid was (analytical clear) two-times distilled water.

Apparent contact angles for liquid probes on test sheets were measured using a PG-X Goniometer. A 5 µl liquid drop (3 µl for DIM) was delivered to the surface of the sample. At least 10 measurements were taken for each liquid probe. The surface energy of the test sheets were calculated using the following equation:

$$\sqrt{\gamma_S^D * \gamma_l^D} + \sqrt{\gamma_S^P * \gamma_l^P} = \frac{\gamma_l(\cos\theta + 1)}{2} \quad (3)$$

With  $\gamma_S^D$ : dispersive component of the surface energies of the solid [mJ/m<sup>2</sup>]

$\gamma_l^D$  : dispersive component of the surface energies of the liquid [mN/m]

$\gamma_S^P$  : polar component of the surface energies of the solid [mJ/m<sup>2</sup>]

$\gamma_l^P$  : polar component of the surface energies of the liquid[mN/m]

$\gamma_l$ : surface energies of liquid [mN/m]

$\theta$ : contact angle [°]

#### 1.2.5 Mechanical properties

Bending force was measured based on ISO 2493. The test was performed on a Büchel Stiffness Tester, with 15° bending angle, 50 mm test span length and 38 mm sample width. A mean value was calculated from 10 measurements.

To determine the tensile strength and elongation at breakpoint of the films tensile test was performed by using an Instron 3345 tensile tester. Five-five samples were fixed between the grips of the device with a gauge length of 36 mm then 20 mm/min crosshead speed was applied. The width of the samples was 10 mm. The measurements were conducted at 23 ± 2°C, with the relative humidity of 50 ± 5%.

The compressive strength, which indicates the maximum compressive force per unit width of cellulose fiber sheets without failing, were determined according to MSZ EN ISO 9895 using short-span (0.7 mm) compressive tester. The width of the sample was 15 mm. The compressive strength was expressed in kN/m.

### 1.2.6 Air resistance (Gurley method)

The necessary time to pass 100 ml air through the handshets was determined by Gurley method (based in ISO 5636-5), with a L&W Gurley densometer. The air resistance was measured on the opposite side of the sieve side and expressed in s/100ml of air.

## 2. Results

### 2.1 Colour difference of test sheets

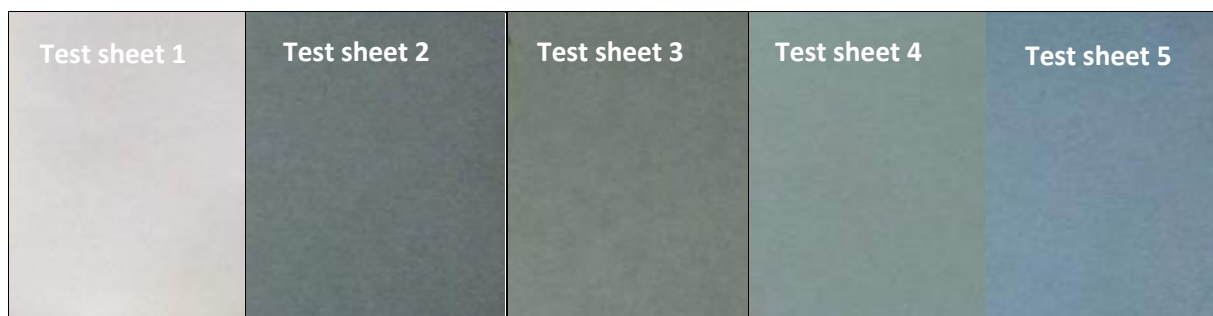


Figure 1: Different colours of tests sheets

	L	a	b	$\Delta E^*$	$\Delta E^{**}$
Test sheet 1	92.75±0.22	-1.34±0.41	3.52±0.21		
Test sheet 2	65.9±0.15	-3.05±0.26	3.97±0.33	17.67	
Test sheet 3	66.54±0.51	-3.59±0.34	6.61±0.46	26.48	9.14
Test sheet 4	75.08±0.22	-10.65±0.77	1.92±0.75	28.48	8.50
Test sheet 5	83.86±0.41	-18.46±0.50	-4.46±0.78	20.87	

Table 2: CIELab measurement results of different test sheets

\*colour difference of sheets compared to unmodified cellulose sheet (Test sheet 1)

\*\* colour difference of potassium-humate containing sheets compared to each other

The results of CIE Lab color measurement are summarized in Table 2. Examining luminance (L \*) results, it can be observed that samples of potassium-humate (TS 2-4) have lower luminance values, i.e., the samples are darker than those without humate (TS 1; 5).

This means that humate can form a chemical bond on the surface of cellulose fibers, thus sticking to it. The a\* value of the red-green axis values the samples. The lower this value, the greener the pattern. The test sheet (TS 5) value is -18.46, while the other test sheets are -10.65, -3.59, -3.05, -1.346, which indicates that the test sheet 5 has a lot more green color, this difference is also visible to the naked eye (Figure 1). From the samples containing copper-sulphate (TS 2-5) test sheet 5 does not contain potassium-humate. Because of the intense color of copper-sulphate, test sheet 5 contains more green colors compared to other samples. b\* is the value of the blue-yellow axis, the higher this value the more yellow is found in the sample. Test sheet 2, 3 and 4 have more yellow than control test sheet (TS 1). Test sheet 5 is much lighter than the other tested samples. The bluish color of copper-sulphate dominates in test sheet 5. Compared to control test sheet (TS 1), the value of  $\Delta E$  was 26.91 for sample test sheet 2, 20.05 for test sheet 3, 20.05 for test sheet 4, and 20.88 for test sheet 5 (Table 2.). The

changes in  $\Delta E$  are classified as "very intensive" color difference (Table 3) [16] [21] compared to the control sample. Compared to the  $\Delta E$  values for 10 w% potassium-humate (TS 2). The  $\Delta E$  values of the samples are increasing containing humate. 25 w% potassium-humate sample (TS 3)  $\Delta E$ : 9.14, 50 w% sample containing potassium-humate (TS 4)  $\Delta E$  is 8.5.

Colour difference( $\Delta E$ )	Colour variation estimation
$\Delta E \leq 0.2$	undiscernible
$0.2 < \Delta E \leq 0.5$	Very light
$0.5 < \Delta E \leq 1.5$	light
$1.5 < \Delta E \leq 3.0$	clear
$3.0 < \Delta E \leq 6.0$	Very clear
$6.0 < \Delta E \leq 12$	intensive
$12 < \Delta E$	Very intensive

Table 3: Correlation between sense perception and colour difference ( $\Delta E$ ) according to Straze et al. (2008) and Jirouš and Ljuljka (1999)

## 2.2 Surface wettability and surface energy

The surface energy of sheets was characterized and the dispersion ( $\gamma_{SD}$ ) and polar ( $\gamma_{SP}$ ) components of surface free energy were determined by contact angle measurements against water and diiodomethane.

All test sheets has water contact angles of about  $40^\circ$ , indicating good wetting property and high hydrophilicity [22]. The contact angles against diiodomethane is around  $34^\circ$  (Table 4). The additives did not changed the hydrophilicity of the cellulose fibers.

Based on the contact angle values, the surface free energy of test sheets was calculated. Results prove that the total surface free energy values hardly differ in different test sheets at 0,1 s, 69.16-84.9 m Nm<sup>-1</sup>, at 5s 46.33-63.05 m Nm<sup>-1</sup> ( Figure 2). The total surface free energy values are nearly the same for the test sheets derived from different concentrations of potassium-humate.

The sheets can be easily printed and glued as the surface energy values are within 40–70 m Nm<sup>-1</sup> [23], which means that test sheets are still in the range.

Characteristics	Type of test sheets	Concentration of potassium-humate (%)			
		0 (TS 5)	10 (TS 2)	25 (TS 3)	50 (TS 4)
Water contact angle ( $^\circ$ )	Cellulose (TS 1)	49 $\pm$ 10			
	Copper-cellulose	40.96 $\pm$ 8	32.96 $\pm$ 8	33.43 $\pm$ 7.5	42.61 $\pm$ 9.3
Diiodomethane contact angle ( $^\circ$ )	Cellulose (TS 1)	35.9 $\pm$ 0.47			
	Copper-cellulose	32.6 $\pm$ 2	32.9 $\pm$ 4	35.73 $\pm$ 3.75	36.48 $\pm$ 5.5

Table 4: Contact angles against water and diiodomethane of liner-cellulose with different concentration of potassium-humate at 0.031 s

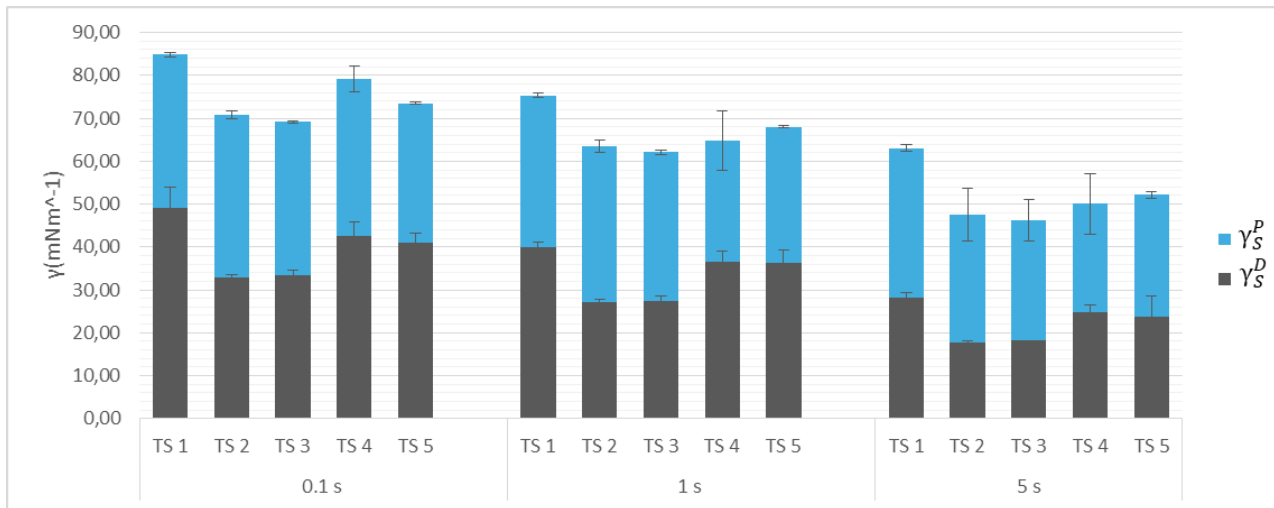


Figure 2: surface free energy ( $\gamma_s$ ) with its components dispersive ( $\gamma_s^D$ ) and polar ( $\gamma_s^P$ ) for all test sheets

## 2.3 Mechanical properties

The modification of cellulose fibres with  $\text{CuSO}_4$  did not affect the flexibility remarkably. However, adding humate the bending resistance was remarkably increased (Table 5). 10 and 25 w% humate doubled the bending resistance, whilst 50 w% humate caused 436% increase compared to the neat handsheet. The bending properties are the function of thickness and the bonding between the cellulose fibres and the fillers [18]. Due to the presence of humate the sheets became thicker which can be the main reason for the higher bending resistance. It can be assumed from the tensile and compressive strength results that the humate could presumably increase the  $\text{CuSO}_4$  modified fiber-fiber connections as well.

Based on the results (as seen in Table 5) the tensile strength and also the strain at break showed lower values for all the samples compared to the sheet prepared from unmodified fibers. Although the TS 2 sample, containing 10 w% potassium-humate, had the lowest strengths the tensile strength was increased by the humate content. Adding the highest amount (50w %) of PH increased the tensile strength to 7.8 kN/m which is comparable to the control sample, where 8.5 kN/m was obtained. The strain was also improved by the humate compared to the cellulose sheets prepared from  $\text{CuSO}_4$  modified fibers.

Results of short-span compression test showed (Table 5) the same tendency as bending resistance or tensile test. The potassium-humate induced improvement of compressive strength compared to the acidically modified fiber sheet. By increasing the humate content the improvement was 10, 13 and 70%. Comparing the TS 4 and TS 1 samples the increase was 5%.

As it is known the mechanical properties are deteriorating by the acidic fiber treatment [19] [20], however, using appropriate amounts of alkali humate the initial mechanical properties of the neat test sheet could be maintained.

	Bending resistance (mN)	Compressive strength (kN/m)	Tensile strength (kN/m)	Strain at break (%)	Air resistance (s/100 ml)	Grammage (g/m <sup>2</sup> )	Thickness (mm)
TS 1	24.0±1.7	3.8±0.6	8.5±0.3	3.5±0.2	624.9±132.4	142±10	165±17
TS 2	31.7±0.6	2.6±0.5	4.4±0.2	1.6±0.1	136.03±33.1	149±16	226±28
TS 3	48.2±3.5	2.9±0.3	5.9±0.1	1.7±0.1	169.96±50.5	153±19	226±21
TS 4	104.7±6.1	4.0±0.5	7.8±0.4	1.9±0.3	262.52±149	249±21	308±32
TS 5	29.3±9.9	2.3±0.2	5.5±0.2	1.4±0.2	120±62.5	147±17	171±22

Table 5: Grammage, thickness, mechanical and air resistance properties of different handsheets

## 2.4 Air resistance

The porosity of the sheets containing CuSO<sub>4</sub> modified fibers was drastically decreased (Table 5). The enhanced air permeability is presumably due to the partial acidic hydrolysis of the fines and thin fibrils which could decrease the free space between the cellulose fibers in TS 1. As it can be seen in Table the presence of humate decreased the porosity and compared to TS 5, the test sheets TS 2, TS 3 and TS 4 showed 13, 41 and 117% decrease, respectively. Handsheet with 50 w% PH had still 50% lower air resistance compared to TS 5.

## 3. Conclusions

During our research we prepared potassium-humate and CuSO<sub>4</sub> modified linter cellulose sheets to get an overview how the copper sulfate and alkali humate affects the colour, wettability, mechanical and air resistance properties of the hand sheets.

According to the results the humate adsorbed well onto the copper sulfate modified cellulose fiber surface which was shown by the intensive colour difference. The wettability and surface energy was not highly affected by adding copper sulfate or humate to the fibers. Compared to the CuSO<sub>4</sub> modified cellulose sheets, humate containing sheets showed slightly lower values which was increased by the humate amount.

The treatment with copper sulfate led to the decrease of the mechanical and air resistance properties of the handsheet. By adding the alkaline humate the mechanical properties were improved in the function of the humate content, the properties became comparable to the control cellulose sheet. With 50 w% humate content the bending resistance exceeded the resistance of the neat sheet.



Although, the suitability of copper sulfate and humate modified sheets as active packaging material is needed to be examined, the high air permeability and the unaffected hydrophilicity can be beneficial at the planned gas and aqueous liquid absorption.

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