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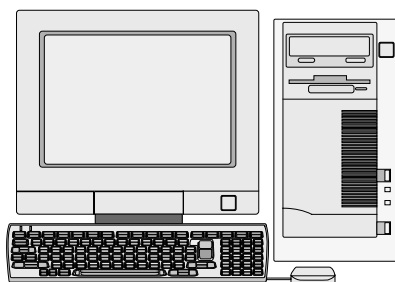
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PRINT GLOSS OF SCREEN PRINTED EFFECT PIGMENTS ON RICH MINERAL PAPER

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Abstract

In the present paper effect pigments, which were differed in composition, interference colour and particle size were investigated. The investigation was focused on the print gloss of effect pigments, which were measured at different reflectance angles. Six types of effect pigments (colourful transparent effect pigment: EP1, conductive pigment: EP2, interference pigments: EP3, EP4, EP5 and multicolour effect pigment: EP6) were printed on double coated Rich Mineral Paper. Effect pigments were applied into printing base (PVC transparent base) in 15wt. % concentration and were printed in screen printing technique. On the bases of measurements of print gloss it was established that colourful transparent effect pigment (EP1) obtained the highest print gloss, meanwhile the conductive pigment (EP2) the lowest. The most obvious impact on the end print gloss has the particle sizes of certain pigments.

Key words: *Print Gloss, Effect Pigments, Rich Mineral Paper, Screen Printing.*

Rezumat

În această lucrare se studiază pigmenții efect, care prezintă diferențe în compoziție, interferența culorii și mărimea particulei. Studiile s-au axat pe evaluarea pigmenților efect asupra luciului la tipărire, care a fost măsurat la diferite unghiuri de reflectanță. S-au analizat șase tipuri de pigmenți (pigmenți cu efect transparent: EP1, pigmenți cu proprietăți conductive: EP2, pigmenți cu interferență: EP3, EP4, EP5 și pigmenți cu efect multicolor: EP6) care au fost tipăriți pe un material de hârtie dublu cretat (Rich Mineral Paper). Pigmenții efect au fost aplicați pe un suport de tipărire (suport transparent din PVC) în concentrație de 15%, utilizând tehnica serigrafică. Pe baza rezultatelor obținute pentru luciul la tipărire, s-a constatat că cea mai mare valoare a fost obținută în cazul pigmentului cu efect transparent (EP1), în timp ce pigmentul cu proprietăți conductive (EP2) are cea mai mică valoare pentru luciul la tipărire. Cel mai pronunțat efect asupra luciului final l-a avut mărimea particulelor pigmenților testați.

Cuvinte cheie: *Luciu la tipărire, Pigmenți efect, Hârtie cu conținut ridicat de minerale, Serigrafie.*

INTRODUCTION

The worldwide importance of specialty printing processes is constantly increasing, and one of them is also printing by effect pigments. Contemporary requirements for environmental friendly and visually attractive packaging are one of the utmost requirements for product distribution to worldwide markets.

The print quality of special effect pigments is influenced by techniques of application, as well as by the physical-chemical properties of the printing ink and print substrate [1].

Special effect pigments are used as colorants or part of colour formulations for all systems where traditional pigments are applied, but where additional colour depth, brilliance, iridescence, colour travel, and other specular effects are required. Effect pigments comprise from two main groups including pearl luster pigments (pearlescent pigments, nacreous pigments, interference pigments) and metal effect pigments. All these pigments consist of small thin platelets that show strong lustrous effect when oriented in parallel alignment in application systems [2].

Gloss is important for the print quality [1]. It is an optical property of a printed surface which causes a shiny or lustrous appearance [3]. When light falls onto a pigmented ink film, four optical processes can occur. These are reflection and refraction of light at the surface on the ink film, and scattering and absorption within the ink film. All four will occur to a greater or lesser extent. If the surface of the ink film is smooth, with a mirror-like finish, the incident light will be reflected specularly, obeying the small laws of reflection. The film will appear glossy. If the surface is rough, light will be reflected diffusely in all directions and the gloss will be reduced [4]. The gloss is depending on the surface roughness and the refractive index of the material. A material with rough surface scatters the light more than a smooth surface and the result will be a less glossy appearance.

By definition gloss is a measure of the proportion or direct reflection. When measuring gloss a sample is illuminated with parallel light from a certain angle. The reflected light is then recorded at the same reflection specular angle. The choice of angle is to some extent determined by the gloss level of the material to be characterized. One rule is that a lower angle is more suitable to use for glossy materials [1].

The gloss characteristics of coated papers and film influence the gloss of the inks that are applied to them. High gloss finishes are very shiny, and tend to be reflective. Gloss also depends upon the printing substrate; penetration will reduce gloss, as will insufficient wetting or affinity between the ink and the substrate. Two papers with identical colour may produce very different prints if they have different gloss and absorbencies.

Gloss can increase by applying an overprint varnish or lamination and is also influenced by effect pigments. The smoother the substrate surface, the better effect pigments can demonstrate their typical features [5-7].

The aim of this study was to gain a better understanding how different effect pigments influenced the end print gloss on rich mineral paper.

RESEARCH METHODS

Six different effect pigments were used: Miraval[®] 5424 Magic Blue (further as a EP1), Minatec[®] 40 CM (EP2), Iriodin[®] 524 Red Satin (EP3), Iriodin[®] GP Rutile Blue-Green WNT (EP4), Iriodin[®] 9605 Blue-Shade Silver SW (EP5) and Colorstream[®] T10-01 Viola Fantasy (EP6). Basic properties of all effect pigments are presented in Table 1.

Table 1 Properties of effect pigments

Pigment type	Composition	Form	Interference color	Particle size
Miraval [®] 5424 Magic Blue (EP1)	Calcium Aluminium Borosilicate: 59-77% SiO ₂ : 1-8% TiO ₂ (Rutile): 22-32% SnO ₂ : 0-1%	Dry, free-flowing powder	Varicolored Glitter Blue	20-200 μm
Minatec [®] 40 CM (EP2)	Mica / SiO ₂ : 52-67% (Sn/Sb)O ₂ : 33-48%	Dry, free-flowing powder	Light Grey	98 % < 15 μm
Iriodin [®] 524 Red Satin(EP3)	Mica: 39-45% Fe ₂ O ₃ : 55-61%	Dry, free-flowing powder	Red	5-25 μm
Iriodin [®] GP Rutile Blue-Green (EP4)	Mica: 41% TiO ₂ (Rutile)+CoTiO ₃ : 57.5% ZrO ₂ : 1% SnO ₂ : 0.5%	Dry, free-flowing powder	Turquoise	5-40 μm
Iriodin [®] 9605 Blue-Shade Silver SW (EP5)	Mica: 68-76% TiO ₂ (Rutile): 23-32% TiO _x ²⁾ , SnO ₂ : 0-1%	Dry, free-flowing powder	Steel Blue	98 % <40 μm
Colorstream [®] T10-01 Viola Fantasy (EP6)	SiO ₂ : 81-90% TiO ₂ (Rutile): 8-14% SnO ₂ : 2-5%	Dry, free-flowing powder	Lilac/Silver/ Green/Blue	5-50 μm

Effect pigments were applied into printing base (PVC transparent base) in 15wt. % concentration and were printed in screen printing technique (Screen Printer TSH Print Swiss S550) on double-coated Rich Mineral Paper (Taiwan Lung Meng Tech Co LTD). The mesh density was 120 threads/cm. The print gloss was measured at three different angles (20°, 60°, 85°) using QIP GlossMaster multiangle gloss meter. Measurements conform to the ASTM D523 standard measurement protocol for specular gloss measurements.

RESULTS AND DISCUSSION

The Rich Mineral Paper (RMP) is waterproof and durable material. It is constituted from the main raw material based on rocks containing variants of calcium carbonate, such as calcite, marble and limestone. Furthermore, RMP is eco-friendly and does not involve pollution of water, toxic gases or waste products in its production process. As well, RMP is biodegradable and easy recycled. It is used in many applications, such as calendars, posters, maps, notepads, tags, paper bags, packaging paper, plastic floor, art craft paper, wall paper, advertising paper for light boxes and billboards [8-9].

In Figure 1 (a, b, c, d, e, f) the print gloss (20°, 60°, 85°) of different effect pigments printed on Rich Mineral Paper are presented.

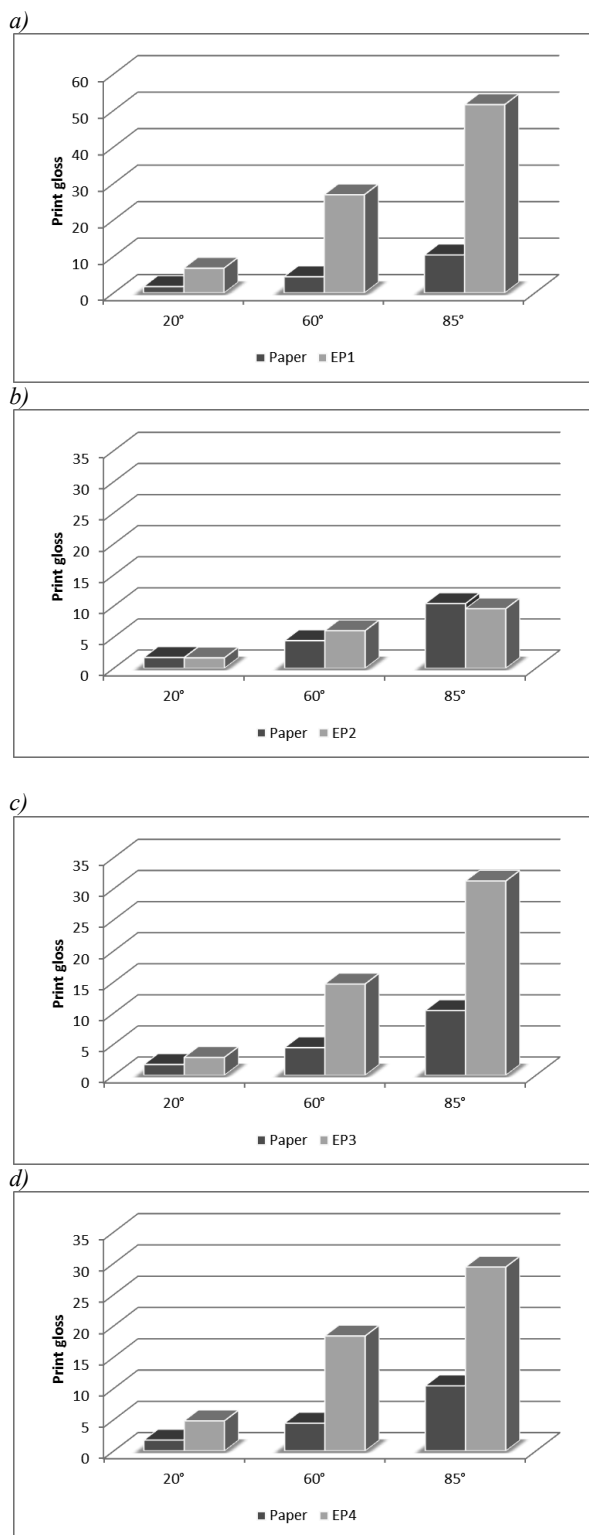


Figure 1: The print gloss of different effect pigments printed on Rich Mineral Paper.

The paper and the applied ink or transparent carrier itself have effect on the gloss [10]. Different measurement angles gives a different results of print gloss as can be seen in Figure 1. Also different effect pigments have impact on the print gloss, which can be observed by comparing all six types of effect pigments printed on Rich Mineral Paper. The effect

pigments differed among themselves in the composition, interference colour and particle sizes. Pigment EP1 belong to the group of colourful transparent effect pigment, pigment EP2 to the group of conductive pigments, pigments EP3, EP4 and EP5 to the group of interference pigments and pigment EP6 to the group of multicolour effect pigments. The Rich Mineral Paper obtained 1.7 gloss unit at angle of 20°, 4.4 gloss units at angle of 60° and 10.4 gloss units at angle of 85°. It was established, that almost all effect pigments increased the print gloss when where printed on Rich Mineral Paper. Among all effect pigments, the EP1 gave the highest print gloss. The print gloss at angle of 20° achieved the 6.7 gloss units, at angle of 60° the 26.9 gloss units and at angle of 85° the 51.6 gloss units. The EP1 (see Table 1) has the largest pigment particles (20-200 μm). The size of pigment particles in the dried ink film play an important role in determining the gloss characteristics of the film [4]. The larger pigment faced reflect more specular light and thus results in larger specular print gloss. On the other hand, the pigment EP2 gave the lowest print gloss (Figure 1/b). The EP2 is a light-coloured, conductive pigment. It is appropriate for coating with intense colours and formulae that required a high level of transparency [11]. The particle sizes of EP2 are in 98% smaller from 15μm (see Table 1), which correspond to lower print gloss. The print gloss of EP2 at angles of 20° and 85° achieved the lower values compared to unprinted paper, meanwhile at angle of 60° the print gloss increased only for 1.6 gloss units. The pigments EP3, EP4 and EP5 behaved similarly, especially when were measured at angle of 85°. Pigment EP3, which have the particle sizes from 5 to 25 μm, obtained a bit lower values of print gloss at angle of 20° (2.8 gloss units) and at angle of 60° (14.6 gloss units) compared to pigments EP4, EP5 and EP6. Pigment EP6 belongs to the group of multicolour effect pigments, which achieved unique colour effect. It is based on synthetically produces silicium dioxide platelets coated with metal oxides [12]. When comparing the print gloss of pigment EP6 with interference pigments (EP3, EP4, and EP5), there has been no large deviations between enhanced print glosses of pigments.

CONCLUSIONS

The evaluation of screen printed effect pigments on Rich Mineral Paper resulted in the conclusion that the particle size and type of effect

pigments plays an important role on the end print gloss. The results clearly demonstrate that effect pigments gave differed values of print gloss when were measured at different angles. The highest print gloss gave all effect pigments at angle of 85°, meanwhile at angle of 20° the lowest. It was also established that all effect pigments increase the print gloss when comparing to unprinted paper, except pigments EP2 at angles of 20° and 85°. There was also a noticeable difference in print gloss depending on which type of effect pigment that have been used. The colourful transparent effect pigment (EP1) gave the most glossy surface, meanwhile the conductive pigment (EP2) the less.

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ON WATER FOOTPRINT OF PAPER

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Abstract

Over the coming years, a global increase in water demand will draw more attention to how businesses manage water responsibly. The paper industry is a large user of fresh water although most of this water is returned to surface water bodies after treatment. The paper producers recognize the importance of sustainable water management and desire to know more about the role of freshwater consumption and emissions along the whole production chain of paper. In the recent years, the water footprint quantification gained a special attention among the pulp and paper producers. Water footprint became an useful tool for water monitoring during life cycle of paper and paper products

In this paper, the water footprint concept is presented, together with the definition and the components of the water footprint. The phases of the methodology for evaluation of water footprint of a product (particularly of paper) are discussed. The values of water footprint of paper are very different depending of paper grade, paper composition and technological level of the pulp and paper mill. This study shows that the green water footprint has the highest contribution to the total water footprint of paper, due to the contribution of wood used in pulp production. The contribution of the blue water footprint of paper is small and consists of the water that is lost by evaporation during the production process. The use of recovered paper may be particularly effective in reducing water footprints of paper products.

Key Words: *Water Footprint, Paper, Water Management, Sustainability*

Rezumat

În perioada următoare, creșterea consumului de apă la nivel global va accentua preocuparea mediului de afaceri în privința utilizării raționale a apei. Industria hârtiei este un mare consumator de apă, chiar dacă cea mai mare parte a apei consumate este tratată și apoi evacuată în apele de suprafață. Producătorii de hârtie sunt conștienți de importanța managementului durabil al apei și doresc să acumuleze informații noi legate de consumul de apă și de volumul emisiilor generate în procesul de producere a hârtiei. În anii anteriori, determinarea amprentei de apă a căpătat o atenție deosebită din partea producătorilor de hârtie. Amprenta de apă a devenit un mijloc eficace pentru determinarea consumului de apă de-a lungul ciclului de viață a hârtiei și a produselor din hârtie.

În lucrare se prezintă conceptul amprentei de apă, împreună cu definiția și elementele componente. Se discută fazele procedurii de evaluare a amprentei de apă a unui produs, în particular a hârtiei. Valorile amprentei de apă a hârtiei diferă sensibil în funcție de sortiment, compoziție și de nivel tehnologic al fabricii. Lucrarea arată că amprenta verde are contribuția cea mai mare la amprenta totală de apă a hârtiei, datorită lemnului utilizat la producerera celulozei. Contribuția amprentei albastre este redusă și se referă la apa pierdută prin evaporare. Folosirea maculaturii determină reducerea semnificativă a valorii amprentei de apă a hârtiei.

Cuvinte cheie: *Amprenta de apă, Hârtie, Managementul apei, Dezvoltare durabilă*

INTRODUCTION

Human activities consume and discharge large volumes of polluted water. At global scale, most of the water use occurs in agricultural production, but there are also substantial water volumes consumed and polluted in the industrial and domestic sectors. Water consumption and pollution can be associated with specific activities such as: irrigation, bathing, washing, cleaning and processing. Total water consumption and pollution are generally regarded as the sum of a multitude of independent water demanding and polluting activities [1].

Total water consumption and pollution relate to what and how communities consume and to the structure of the global economy that supplies the various consumer goods and services. Until the recent past, there have been few thoughts in the science and practice of water management about water consumption and pollution along whole production and supply chains. As a result, there is little awareness about the fact that the organization and characteristics of a production and supply chain does actually strongly influence the volumes of water consumption and pollution that can be associated with a final consumer product. It was shown that visualizing the hidden water use behind products can help in understanding the global character of fresh water and in quantifying the effects of consumption and trade on water resources use [2]. The improved understanding may form a basis for a better management of the global freshwater resources.

The goals of this paper are to discuss the water footprint concept and to present the steps for accounting the water footprint of a paper product.

THE WATER FOOTPRINT CONCEPT

The idea of considering water use along supply chains has gained interest after the introduction of the *water footprint* concept by Hoekstra in 2002 [3]. The water footprint is an indicator of freshwater use that looks not only at direct water use of a consumer or producer, but also at the indirect water use. The water footprint can be regarded as a comprehensive indicator of freshwater resources appropriation, next to the traditional and restricted measure of water withdrawal.

Water footprint is defined as the total volume of freshwater that is used to produce the goods and services consumed by an individual or a community. A water footprint can be calculated for a particular product, for any well-defined group of consumers (e.g. an individual, family,

village, city, province, state or nation) or producers (e.g. a public organization, private enterprise or economic sector). The water footprint is a geographically explicit indicator, not only showing volumes of water use and pollution, but also the locations. There are the following water footprint types:

- The water footprint of a product is the sum of the water footprints of the process steps taken to produce the product (considering the whole production and supply chain);
- The water footprint of a consumer is the sum of the water footprints of all products consumed by the consumer.
- The water footprint of a community is the sum of the water footprints of its members.
- The water footprint of national consumption is the sum of the water footprints of its inhabitants.
- The water footprint of a business is the sum of the water footprints of the final products that the business produces.
- The water footprint within a geographically delineated area (e.g. a municipality, province, state, nation, catchment area) is the sum of the process water footprints of all processes taking place in the area.

The components of a water footprint include the blue, green and grey water footprints. The *blue water footprint* refers to consumption of blue water resources (surface and ground water) along the supply chain of a product. Blue water comprises loss of water from the available ground-surface water body in an area, which happens when water evaporates, returns to another area or the sea or is incorporated into a product. It excludes the part of the water withdrawn from the ground or surface water systems that returns in that system directly after the use or through leakage before it was used. The *green water footprint* refers to volume of rainwater that evaporated during the production process. This is mainly relevant for agricultural products (crops or trees). The *grey water footprint* refers to pollution and is defined as the volume of freshwater that is required to assimilate the load of pollutants based on existing water quality standards. Figure 1 shows the origin of green and blue water footprints. The green water footprint refers to the human use of the evaporative flow from the land surface, mostly for growing crops or production forest. The blue water footprint refers to the consumptive use of the run-off flow, in other words, the abstraction of run-off from the catchment insofar as it does not return to the catchment in the form of return flow.

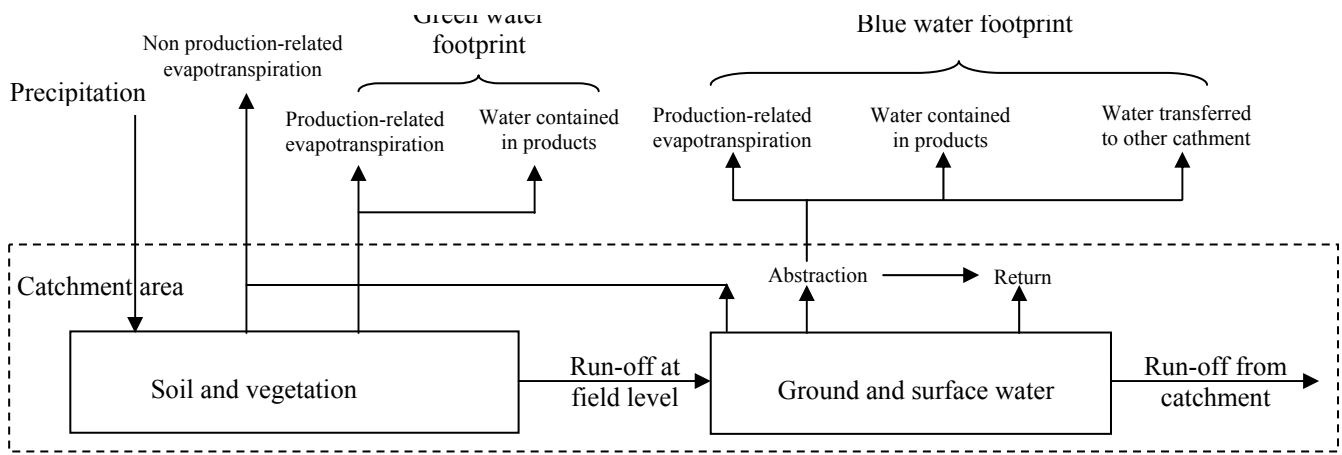


Fig. 1 The green and blue water footprint in relation to the water balance of a catchment area

The difference between “green” and “blue” water is their point of origin. The freshwater in aquifers, lakes and rivers is referred to as blue water, while green water is bound in the soil and plants and released by evapotranspiration and returned to the atmosphere. Blue water can be transported and is therefore the only source for drinking water. Green water cannot be transported since it is bound in the soil.

Figure 2 presents the schematic representation of the components of a water

footprint. Direct water use refers to the water use by the consumer or producer himself. Indirect water use refers to the water use in the production chain of products bought by the consumer or producer. It shows that the non-consumptive part of water withdrawals (the return flow) is not part of the water footprint. It also shows that, contrary to the measure of ‘water withdrawal’, the water footprint includes green and grey water and the indirect water-use component.

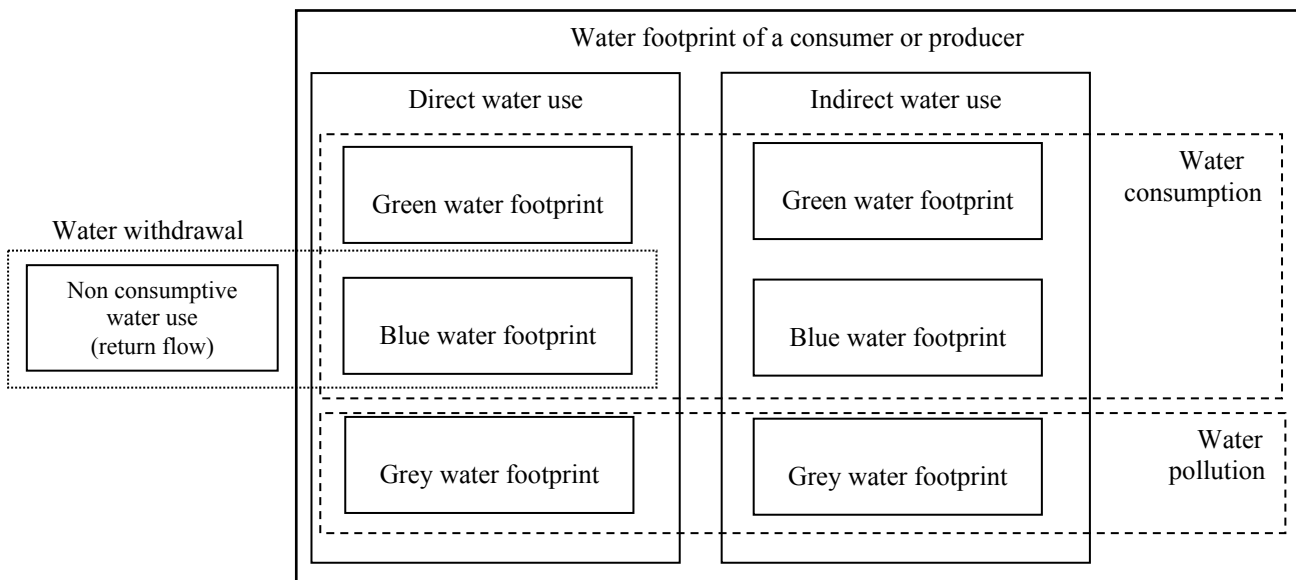


Fig. 2 Schematic representation of the components of a water footprint [4]

Figure 1 also shows that, as an indicator of water use, the water footprint differs from the classical measure of water withdrawal in three respects:

- it is not restricted to blue water use, but also includes green and grey water;
- it is not restricted to direct water use, but also includes indirect water use;
- it does not include blue water use insofar this water is returned to where it came from.

The water footprint thus offers a wider perspective on how a consumer or producer relates to the use of freshwater systems. It is a volumetric measure of water consumption and pollution. The water footprint is not a measure of

the severity of the local environmental impact of water consumption and pollution. The local environmental impact of a certain amount of water consumption and pollution depends on the vulnerability of the local water system and the number of water consumers and polluters that make use of the same system. Water footprint accounts give spatiotemporally information on how water is appropriated for various human purposes. They can feed the discussion about sustainable and equitable water use and allocation and also form a good basis for a local assessment of environmental, social and economic impacts.

The water footprint of different commodities is listed in table 1 [5].

Table 1 Water footprint of different commodities

Commodity	Unit	Global average water footprint (litres)
Apple or pear	1 kg	700
Banana	1 kg	800
Cheese	1 kg	5,000
Chicken	1 kg	3,900
Chocolate	1 kg	24,000
Eggs	one, 60 g	200
Leather	1 kg	17,000
Maise	1 kg	900
Milk	1 glass 250 mL	250
Paper	1 A4 sheet (copy paper)	10
Pork	1 kg	4,800
Tomato	1 kg	180
Wine	1 glass 125 mL	120

ASSESSMENT OF WATER FOOTPRINT OF PAPER

The water footprint of a product is defined as the total volume of fresh water that is used directly or indirectly to produce the product. It is estimated by considering water consumption and pollution in all steps of the production chain. The accounting procedure is similar to all sorts of products, either product derived from the agricultural, industrial or service sector. The water footprint of a product breaks down into a green, blue and grey component.

The methodology for evaluation of water footprint of a product (particularly of paper) includes three phases [6]:

1. Setting goals and scope of water footprint assessment
2. Water footprint accounting
3. Water footprint sustainability assessment

Setting goals and scope of water footprint assessment

In order to produce paper there are a wide range of different suppliers contributing raw materials. However, it is out of this scope to assess the water footprint for each of these individual suppliers. Therefore a selection was made based on the actual weight contribution of each raw material to the final paper product. The main raw material inputs selected for the water footprint of a common paper grade are: chemical or mechanical pulp, recovered paper, additives, fillers, starch. Water contained by paper as moisture should be also taken into consideration. Natural gas, although it is not a direct material input to paper itself, it is an important energy input to the operational side of paper production. Data regarding the water footprint of these inputs are available from the literature. Labor and

transport are usually excluded from the water footprint assessment, as they are expected to have a minor contribution to the overall water footprint of a paper product. For the same reason, thermal pollution is also excluded from the grey water footprint assessment.

Water footprint accounting

Water footprint of paper, $WF [p]$, accounts as the sum of green water footprint, $WF_{forestry}$, blue water footprint $WF_{proc.blue}$, and grey water footprint $WF_{proc.grey}$, according to the equation (1):

$$WF [p] = WF_{forestry} + WF_{proc.blue} + WF_{proc.grey}, \quad (1)$$

Green Water Footprint

The green water footprint of paper mainly refers to rainwater that is evaporated during tree growth, and can be determined using equation (2).

$$WF_{forestry}[P] = \left(\frac{ET_a + (Y_{wood} + f_{water})}{Y_{wood}} \right) \times f_{paper} \times f_{value} \times (1 - f_{recycling}), m^3 \quad (2)$$

- ET_a is the evapotranspiration from a forest/woodland ($m^3/ha.year$);
- Y_{wood} is the wood yield from a forest/woodland ($m^3/ha.year$);
- f_{water} is the volumetric fraction of water in freshly harvested wood (m^3/m^3);
- f_{paper} the wood-to-paper conversion factor (i.e. the harvested volume needed to produce a metric ton of paper product - m^3/ton);
- f_{value} the fraction of total value of the forest which is associated with paper production (dimensionless);
- $f_{recycling}$ the fraction of pulp derived from recovered paper (dimensionless).

Equation (2) shows that the green water footprint mainly depends on the forest evapotranspiration rate, ET_a , which largely differs among vegetation areas. The evapotranspiration rate of a tropical forest is up to three times higher as of a boreal forest.

The forest water data depend on the vegetation zone, as is exemplified in table 2 for two countries [7].

Table 2 Example of forest water data

Forest water data	Finland	Uruguay
Forest evapotranspiration, $m^3/ha.year$	3600	9300
Boreal forest		
Subtropical forest		
Wood yield, $m^3/ha.year$		
Broadleaves	7	
Pine	6	
Spruce	7	
Eucalyptus		33
Volumetric fraction of water in harvested wood, $m^3 water/m^3 wood$		
Broadleaves	0.45	
Pine	0.55	
Spruce	0.53	
Eucalyptus		0.50

The values for wood-to-paper conversion factor, f_{paper} are listed in table 3.

Table 3 Wood-to-paper conversion factor

Product	Wood-to-paper conversion factor, $f_{paper} m^3/t$
Mechanical pulp	2.50
Semi-chemical pulp	2.67
Chemical pulp	4.49
Dissolving pulp	5.65
Recovered paper	-
Newsprint	2.87
Printing & Writing paper	3.51
Other paper and board	3.29

The equation (2) also shows that the use of recovered paper may be particularly effective in reducing water footprints of paper products, due to the fact that the pulp from recycled paper has no forestry-related water footprint. Water footprint of paper grades based on recovered paper are much lower comparing with those containing chemical pulps. In addition, the global water footprint of paper can be reduced by choosing production sites and wood types that are more water-efficient.

Blue Water Footprint

Blue water footprint is freshwater withdrawn from rivers, lakes or groundwater reservoirs that is used in the pulp and paper production which does not return to the place of origin during the same period of time, either because it is evaporated, incorporated into the product, transferred to another basin or returned later on. Blue water footprints have to be calculated by assessing the water flows of the pulp and paper mills and that of externally produced starch and pigments. The blue water footprint assessment includes:

1. Water that evaporates in the drying section of pulp and paper production, (*Blue Water Evaporation*);
2. Water stored in the pulp and paper product, (*Blue Water Incorporation*);
3. Water in the effluent sludge that is a by-product from the waste water treatment plant and other losses including water leakage and water that is not returned to the same catchment area, (*Lost Return Flow*)

For each production site the process blue water footprint is calculated according to equation (3).

$$WF_{proc.blue} = \text{Blue Water Evaporation} + \text{Blue Water Incorporation} + \text{Lost Return Flow}, m^3 \quad (3)$$

Grey Water Footprint

Grey water footprint is the volume of freshwater needed to assimilate a given load of pollutants on reaching freshwater sources (for example a production process effluent discharged to a receiving water body), based on natural background concentrations and existing ambient water quality standards. For pulp and paper production the grey water footprint is calculated by assessing the effluent flows of the mill. For the grey water footprint calculation equation (4) is used.

$$WF_{proc.grey} = \frac{L}{C_{max} - C_{nat}} = \frac{Effl \times C_{effl} - Abstr \times C_{act}}{C_{max} - C_{nat}}, m^3 \quad (4)$$

- L : additional pollutant load contained in the receiving water body, mass/time;
- $Effl$: effluent volumetric flow rate, volume in time;
- $Abstr$: volumetric flow rate of the abstraction, volume in time;

- C_{effl} : actual concentration of the effluent, mass/volume;
- C_{act} : actual concentration of the intake water, mass/volume;
- C_{nat} : the natural concentration of the pollutant in the receiving water body (river, lake etc.). For human-made substances that naturally do not occur in water $C_{nat} = 0$;
- C_{max} : ambient water quality standard, mass/volume

The emission load includes measures of chemical oxygen demand (COD), biological oxygen demand (BOD), absorbable organic halogens (AOX), total organic carbon (TOC), ammonium, chlorides, phosphates and nitrates. Data on $Effl$, $Abstr$ and C_{act} come from the mill own databases and data on C_{nat} and C_{max} are usually obtained via the local environmental authorities.

The values of water footprint of paper are very different depending of paper grade, paper composition and technological level of the pulp and paper mill. Green water footprint has the highest contribution to the total water footprint of paper, due to the contribution of the wood used in pulp production. The contribution of the blue water footprint of paper is minor (1%) and consists of the water that is lost during the production process. It mainly consists of process water that is vented to the atmosphere, where it again becomes part of the global water cycle. In the paper and pulp industry it is not very common to measure the evaporation of water. Water footprint of newsprint ranges between 200-1500 m^3/t and of printing & writing paper between 300-2600 m^3/t . [8].

Water footprint sustainability assessment

The accounting phase measures the quantity of freshwater that is consumed throughout the production chain and categorizes it in green, blue and grey water footprints. However, in order to make a water footprint study more realistic and meaningful, the local context needs to be taken into account. This is achieved by a sustainability assessment phase where water scarcity hotspots are identified and water footprints are compared to actual water availability. The pulp and paper mills must provide information on their operations environmental permits, sustainable forestry management and use of freshwater resources in the production process. At a water catchment level further information are needed from external sources such as local authorities. The World Business Council for Sustainable Development

(WBCSD) Global Water Tool [9] is used to support the assessment of the local water scarcity situation for each of the specific catchment areas.

A sustainability assessment has three components: social, economic and environmental. The social assessment looked at the local freshwater availability and the potential for conflict over freshwater resources in the region over time. The WBCSD Global Water Tool allowed for mapping on each of the mills local projected annual renewable supply per person for year 2025. The WBCSD Global Water Tool also provided information on the physical and economic water scarcity of the region. If freshwater is abundant for current and future operations then water can be allocated and used in an economically efficient way, taking into account the different stakeholders' and environmental flow requirements. The WBCSD Global Water Tool mapping exercise itself is useful to identify freshwater hotspots and potential conflicts over water. It is however not a conclusive tool to claim that operations are sustainable.

From environmental point of view, a mill can demonstrate good performance by complying with local permit level allowances for water uptake and discharge, improving operational efficiency over time, and setting targets to further improve effluent quantity and quality. In addition, certified management systems, and certification to eco-labels demonstrate a good environmental management. (e.g. ISO 14001 and EU eco-label).

These criteria contribute to sound environmental management but do not prevent a mill from having a grey or blue water footprint. Therefore it is important to assess the environment sustainability of both the blue and grey water footprints. The sustainability of a grey water footprint is assessed using "water pollution level" (*WPL*), where a water pollution level of 100% means that the load assimilation capacity of the river has been fully consumed. Ambient water quality standards would be assessed as violated in cases where the *WPL* is beyond 100%. *WPL* is calculated according to equation 5:

$$WPL[x,t] = \frac{\sum WF_{grey}[x,t]}{R_{act}[x,t]}, \% \quad (5)$$

– R_{act} : actual run-off from the catchment, this data comes from local authorities or is measured by the mills;

– $\sum WF_{grey}$: summ of grey water footprints in a catchment area.

The sustainability of the blue water footprint is assessed by looking at the blue water

scarcity, (WS_{blue}). A blue water scarcity of 100% means that the available blue water has been fully consumed, everything beyond a 100% is considered unsustainable. Blue water scarcity is calculated according to equation 6:

$$WS_{blue}[x,t] = \frac{\sum WF_{blue}[x,t]}{WA_{blue}[x,t]}, \% \quad (6)$$

– $\sum WF_{blue}$: total of blue water footprints in the catchment area;

– WA_{blue} : blue water availability, this data comes from local authorities or is measured by the mills.

Once green, blue and grey water footprints have been quantified it is then possible to reduce them and their linked impacts. For example, the blue water footprint can be reduced by minimizing evaporation losses from direct production processes and closing water cycles in the mills. The grey water footprint can be lowered by removing the pollutant load from the process water. In the supply chain, contracts can include requirements on reducing supplier water footprints, which indirectly have an impact on the final water footprint of paper.

CONCLUSIONS

The water footprint represents a useful tool to understand the role of water in the supply chain and to conclude in what way and in what quality water is consumed. This parameter can be useful to map water-related risks over the whole production chain of a paper product and look for ways to reduce the specific water consumption.

A water footprint can be calculated for a particular product, an individual, family, village, city, province, state or nation. Water footprint can also be determined for a public organization, private enterprise or economic sector. The water footprint is a geographically explicit indicator, not only showing volumes of water use and pollution, but also the locations.

The water footprint of a paper product is the sum of the blue, green and grey water footprints. There are methods that allow the calculation of the water footprint of paper by determining the values of the component footprints. The values of water footprint of paper are very different depending of paper grade, paper composition and technological level of the pulp and paper mill. Green water footprint has the highest contribution to the total water footprint of paper, due to the contribution of the wood used in

pulp production. The contribution of the blue water footprint of paper is minor (1%) and consists of the water that is lost during the production process.

By determining of the water footprint of a paper product, useful information for paper mill regarding water consumption and emissions along

the production chain are obtained. This is a valuable tool to identify the causes of potential future water risks. The information also provides valuable insights for making decisions in future operations from the water usage point of view.

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CERCETAREA ȘI IMPLEMENTAREA UNOR NOI SISTEME DE SECURIZARE A HÂRTIEI DESTINATĂ TIPĂRII DOCUMENTELOR DE VALOARE FOLOSIND ELEMENTE DE SECURIZARE NANOPARTICULE

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Rezumat

În lucrare sunt prezentate o serie de studii și experimentări privind utilizarea nanoparticulelor magnetice coloidale, obținute prin metoda coprecipitării chimice, ca elemente de securizare pentru hârtiile destinate documentelor de valoare. Introducerea nanoparticulelor magnetice din coloizi în compoziția hârtiei s-a realizat în masă, prin tehnici speciale de reținere pe fibră. În urma experimentelor realizate s-a obținut un randament de retenție bun și o distribuție uniformă a nanoparticulelor în foaia de hârtie, iar proprietățile fizico-mecanice ale hârtiei nu au fost afectate. De asemenea, s-a constatat că nanoparticulele de coloid favorizează formarea de legături chimico-coloidale cu fibrele celulozice.

Cuvinte cheie: Hârtie securizată, Nanoparticule, Coloizi, Magnetită

Abstract

In this paper are presented some studies and experiments regarding the use of colloidal magnetic nanoparticles to securing value documents paper. These magnetic nanoparticles are obtained by chemical co-precipitation method. Introducing of colloidal magnetic nanoparticles into cellulose fibres network was realised by mass treatments, using special techniques of fibres loading. After the experiments has been obtained a good retention and uniform distribution of nanoparticles into paper web, preservation of physical-mechanical properties of paper. Colloidal nanoparticles allow the formation of chimico-colloidal bonds with cellulose fibres, also.

Key words: Security paper, Nanoparticles, Colloids, Magnetite.

INTRODUCERE

Hârtiile destinate tipăririi documentelor de valoare fac parte din categoria hârtiilor speciale. Deși cantitativ au o pondere redusă în producția mondială de hârtii și cartoane, acestea au o importanță economică deosebită și un anumit rol personal și social bine definit.

Cel mai mare risc la care sunt expuse documentele de valoare îl reprezintă riscul contrafacerii și falsificării. Se falsifică documentele de valoare fixă (bancnote, cekuri, documente de proprietate etc.), documente cu valoare negociabilă (cekuri bancare, etc.) și documente sociale personale (acte de identitate, pașapoarte, diplome de studii etc.).

Hârtiile de valoare sunt hârtii de calitate superioară având caracteristici fizico-mecanice - rezistență mecanică ridicată, comportare foarte bună la tipărire (pe aceste hârtii se pot imprima desene de mare finețe, în mai multe culori, pentru evitarea falsificării) și rezistență deosebită în circulație. În afară de aceste caracteristici hârtia destinată tipării actelor de valoare trebuie să conțină o serie de elemente de securitate care să o facă greu de falsificat.

Pentru ca securitatea documentelor să fie cu un pas înaintea tehnicilor, în evoluție, folosite de către cei care se ocupă de contrafaceri și falsificări, se impune ca și sistemul de securizare să fie mereu dinamizat cu noi elemente de securitate, cât mai complexe. Pe de altă parte, fiecare document se realizează pe un anumit sortiment de hârtie securizată, ceea ce înseamnă că tipărirea unei game largi de documente de valoare impune automat și diversificarea continuă a grupele de hârtii securizate.

Elementele care pot fi utilizate pentru securizarea hârtiilor pot fi: microparticule /nanoparticule complexe în următoarele variante:

- Pigmenți organici sau minerali fluorescenți
- Pigmenți sub formă de pulberi magnetice fluorescente sau coloizi magnetici
- Microparticule inteligente de tip MHC – microparticule metalizate holografice codate

Astfel, pigmenții - microparticule de natură minerală sau organică - asigură prin înglobarea lor în compoziția hârtiei funcția de element de securizare. Detecția acestor microparticule este dată prin culoarea pe care o prezintă în domeniul vizibil și de prezentarea fenomenului de fluorescență în prezența radiațiilor UV.

O altă grupă nouă de microparticule, care pot fi introduse în structura hârtiei se referă la pulberile magnetice fluorescente sau coloizi magnetici. Spre deosebire de prima categorie de microparticule, pulberile magnetice fluorescente vin în plus cu o proprietate care poate fi valorificată în procesul de securizare a hârtiei și anume – proprietățile magnetice ale acestora, care pot fi validate electronic cu ajutorul unui echipament de detecție, specializat în acest sens.

Următoarea grupă de microparticule este reprezentată de microparticule inteligente de tip MHC (metalice holografice codate). Aceste elemente metalice holografice au dimensiunile cuprinse între 50 nm și 1 mm și se amplasează pe una dintre suprafețele hârtiei. Conțin un substrat cu o structură de difracție în relief – o imagine holografică, iar printr-o deschidere a elementului

metalic (decuparea suportului metalic) se inscripționează un cod alfanumeric de autentificare. Elementele de codare a microparticulei inteligente pot fi identificate cu ajutorul unei lupe sau a unui microscop.

Pornind de la aceste date, lucrarea și-a propus să extindă gama de hârtii securizate folosind ca elemente de securizare nanoparticule din coloizi cu proprietăți magnetice.

Noua tehnologie de securizare va avea particularități specifice fiecărui tip de microparticulă care va intra în componența hârtiei (în masă sau la suprafața hârtiei).

În acest fel, cercetarea va oferi producătorului de hârtii și implicit tipografiilor autorizate în domeniul realizării documentelor de valoare, o varietate mai mare de elemente de securitate bazate pe realizarea unor combinații diverse între indicatorii de securizare sau oferirea întregului sistem. Aceasta deschide posibilitatea obținerii unor soluții particularizate și unice pentru fiecare document. Pe baza acestor caracteristici, se poate asigura trasabilitatea produsului pentru fiecare lot, plecând de la producătorul de hârtie, tipografia care a realizat documentul și beneficiarul final al acestuia.

PARTEA EXPERIMENTALĂ

Pentru securizarea hârtiei au fost folosite nanoparticule magnetice de magnetită dintr-un coloid magnetic pe bază de apă. Nanoparticulele magnetice au fost elaborate prin metoda coprecipitării chimice [Bica et.al. 2007], după care au fost stabilizate cu un strat dublu de acid lauric și apoi au fost dispersate în apă la o concentrație volumică de aproxim. 2%.

Caracterul inovativ al acestor elemente de securitate este dat de unicitatea folosirii lor în structura hârtiei, lărgind astfel aria de utilizare a nanoparticulelor.

Introducerea nanoparticulelor magnetice din coloizi în compoziția hârtiei s-a realizat în masă, prin tehnici speciale de reținere pe fibră. Astfel se asigură o reținere avansată a acestora în structura hârtiei, obținându-se un efect bun de securizare a hârtiei.

Experimentările au avut ca obiective:

- înglobarea în structura fibroasă a hârtiei a nanoparticulelor magnetice de magnetită din coloid,
- influența lor asupra caracteristicilor fizico – mecanice și de tipărire a hârtiei.

S-au folosit diferite rețete de materiale fibroase la diferite grade de măcinare, stabilindu-se compoziția optimă a foilor de hârtie. Pentru experimentări s-au folosit ca materiale fibroase:

- celuloză sulfat albită fibră scurtă- produsă de Grupul ILIM – Rusia în proporție de 70%
- celuloză sulfat albită fibră lungă- produsă de Bukocel - Slovacia în proporție de 30%

Coloidul cu proprietati magnetice utilizat are o densitate de 1,0779 g/cm³. Concentratia volumica de

nanoparticule in colid a fost de aproxim. 2%.

Celulozele au fost măcinate în holendru Valley la un grad de măcinare de 30 - 32°SR pentru celuloză sulfat albită fibră scurtă și, respectiv, la un grad de măcinare de 40 - 42 °SR, pentru celuloză sulfat albită fibră lungă.

S-au realizat 4 seturi de probe cu adaosuri procentuale de coloid cu proprietăți magnetice situate in domeniul 0.0 – 25% raportat la fibra a.u.

Măsurarea volumului de coloid necesar pentru fiecare probă s-a făcut cu o microbiuretă electronică automată.

Suspensia astfel obținută s-a deshidratat pe aparatul Rapid Kothen, iar foile formate s-au uscat la temperatura de 93°C, timp de 6 min.

REZULTATE ȘI DISCUȚII

Analiza proprietăților fizico-mecanice ale foilor de hârtie

Probele de hârtie au avut următoarele adaosuri de coloid raportate la fibra a.u.: P0 – 0% coloid, P1- 1% coloid, P2 – 5% coloid, P3 – 10% coloid, P4 – 25% coloid.

Probele de hârtie obținute cu diferite adaosuri de coloid au fost condiționate și analizate fizico – mecanic în **Laboratorul de încercări fizico-mecanice al S.C. CEPROHART S.A.**, acreditat RENAR. Rezultatele obținute sunt prezentate în tabelul 1.

Tabelul 1 Caracteristicile probelor de hârtie cu diferite adaosuri de coloid (0.0 – 25%)

Nr.crt.	Caracteristica determinată, UM	Proba de hârtie cu diferite adaosuri de coloid				
		P0	P1	P2	P3	P4
1.	Gramaj, g/m ²	69,7	70,5	71,3	72,7	71,1
2.	Grosime, mm.	0,098	0,098	0,101	0,101	0,100
3.	Densitate, g/cm ³	0,71	0,72	0,71	0,72	0,71
4.	Lungime de rupere, m.	6.293	7.030	6.940	7.007	6.769
5.	Porozitate Gurley, F/S	115/115	129/125	138/126	128/123	125/124
6.	Grad de alb, %	56,32	39,55	33,58	27,99	21,07

Din rezultatele obținute la determinările fizico – mecanice ale probelor de hârtie analizate putem observa următoarele :

1. Adaosul de coloid nu influențează semnificativ caracteristicile fizico – mecanice ale hârtiei idiferent de adaosul de coloid folosit, putem însă observa o ușoară îmbunătățire a caracteristicii – luginii de rupere, ceea ce evidențiază un aport la imbunatatirea legaturilor interne din structura benzii de hartie.
2. Coloidul este ușor adsorbit pe suprafața activă a celulozei. Retenția coloidului în probele de hârtie analizate este foarte bună, analiza colorimetrică a apelor rezultate la deshidratarea suspensiilor formate din amestecuri de celuloză și coloid evidențiind acest lucru.
3. Gradul de alb este influențat semnificativ datarita culoarii brun inchis a coloidului.

Gradul de alb al hartiei se micșorează accentuat cu marirea adaosului de coloid magnetic in domeniul 1,0 – 25%.

Foile obținute cu adaosuri diferite de de coloid au fost analizate optic la spectrometru Matrix – F, produs de BRUKER OPTICS cu absorbție în IR apropiat. Rezultatele obținute sunt prezentate în figura următoare (Figura 1).

Valoarea absorbției luminii în spectrul IR apropiat crește odată cu creșterea concentrației nanoparticulelor adsorbite pe suprafața fibrelor celulozice din hârtie. Această proprietate a nanoparticulelor magnetice folosite ca element de securizare în hârtie poate largi aria de detecție folosită.

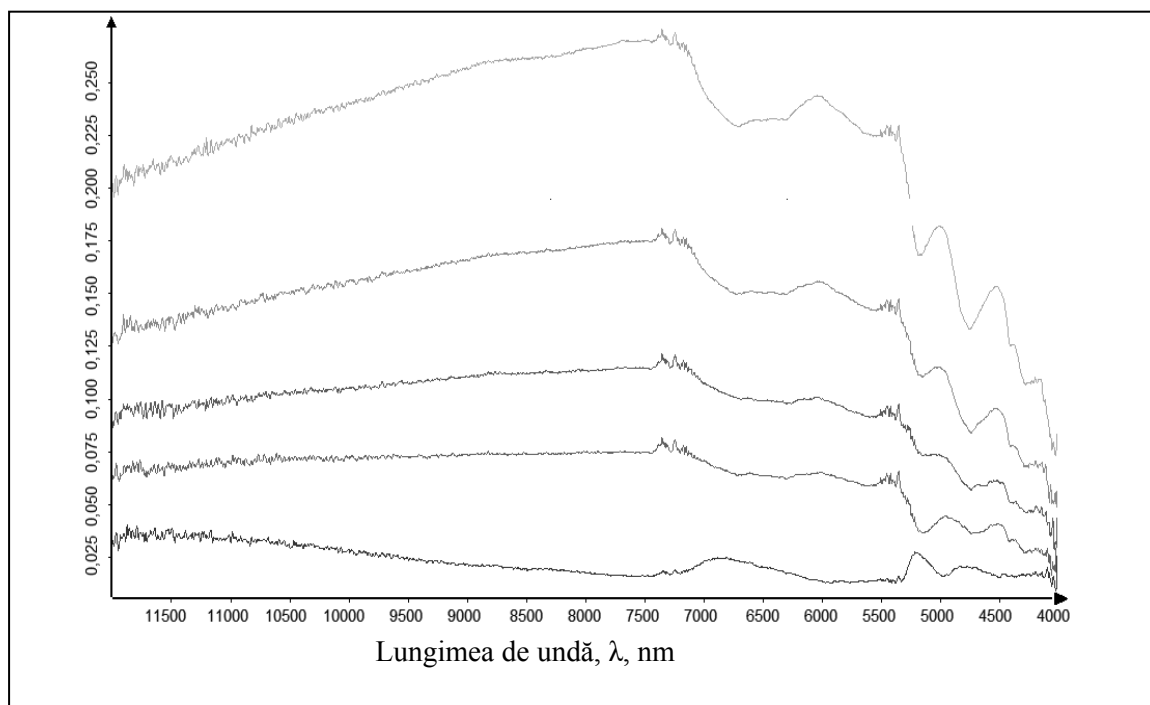


Fig.1. Curbele de absorbție a luminii în spectrul IR apropiat

Pentru a diminua influența asupra gradului de alb s-a optat pentru utilizarea unui adaos de coloid sub 1%, care să nu compromită proprietățile de securizare ale hârtiei. Pentru verificarea acestui adaos și influența lui în proprietățile fizico - mecanice ale hârtiei s-au realizat cinci seturi de probe în suspensie păstrându-se constante caracteristicile materialului fibros folosit, adăugându-se diferite concentrații

de coloid în domeniul: 0,1%-0,8%, suspensiile astfel obținute au fost deshidratate, foile de hârtie obținute au fost uscate, condiționate și analizate fizico-mecanic, rezultatele obținute sunt prezentate în tabelul 2. Foile de hârtie analizate au avut următoarele adaosuri de coloid: P1/0-0% coloid, P1/1-0,1% coloid, P1/2-0,2% coloid, P1/3-0,4% coloid, P1/4-0,6% coloid, P1/5-0,8% coloid.

Tabelul 2 Caracteristicile probelor de hârtie șarjate cu adaosuri de coloid între 0,1% și 0,8%

Nr.crt.	Caracteristica determinată, UM	Proba de hârtie cu diferite adaosuri de coloid					
		P1/0	P1/1	P1/2	P1/3	P1/4	P1/5
1.	Gramaj, g/m ²	73,1	72,6	72,9	73,2	74,6	75,9
2.	Grosime, mm.	0,114	0,113	0,114	0,113	0,114	0,118
3.	Densitate, g/cm ³	0,64	0,64	0,64	0,65	0,65	0,64
4.	Lungime de rupere, m.	6.493	6.600	6.540	6.607	6.769	6700
5.	Porozitate Gurley, F/S	41/40	42/40	43/42	40/39	41/40	43/42
6.	Grad de alb, %	65,44	62,56	63,51	62,54	61,96	61,21

Din rezultatele prezentate se poate observa o scădere mică a gradului de alb cu aproximativ 2-4 unități, dar caracteristicile fizico-mecanice analizate rămân nemodificate față de rezultatele obținute la analizele inițiale. Rezultatele obținute în acest domeniu al adaosului de coloid, permit continuarea cercetării cu aceste concentrații de nanoparticule magnetice în hârtie, analizându-se și proprietățile magnetice

Analiza proprietăților magnetice ale foilor de hârtie

Caracterizarea magnetică a probelor de hârtie cu adaos de nanoparticule magnetice de magnetită a fost realizată în *Centrul National pentru Ingineria Sistemelor cu Fluide Complexe din cadrul Universitatii "Politehnica" Timisoara."*

Magnetizația masică a probelor a fost măsurată prin metoda probei vibrante (Vibrating Sample Magnetometry - VSM) cu un magnetometru VSM 880 (DMS/ADE Techn., USA) la temperatura camerei (~25 °C).

În figura 2 sunt prezentate curbele de magnetizație masică (emu/g_{hartie}) funcție de câmpul magnetic aplicat (A/m) pentru cele 5 probe de hârtie.

Probele de hârtie cu nanoparticule de magnetită (P1 – P4) prezintă o magnetizație de saturație crescătoare, corespunzător cu procentul de coloid magnetic adăugat. Proba P0, fără coloid, prezintă magnetizare. Curba de histereză a

magnetizării indică prezența unui material feromagnetic în structura hârtiei, provenind din conținutul de fier al celulozelor folosite. S-a estimat o cantitate de 68 micrograme Fe la 1 Kg hartie. Proba P1, cu cel mai mic procent de coloid adăugat (1%), prezintă o magnetizație de saturație semnificativ mai mare decât proba P0.

În urma rezultatelor obținute se poate aprecia ca este posibilă realizarea unei tehnici de detecție precum și a unui instrument portabil, la nivelul de sensibilitate cerut pentru a detecta semnale sub 0,1 emu/g, corespunzător unor adaosuri de coloid sub 1%.

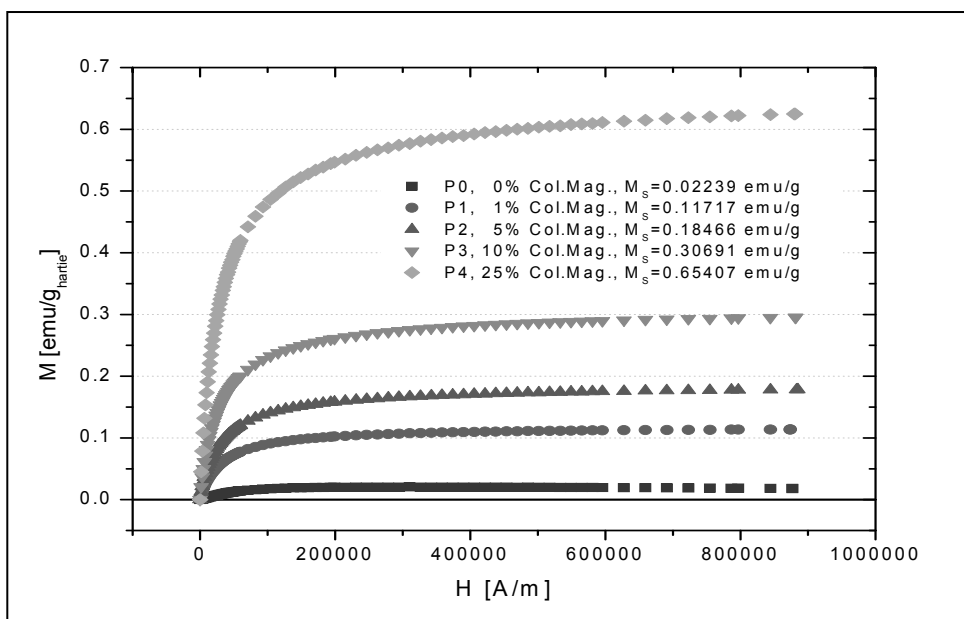


Fig. 2 Curbele de magnetizație masică

Analiza microscopică a foilor de hârtie

Analiza microscopică a foilor de hârtie pentru cele 4 probe analizate au arătat o distribuție

uniformă a nanoparticulelor în structura fibroasă a hârtiei, după cum se poate observa în imaginile de mai jos.(figura 3).

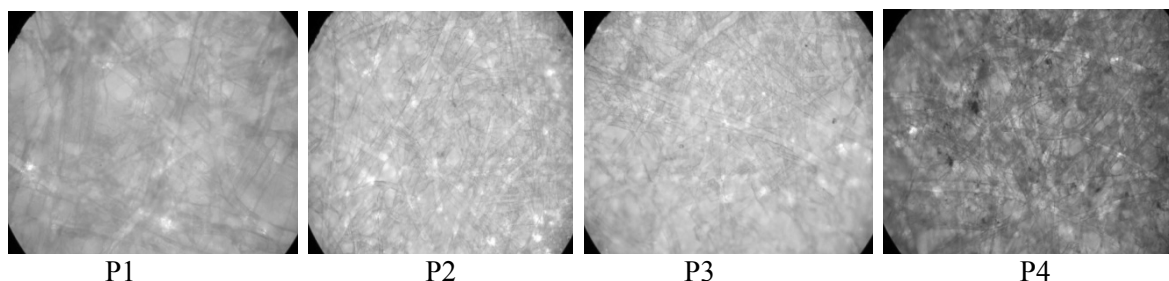


Fig. 3. Structura hârtiilor – imagini la microscop

CONCLUZII

1. Experimentările au demonstrat că nanoparticulele magnetice de magnetită pot fi utilizate ca elemente de securizare a hârtiilor speciale destinate tipării documentelor de valoare.
2. Nanoparticulele nu afectează proprietățile fizico-mecanice ale hârtiei indiferent de adaosul de coloid folosit.
3. Influența negativă asupra gradului de alb poate fi diminuată prin reducerea adaosului de coloid fără a compromite proprietățile de securizare. Curbele de măsurare a magnetismului evidențiază acest lucru.
4. Datorită dimensiunilor nano pot fi utilizate cantități mici de coloizi pentru securizarea hârtiei.
5. Randamentul de retenție bun și distribuția uniformă pe suprafața de hârtie, fac posibilă utilizarea economică a nanoparticulelor.
6. S-a ales dozarea nanoparticulelor din coloid care favorizează formarea de legături chimico-coloidale nanoparticule – fibre celulozice, comparativ cu nanoparticulele din pulberi la care înglobarea nanoparticulelor se face doar prin legături fizice.
7. Prin faptul că nanoparticulele au rezistență chimică, rezistență la temperaturi ridicate și dimensiuni mici sunt greu de a fi imitate/contrafăcute în afara procesului de fabricare a hârtiei.
8. Securizarea hârtiei folosind nanoparticule asigură trasabilitatea produsului, permite identificarea legală și în cazul documentelor arse. Suplețea acestei tehnologii este dată de precizie, fiabilitate, productivitate foarte înaltă și nu în ultimul rând de posibilitatea ridicată de a conduce automatizat procesele de producție.

Această cercetare contribuie la diversificarea sortimentelor de hârtii speciale - grupa hartiilor securizate - prin realizarea unui nou element de securizare a hârtiilor destinate obținerii documentelor de valoare a căror autenticitate se poate verifica în viitor concomitent prin două metode: detecție magnetică și detecție optică - cu ajutorul radiațiilor UV.

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WATERMARKING. A ROLE IN SECURITY IN THE 21ST CENTURY

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Abstract

This paper outlines the origins of Watermarking, the methods of production and applications throughout the evolution of this process and its role as a fundamental security feature in today's marketplace.

Key words: Watermark, Paper making, Security paper, Paper structure

Rezumat

În lucrare sunt prezentate aspecte privind originea filigranului, metodele de obținere, aplicațiile și evoluția întregului process, precum și rolul filigranului ca element de securitate fundamental în producția și piața hârtiilor speciale.

Cuvinte cheie: Filigran, Fabricarea hârtiei, Hârtie securizată, Structura hârtiei

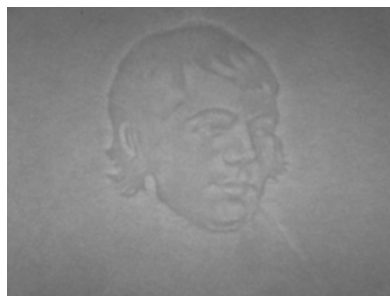
INTRODUCTION

A Watermark in a sheet of paper is not a new invention. It is not an old invention; it is a very old invention.

In Europe it is believed that Watermarks in paper started at Cartiere Miliani Mill in the Italian town of Fabriano circ.1276. At that time all paper was handmade in a wooden framed mould with a metal mesh and the image, made out of wire and placed on the mesh, created a thinner area in the paper which showed up as a light line when the paper was held up to the light.



These Watermarks would have originally been used to differentiate the product of individual master papermakers and a papermaker could be prohibited from using the mark of a different papermaker. As papermaking grew throughout Europe, Paper Mills too would have individual identifying watermarks. The origins of an anti-fraud system.



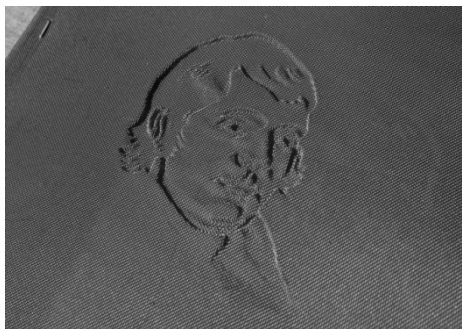
During the Seventeenth and Eighteenth Centuries, British papermakers used certain symbols to designate the paper's intended size. Marks such as the foolscap, hand, post and pott

came into use and over a period of time papermakers began to use these marks to denote particular sized papers. "Royal" sized papers (19x24 inches) were marked with the symbol of a crown. "Post" sized papers (15¼x19 inches) were marked with the image of a horn. "Pott" sized papers (12½x15 inches) were marked with the image of a chalice for examples.

This capability found its way into Government papers and Banknotes and in 1773 the Parliament of England passed a Law in which it was decreed that the death penalty would be levied on anyone found guilty of copying or imitating the watermarks used in the bank-notes of the British Isles. So from the very simple idea of displacing paper fibres, it grew to become a cornerstone of the security of a Nation's currency.

The next major step in the history of watermarks came in the late Eighteenth and early Nineteenth Centuries with the introduction of finer mesh brass screens. The finer mesh allowed more detail to be captured when a shape was pressed into it.

An Englishman by the name of William Henry Smith is often credited with having created the first *light & shade watermark* in 1848. By pressing a shape into the wire mesh screen of the paper mould the wire mesh screen contained a *relief* surface rather than a flat one, the resulting impression of the paper would take on the relief itself and the deepest areas would accumulate more pulp fibers than the thinnest ones.



Those first *light & shade watermarks* were created by carving a relief sculpture into a plate of wax. The papermakers discovered that short fibered pulp produced the best results with a *light & shade watermark*

Mechanisation

With intricate and complicated Watermarks now established, the art of papermaking also developed from Handmade to a more mechanized production. The *Fourdrinier* paper machine was patented on 24 July 1806 by Henry Fourdrinier. It comprised of a moving wire

on a table where the paper stock was poured out onto. The original Fourdrinier paper machine was housed in the Two Waters Paper Mill in Hertfordshire, England.



In 1809 John Dickinson received a patent for the *cylinder* paper machine. The difference between this new type of paper machine and the *Fourdrinier* lay in the way in which the paper was formed. A cylinder, covered with a woven wire fabric, was half immersed in the pulp vat. Inside the cylinder a vacuum was installed so that it would draw the pulp to the surface of the fabric which covered the cylinder.

All three of these paper manufacturing methods, Handmade, Fourdrinier and Cylinder Mould, are still in use today.

Handmade is in the preserve of artists specializing in small, high quality paper where the runs are measured in the number of sheets.

The Cylinder Mould Vat machine method is commonly used for Banknote production and other high value security documents like Passports and ID papers. The machine speeds range from 25mpm up to 130mpm on the most modern machines. Watermarks are put into the cover of the roll, usually around 1.2m diameter, and are in contact with the forming paper for approximately 80% of the circumference of the roll.

Fourdrinier paper making is the most widely used form of paper manufacture with grades from card and board to writing papers and security papers. Machine speeds of 100mpm to 1000mpm are possible and as such offer a commercial advantage over the other methods. A watermark is formed in the paper on a cylinder called a Dandy Roll. This roll runs on top of the forming table where the paper is still around 98% water, and only makes contact for a brief moment.

Watermarks, both line and shadow marks are possible and everything from branded paper, cheque papers and high security papers can be made on Fourdrinier machines.

Watermarking Market

The different styles of Watermarking and different production methods makes this available to the mass market for many applications. Technologies exist to provide a watermarked paper in small enough quantities to be an attractive feature to small businesses looking for Brand awareness, security or prestige. The accurate positioning of watermarks in a sheet of paper can realise a Designers inspirations. Watermark density can be altered to suit a Cheque or Voucher sized paper and designs can be made to fit small sheets like Tax and Excise labels.



Textures can be introduced and prominence in the sheet altered. The variations are numerous and assistance and advice is available to achieve the desired result from Branding to Banknote.

Branded watermarks: Where a Paper Mill or Company have their own branded paper sold to all markets in different layouts, sheet sizes and colours. Conqueror by Antalis is the market leader.

Usually cut to specific sheet sizes, RA2, SRA2 and A4, also envelopes, mostly with a registered electrotype watermark offered as a Wove or Laid paper. Grammage range from 60gsm² to 140gsm².

Sales and Marketing teams required to establish the Brand and sell worldwide, targeting paper Merchants and Printers.

Branded paper in Europe is in decline as less stationary paper is used. Asian markets still use this.

Private Watermarks: where a business has their own company logo or identification in an A4 sheet

for prestige and security. The quantities can range from 250Kg to several tonnes. A wide range of options of layouts and styles of watermark can be required.

Requirement to cut to register or supply paper in reels or webs is common.

Sales and marketing teams targeting paper Merchants and Printers or direct selling to this large market sector.

Motor manufacturers, Insurance Companies, Legal and Accountancy firms and Media groups are the type and size of business that require this.

Security Watermarks: where a watermark is a fundamental security feature. Usually single or multi-toned shadow marks of a specific design either registered as in a passport or certificate or in an all over formation to suit any sheet size like a cheque or bonded paper. This type of paper may also require extra security features such as coloured fibres and planchettes or chemical sensitivity, even metallic threads. Grades such as CBS1 specification or paper with UV dull properties may be required.

The requirement for manufacturers or Merchants to offer secure storage for equipment and paper stock, and the possibility for third party inspections and audits are usual procedures.

Sales and Marketing teams required to sell worldwide, targeting Paper Merchants, Security Printers, Banks and Government Agencies.

Unique Security:

A watermark is part of a papers structure and therefore cannot be replicated at a later date. It adds value to a paper, offering a level of security that any printed process cannot and as such remains as a fundamental security feature demanded by all Treasury's and Banks.

Even in today's computer led High-Tec solutions, which require constant evolution to stay ahead of the fraudsters and hackers, leaving earlier versions still in circulation vulnerable, paper based security documentation still has an important place. UV light, magnetic readers, computer chips, barcode scanners, sensitised inks, and many others, all have a place in the ever more complicated suite of defences required in today's world. Reliant on energy and in dread of a successful computer virus, the Hi-Tec options are exposed to a power cut or a clever bedroom computer geek.

But watermark identification requires no sophisticated software or equipment to verify

authenticity. The most remote border outpost can easily check a watermark to verify a passport. The most inexperienced of bank tellers can verify a banknote. No sophisticated technology or equipment is required, just the simple act of holding the paper up to the light is all it takes.



Woollard & Henry Ltd.

CONCLUSION

The simplest of solutions often turns out to be the easiest to use, the most enduring and one of the best. This is why in the 21st century, a 900 year old technology is still very relevant.

Woollard & Henry Ltd. has been producing Dandy Rolls and watermarks for over 130 years and are now the largest manufacturer in the world. We have an International reputation for quality, expertise and experience that is unmatched. As such we are uniquely placed to offer an overview of the Security Watermarking market and offer advice on any requirement.

A CHANCE FOR ARCHIVE FUTURE: DISINFESTATIONS BY IONIZATION RADIATION TREATMENT - PHYSICO – MECHANICAL TESTS ON THE MATERIALS FROM THE TREATED ARCHIVES

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Abstract

Within the experimental programme were irradiated paper grades naturally aged at different radiation doses. The paper were analysed in order to asses the effect of the Gamma radiations on the physico - mechanical properties that influence the papers' durability. Were realized determinations of the main characteristics that defines the papers' durability: breaking length SR EN ISO 1924- 2:2009, opacity ISO 2471:2008, sizing STAS 4748:1985, whiteness ISO 2470-1:2009, smoothness SR ISO 5627:1995, bursting strength SR EN ISO 2758:2004, tearing resistance SR EN 21974:97 Cobb size test SR EN 20535:96, folding endurance SR ISO 5626:96.

Key words: Paper durability, Ionization radiations, Archive papers, Disinfestation

Rezumat

În cadrul programului experimental au fost iradiate o serie de probe de hârtie îmbătrânite natural, cu doze diferite de radiații Gamma. Mostrele de hârtie au fost apoi analizate în vederea evaluării efectului radiațiilor Gamma asupra caracteristicilor fizico mecanice care influențează durabilitatea hârtiei. Astfel au fost analizate următoarele caracteristici: lungimea de rupere - SR EN ISO 1924-2:2009, opacitatea - ISO 2471:2008, gradul de înclieiere - STAS 4748:1985, gradul de alb - ISO 2470-1:2009, rezistența la plesnire - SR EN ISO 2758:2004, rezistența la sfâșiere - SR EN 21974:97, absorbția apei - SR EN 20535:96, numărul de duble îndoiri - SR ISO 5626:96.

Cuvinte cheie: Durabilitatea hârtiei, Radiații ionizante, Hârtii din arhive, Dezinfecție

INTRODUCTION

The elucidation of the degradation mechanism for several organic and mineral materials within the composition and structure of national patrimony objects with the explanation of the phenomena that take place between the systems involved in the destruction process and their elimination or diminishing represents a fundamental problem of the conservation – restoration activity. The most certain mean to

estimate paper durability is natural ageing obtained by long term preservation. But this method implies a long period of time for observations and evaluation. On this account in order to determine the paper capacity to resist to this process we use artificial methods of accelerated ageing.

Assessment of **paper resistance** to the ageing process, assumes that modifications due to ageing, are to be characterized through determination of some properties, generally strength properties (furnish, grammage, tearing

strength, folding endurance, aqueous extract pH, alkali reserve etc)

A paper resistant to ageing after a period of time **still present's minimum values** of those properties that allow the paper to be used in accordance with its initial purpose

Pulp and paper ageing was studied mainly in the last 100 years. The aim of this study was to identify the degradation mechanism but also to elaborate methods to stop and slow down this process in order to protect the world's cultural heritage. Most of the researches in this field were correlated with the elaboration of new conservation methods. They also lead to the development and application of new analytical instruments. Project's main objective is to study the influence of different doses of Gamma radiations used in order to disinfect the archives on the physico mechanical properties of different paper grades/1/. Within the irradiation process with Gamma radiations the archives will be disinfect without a major effect on the physico mechanical properties of the documents on paper support subjected to this process.

EXPERIMENTAL

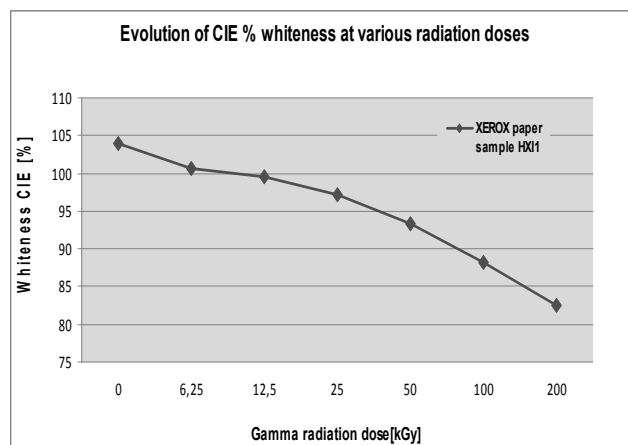
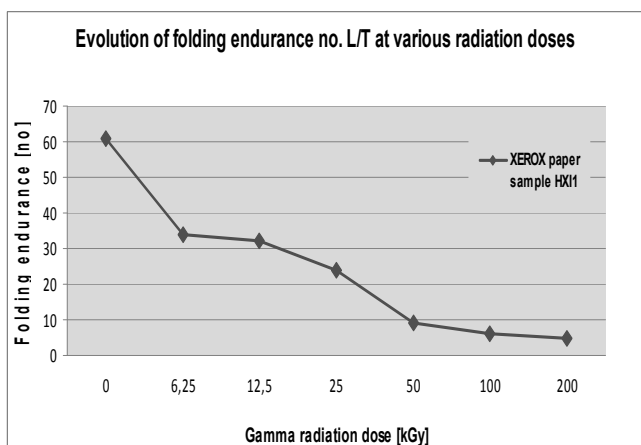
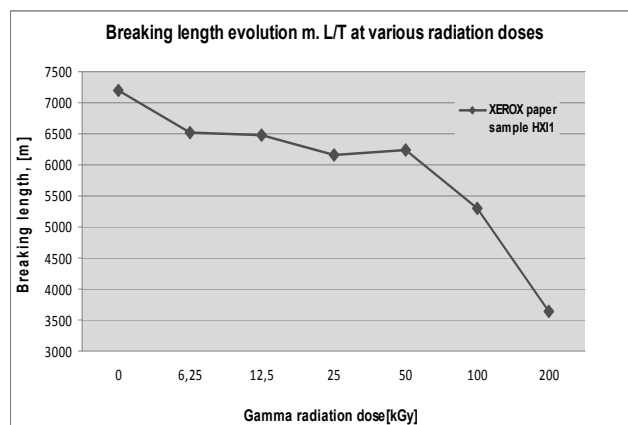
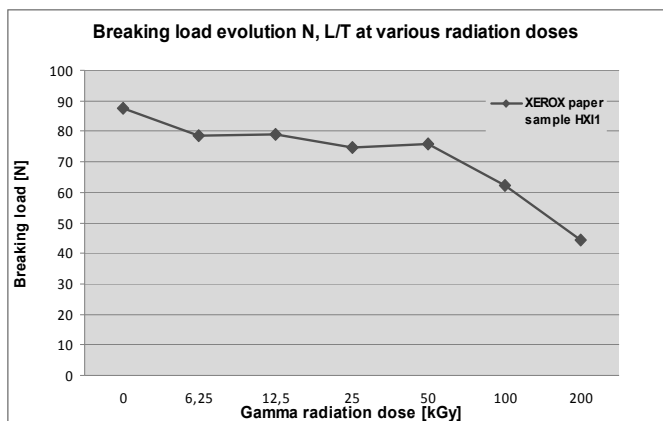
Within the experimental programme SC CEPROHART SA Braila tested the following paper grades/2/:

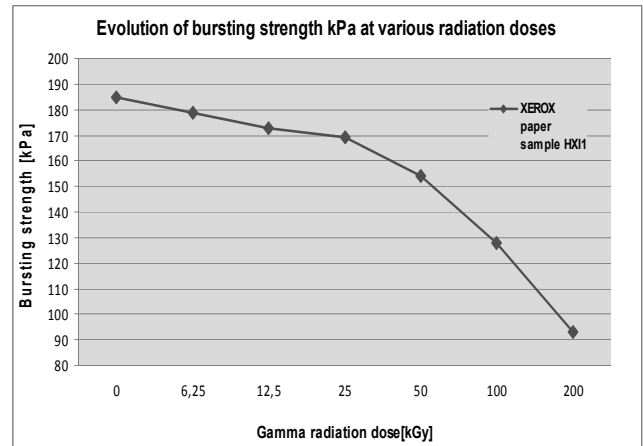
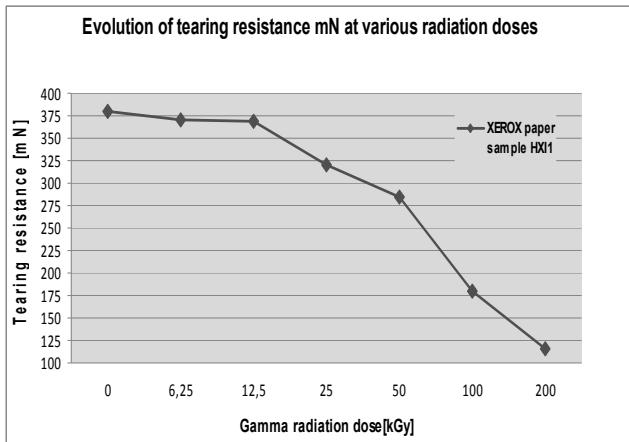
- import copy paper manufactured in July 2009 HXI 1 (0 ÷ 200 kGy);
- import copy paper manufactured in November 2009 HXI 2 (0 ÷ 25 kGy);
- CEPROHART copy paper manufactured in November 2009 HXCPH (0 ÷ 25 kGy);
- naturally aged paper (RSR Official Monitor / 01.08.1968) (0 ÷ 13,7±0,8 kGy);
- Whatman paper manufactured in 2010 ICHR (0 ÷ 13,7±0,8 kGy);
- Business copy paper 80 g/m² manufactured in 2010 (0 ÷ 13,7±0,8 kGy).

The determinations were performed within CEPROHART physico – mechanical laboratory certified according to ISO 17025 by RENAR.

RESULTS AND DISCUSSIONS

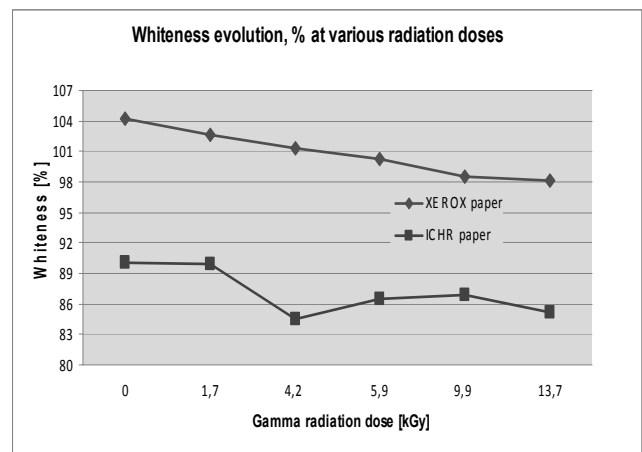
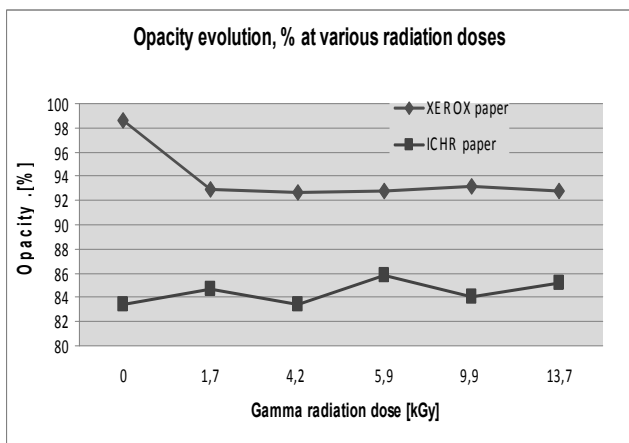
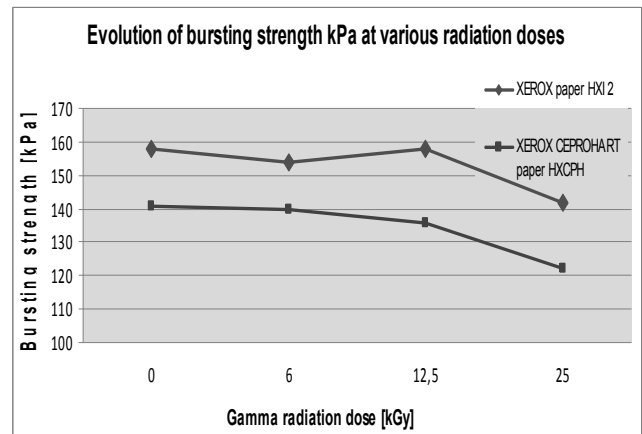
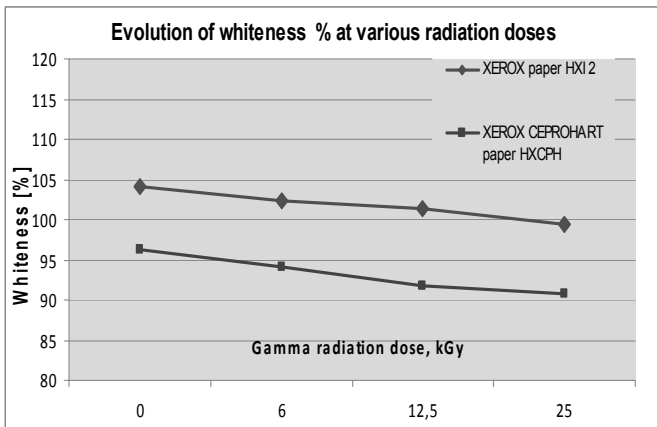
The evolution of the main characteristics for the import copy paper HXI 1 irradiated at Gamma radiation doses of 0 ÷ 200 kGy are illustrated within the following graphs:



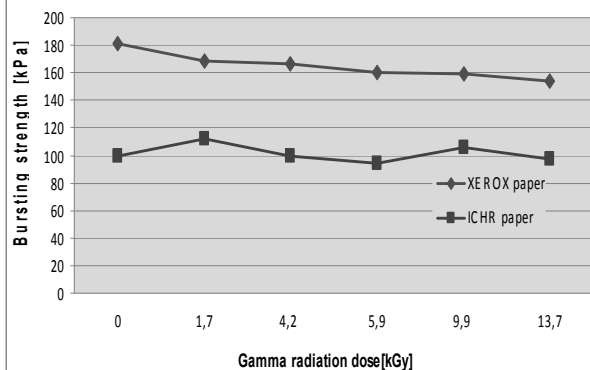


The evolution of the main characteristics for the import copy paper HXI 2 and CEPROHART copy paper manufactured HXCPH irradiated at Gamma

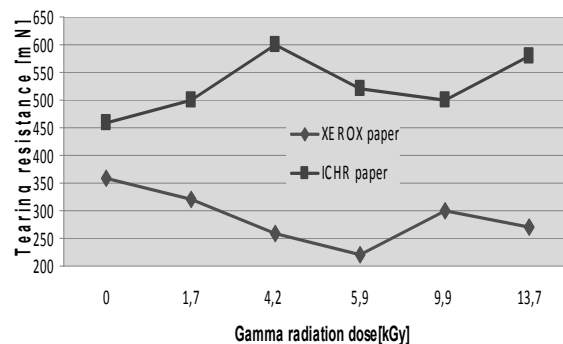
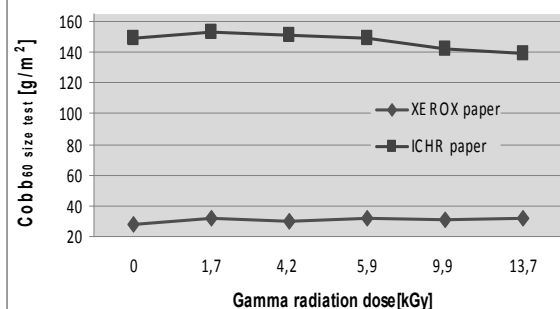
radiation doses of 0 ÷ 25 kGy are illustrated within the following graphs:



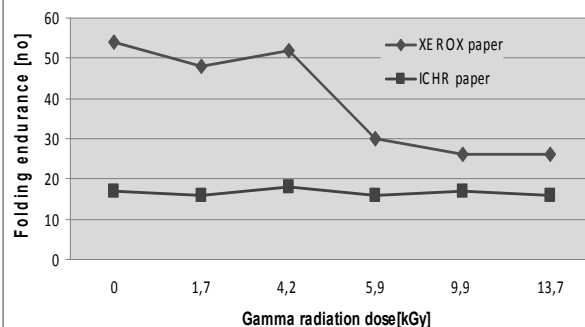
Bursting strength evolution kPa, at various radiation doses



Tearing resistance evolution, mN at various radiation doses

Cobb₆₀ size test evolution g/m² at various radiation doses

Folding endurance evolution, no at various radiation doses



DISCUSSIONS AND CONCLUSIONS

From the analysis of the determined characteristics for each paper grade performed within CEPROHART physico – mechanical laboratory certified according to ISO 17025 by RENAR, we could conclude that:

Import copy paper HXI 1

- The radiation doses of 200 kGy leads to major decreases of the breaking load, breaking length, bursting strength and tearing resistance. The value of the folding endurance collapses affecting irreversibly the physico-mechanical characteristics of the irradiated paper;
- The radiation doses of 200 kGy affects less the optical characteristics of the irradiated paper
- The radiation doses of 25 kGy affects less the physico-mechanical characteristics of the irradiated paper with an exception: the folding endurance that diminishes with 60% comparatively with the initial value

- The radiation doses of 200 kGy do not affects in a significant proportion the optical characteristics of the irradiated paper
- The radiation doses of 12,5 kGy have minor effects on the physico-mechanical characteristics of the irradiated paper with an exception: the folding endurance that diminishes with 47,5% comparatively with the initial value;
- The radiation doses of 12,5 kGy have negligible effects on the optical characteristics of the irradiated paper. The whiteness diminishes only with 4,2% comparatively with the initial value and document's readability is not affected;
- The radiation doses of 6,25 kGy have minor effects on the physico-mechanical characteristics of the irradiated paper, even negligible for the bursting strength and tearing resistance. The influence on the folding endurance remains significant (44%);
- The radiation doses of 6,25 kGy have negligible effects on the optical characteristics

of the irradiated paper. The whiteness diminishes only with 3.13% comparatively with the initial value and document's readability is not affected;

- In the further tests will be correlated the radiation doses with the contamination degree of the documents in order to mitigate the negative effect on the initial values of the paper's physico-mechanical characteristics.

Import copy paper HXI 2

- The most affected are the physico-mechanical characteristics of the paper irradiated with Gamma radiations
- The doses of 25 kGy comparatively with higher doses of gamma radiation are less destructive. The breaking length, breaking load, tearing resistance, bursting strength decrease significantly (10,1 ÷ 23,9 %) and the folding endurance decrease drastically (62,5% in comparison with the initial value).
- The doses of 25 kGy Gamma radiations affects in a small measure the optical characteristics of the irradiated paper (whiteness decrease with 4,6%)
- The effects of the 12,5 kGy Gamma radiations doses are negligible on the optical characteristics (whiteness decrease only with 2.7%)
- The doses of 6,25 kGy Gamma radiations have a diminished effect on the physico-mechanical characteristics of the papers. The bursting strength decrease only with 1.4% and the tearing resistance with 3.6%, but the influence on the folding endurance is significant (34%).
- The effects of the 6,25 kGy Gamma radiations doses are negligible on the optical characteristics (whiteness decrease only with 1,76%)
- In the further test we will correlate the radiation doses with the contamination degree of the documents in order to mitigate the negative effect on the initial values of the paper's physico-mechanical characteristics.

CEPROHART copy paper HXCPH

- The most affected are the physico-mechanical characteristics of the papers irradiated with Gamma radiations
- The doses of 25 kGy comparatively with higher doses of gamma radiation are less destructive. The breaking length, breaking load, tearing resistance, bursting strength decrease significantly (11,3 ÷ 22,9 %) and the folding

endurance decrease significantly with 33.3% in comparison with the initial value.

- The dose of 25 kGy Gamma radiations affects in a very small degree the optical characteristics of the irradiated paper (whiteness decrease with 5.5%)
- The doses of 12,5 kGy have significant effects only on the folding endurance (the decrease is of 23.8% comparatively with the initial value) while the tearing resistance decrease with 20.5%
- The effects of the 12,5 kGy Gamma radiations doses are negligible on the optical characteristics (whiteness decrease only with 4.7 %). The whiteness of the CEPROHART paper decrease more because comprise a higher percent of cellulose fibres
- The Gamma radiation doses have a small effect on the physico-mechanical characteristics even negligible for the bursting strength (1,4%), but with a significant influence on the folding endurance (a decrease with 19%).
- The effects of the 6,25 kGy Gamma radiations doses are negligible on the optical characteristics
- In the further tests we will correlate the radiation doses with the contamination degree of the documents in order to mitigate the negative effect on the initial values of the paper's physico-mechanical characteristics.

Business copy paper 80 g/m² XEROX paper

- The radiation doses had either a positive effect on the breaking length with a small increase of the value (only at 1,7 kGy and 4,2 kGy) either a small decrease of the value at other radiation doses used within the experiments
- At all the used radiation doses the opacity decreased comparatively with the initial value (5,52÷5,95%)
- The most affected characteristics by the ageing and irradiation processes are the mechanical characteristics and not the optical ones
- The whiteness decreasing for all the radiation doses is a minor phenomenon (1,5 ÷ 5,8 %) and could be controlled taking into account the contamination degree of the documents
- The bursting resistance decrease constantly in the range 6,6 ÷ 14,9% reasonable to assure a good durability
- At all used radiation doses the Cobb size test increased gradually in a range of 5,7 ÷ 15,35% illustrating a negative influence

- The decrease of the folding endurance is situated in a wide range of values respectively $3,7 \div 51,9\%$ allowing us to analyze carefully the used radiation dose and to correlate it with the contamination degree and the composition of the document

Whatman ICHR paper

- The used radiation doses had a positive effect on the breaking length leading to increases within the range $2,4 \div 11,5\%$
- At all the used radiation doses the opacity increased comparatively with the initial value within the range $0,04 \div 2,9\%$ confirming us the different behavior of the cotton cellulosic fibers comparatively with the paper complex
- The phenomenon of whiteness decreasing is registered for all the used radiation doses but is minor ($0,5 \div 6,2\%$) and could be controlled taking into account the contamination degree of the documents
- The tearing resistance increase for all the radiation doses ($7,7 \div 30,4\%$) and could be a positive signal for the behavior of the papers with cotton cellulose fibers in composition irradiated with Gamma radiations
- The evolution of the Cobb size test was random the values registering an increase at some radiation doses and a decrease for others. The increases and decreases of the initial value could not be correlated with the radiation doses without a replica of the experiments in order to verify their consistency
- The values of the folding endurance are situated in a small range allowing us to conclude that the radiation effect is not harmful on cotton cellulose fibres. We could run some tests radiation doses $> 13,7$ kGy in order to simulate the utilization of Gamma radiation for documents with high contamination degree.
- We will run some experiments at higher radiation doses trying to simulate the effect of

the radiations on paper support documents with a superior contamination degree

In the future, in order to have a complete image of the phenomenon, we must run some additional test consisting of:

- analyze and establish the optimal doses of radiations that must be used in order to disinfect the documents on paper support and, in the same time, preserving their physico-mechanical properties;
- a preliminary assessment of the homogeneity of the physico-mechanical properties of the irradiated documents aiming to make a relevant interpretation of the obtained results;
- a correlation between the papers' composition, the document's age, the contamination degree, the sizing technique, the storage conditions, the values of the physico-mechanical characteristics of the documents prior the irradiation process at the selected Gamma radiation doses
- irradiations performed on artificially aged documents in different humidity, temperature or other exogenous factors conditions in order to realize a complete data base that could be used as guide for further decontamination processes performed on infested archives.

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SR EN ISO 50001:2011 – SISTEM DE MANAGEMENT AL ENERGIEI – O NOUĂ PROVOCARE PENTRU ORGANIZAȚII

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Rezumat

Managementul energiei, implementat integrat într-o organizație, alături de managementul calității, mediului, sănătății și securității ocupaționale și alte sisteme, întregeste managementul calității totale al organizației. Principalele obiective ale managementului energiei sunt asigurarea consumurilor optime și utilizarea eficientă a energiei, pentru maximizarea profitului prin minimizarea costurilor energetice. Reprezintă astfel o nouă modalitate de a crește competitivitatea organizației pe piață.

Implementarea sistemului de management al energiei în conformitate cu cerințele standardului de referință SR EN ISO 50001:2011 poate fi o provocare pentru toate organizațiile, dar va fi mai la îndemână organizațiilor care deja au implementat un sistem de management de mediu, prin asemănarea celor două standarde de referință.

Cuvinte cheie: *Managementul energiei, Managementul calității, Managementul mediului, Competitivitate*

Abstract

Energy management, fully implemented in an organization, with quality management, environment, occupational health and safety and other systems, completes the total quality management of the organization. The main objectives of energy management are to ensure optimal and efficient consumption of energy to maximize profits by minimizing energy costs. Thus represents a new way to increase competitiveness on the market organization.

Implementation of energy management system in accordance with standard requirements of SR EN ISO 51001:2011 can be a challenge for all organizations, but will be on hand to organizations that have already implemented an environmental management system, due to the similarity of the two standards.

Key words: *Energy management, Quality management, Environmental management, Competivity*

INTRODUCERE

Strategia Lisabona - Strategia Europeană pentru dezvoltarea durabilă a inclus ca priorități actuale :

- Schimbările climatice
- Lupta împotriva încălzirii globale
- Conservarea biodiversității
- Reducerea problemelor de sănătate cauzate de poluare
- Utilizarea mai responsabilă a resurselor naturale

Politica energetică a UE și Politica de mediu țin seama de faptul că reducerea impactului asupra mediului a producerii și utilizării energiei poate conduce spre promovarea economisirii energiei și eficienței energetice, precum și a creșterii ponderii producției și utilizării de energii curate.

Obiectivele și țintele UE pentru energie-schimbări climatice – 2020 sunt:

- **obiectiv strategic al politicii energetice europene** - reducerea emisiilor de gaze cu efect de seră (GES) cu 20% față de anul 2005.
- **obiective conexe:**
 - creșterea ponderii surselor regenerabile de energie (SRE) în totalul mixului primar energetic la 20%,
 - reducerea consumului final prin creșterea eficienței energetice cu 20%,
 - creșterea ponderii biocarburanților în transporturi la 10% (biocombustibili, electricitate sau hidrogen).

Obiectivele mai sunt cunoscute ca așa-numitul **pachet 20-20-20**.

Strategia energetică a României pentru perioada 2007-2020 se aliniază Directivei 2006/32/CE privind eficiența energetică la utilizatorii finali, care prevede reducerea consumului de energie finală cu cel puțin 9% într-o perioadă de 9 ani (2008-2016), comparativ cu media consumului din ultimii 5 ani pentru care există date disponibile (2001-2005).

Potentialul național de economisire de energie, respectiv de reducere a pierderilor energetice, este apreciat la 27 – 35 % din resursele energetice primare (exprimat ca procent din consum) astfel:

- industrie 20 - 25%,
- clădiri 40 - 50%,
- transporturi 35 - 40%

Ce este SR EN ISO 50001:2011 ?

Standardul SR EN ISO 50001:2011 - Sisteme de management al energiei. Cerințe și ghid de utilizare este un Ghid în stabilirea proceselor necesare pentru îmbunătățirea performanței energetice.

Standardul se adresează oricărei organizații care dorește să-și dezvolte și să-și implementeze o politică energetică și obiective energetice, care să ia în considerare informațiile și cerințele legale referitoare la utilizarea semnificativă a energiei.

Sistem de Management de Mediu /Sistem de Management al Energiei

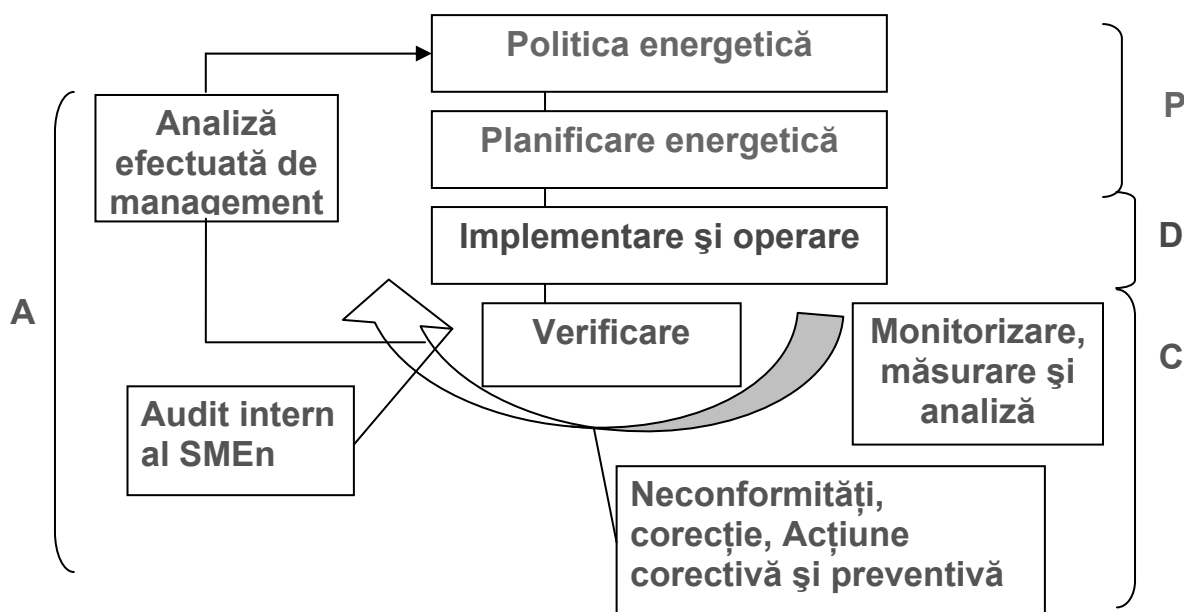
Cele două sisteme de management au și asemănări, dar și deosebiri.

Principalele asemănări:

- Abordare PDCA
- Definirea cerințelor standardelor de referință
- Etape de implementare similare

Diferențele dintre sisteme:

- Vizează sectoarele utilizatoare de energie și cu posibilitățile de îmbunătățire substanțială a indicatorilor de performanță energetică
- Utilizarea valorilor măsurate pentru consumurile de energie



Abordare PDCA

Etapele de implementare a sistemului de management al energiei sunt:

- Analiza energetică inițială pentru a stabili zonele cu utilizări ale energiei, consumuri de energie semnificative și pentru identificarea oportunităților de îmbunătățire a performanței energetice
- Analiza și actualizarea documentației necesare pentru integrarea sistemului de management al energiei în sistemul existent,
- Instruire personal pentru implementarea noilor cerințe ale standardului de management al energiei și documentelor interne nou elaborate/ revizuite,
- Auditarea internă a sistemului de management al energiei,
- Analiza de către top management a funcționării sistemului de management al energiei și stabilirea de decizii de îmbunătățire.

Planificarea energetică vizează:

- analiza utilizărilor energiei și a consumului de energie, identificare zone cu utilizări ale energiei și consumuri de energie semnificative pentru stabilirea nivelului de referință a energiei
- identificare oportunități de îmbunătățire a performanței energetice
- Stabilirea de obiective, ținte și planuri de acțiune pentru îmbunătățirea performanțelor energetice.

Elementele de ieșire ale planificării energetice sunt:

- Nivelul de referință al energiei
- Indicatori de performanță energetică
- Stabilirea obiectivelor și țintelor sale energetice și modului de definire și implementare a sistemului – funcție de puterea economică a organizației
- Stabilirea planurilor de acțiune pentru atingerea obiectivelor și țintelor
- Definirea și documentarea modului de îndeplinire a cerințelor standardului
- Îmbunătățirea continuă a performanței energetice - determină reducerea costurilor și a emisiilor de bioxid de carbon.

Obiective, ținte, programe de acțiune utilizând nivelul de performanță identificat prin analizele energetice.

Pot fi utilizați ca indicatori globali, relevanți pentru energie:

- Eficiență energetică – raportul dintre rezultatele activităților unei organizații, bunuri sau servicii și energia utilizată pentru acest efect
- Intensitatea energetică – consum energetic intern brut / produs intern brut (tone combustibil convențional/\$ sau kW/\$)

Indicatori relevanți pentru mediu:

- Emisiile în mediu – aer, apă, sol, deșeuri....
- Consumuri de resurse – energie, materii prime....

Indicator comun: **emisiile de gaze cu efect de seră.**

În continuare sunt prezentate câteva exemple de măsuri de îmbunătățire a performanței energetice și eficienței energetice care pot fi implementate în organizații din domeniul de fabricare a celulozei și hârtiei:

- Pentru energia termică - abur:

- Reducerea cantității de solide totale dizolvate în apa de cazan care permite funcționarea cazanului fără opriri datorate depunerilor, deci și reducerea pierderilor de energie
- Optimizarea funcționării ventilelor de dezaerare – se reduc pierderile.
- Optimizarea sistemelor de distribuție și izolarea traseelor de conducte de abur / condens recirculat.
- Recuperarea și recircularea condensului are ca efect reducerea pierderilor de energie, consumului de apă de adaos dar și a cantității de chimicale utilizate.

- Pentru energia electrică:

- creșterea factorului de putere corespunzător cerințelor locale de consum a distribuitorului de electricitate și tehnici de corectare a factorului de putere
- înlocuirea motoarelor cu motoare cu eficiență energetică ridicată
- funcționarea echipamentelor cu un consum de energie corespunzător (randament motor)
- asigurarea de cabluri electrice cu dimensiuni corespunzătoare consumului
- funcționarea transformatoarelor la încărcare de min. 40 – 50 %
- amplasarea echipamentelor consumatoare mari de energie cât mai aproape de sursa de putere.

Tabel 1 Exemple de măsuri BAT pentru industria de hârtie

Tehnologii de eficiență energetică	Tipul de energie și cantitatea necesară	% de economie de energie și cantitatea	Observații
Pastă de consistență ridicată	Energie electrică pentru pompe și rotoare, 60 kWh/t	33%, 20 kWh/t	Optimizarea proiectării rotorului
Rafinarea pasteii	Energie electrică pentru acționare motoare, 100-500 kWh/t	20%, 80 kWh/t	Depinde de sortimentul de hârtie fabricat
Formarea la consistență ridicată	Energie electrică, 200 kWh/t	20%, 40 kWh/t	Se aplică la hârtiile din maculatură
Optimizarea sistemului de vacuum	Energia electrică	25%	
Recuperarea aerului cald exhaustat de la partea uscătoare a mașinii de hârtie	Energie termică	10%	Utilizarea schimbatoarelor de caldura aer-aer sau aer – apă
Utilizarea ventilatoarelor de aer, cu arderea directă a gazelor	Energie termică	40%	În principal utilizată la hota mașinii de hârtie tissue

CONCLUZII

Toate companiile industriale pot economisi energie, prin aplicarea principiilor unui bun management și prin aceleași tehnici pe care le utilizează pentru calitate, pentru mediu sau sănătatea și siguranța ocupațională. Aceste practici de management includ responsabilitatea deplină a managementului pentru consumul de energie. Reducerea consumurilor energetice nu înseamnă numai economii financiare ci și reducerea poluării mediului.

Angajamentul top managementului este condiția prealabilă pentru gestionarea cu succes a performanței energetice și indicatorilor de eficiență energetică.

Este dificil să se determine cu exactitate costurile și beneficiile economice aduse de implementarea unui sistem de management al energiei, dar nu trebuie să uităm că economiile nete contribuie direct la creșterea profitului organizației.

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**PROGRAMUL COST –
COOPERARE EUROPEANĂ
PENTRU ȘTIINȚĂ ȘI TEHNOLOGIE**

**COST ACTION FP0901, 2009-2013
ANALYTICAL TECHNIQUES FOR BIOREFINERIES**

www.abo.fi/costfp0901, www.cost.esf.org

Chair of the Action:

Prof. Stefan Willfor, FI, swillfor@abo.fi

COST Science Officer:

Melae Langbein, mlangbein@cost.esf.org

Participating countries: Austria, Belgium, Bulgaria, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Netherlands, Norway, Poland Portugal, Romania, Serbia, Slovak Republic, Slovenia, Spain, Sweden, Switzerland, Turkey, United Kingdom, Brazil, New Zealand, USA, (South Africa).

Strategy:

- Create an interdisciplinary platform for interaction between scientists
- Apply and evaluate methods from other research areas
- Intensify the cooperation between industry and Academia
- Develop and evaluate standardized, rapid, non-destructive on-line methods for the industry
- Stimulate the use of statistical methods
- Identify the need for new ERA-NET or ERA-NET Plus Actions

Working groups:

Working Group 1- Biorefinery feed material sampling and characterization

WG1 Leader: Callum Hill, UK, c.hill@napier.ac.uk

The feed material in Biorefineries covers a wide range from forest to agro-industry; from fresh plants to industrial waste or recycled fibres. Pretreatments, isolation methods, and sample representativeness are important. The isolation and analysis of specific compounds are critical steps to understand their chemistry. Determination of molar mass, polymer structure, physico-chemical properties, and the molecular building blocks are analytical challenges.

Working Group 2- Characterization of processed biochemicals and biomaterials

WG 2 Leader: Claudia Crestini, IT, crestini@stc.uniroma2.it

The sampling methods and pretreatments used in the Biorefinery process and for the products may differ significantly from those used for the feed material. An increasing amount of analysis data is needed directly from the processes which call for analytical on-line applications, hyphenated techniques, and statistical multicomponent analyses to sort the relevant data from the main data stream.

Working Group 3- Characterization and fate of process residues

WG 3 Leader: Elisabeth Sjöholm, SE, elisabeth.sjoholm@innventia.com

The ultimate aim of a Biorefinery is to utilize 100% of the feed material! This is yet difficult to achieve and calls for an understanding of the chemistry of the process residues. When residues are used for bioenergy, a thorough characterization is needed, to avoid problems of corrosion, fouling and low performance.

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PhD theses abstracts**EXTRACTION, SEPARATION AND
CHARACTERIZATION OF NATURAL BIOACTIVE
POLYPHENOLS FROM DIFFERENT RAW MATERIALS**

Candidate: Ioana Ignat

PhD thesis supervisors:

Prof. Valentin I. Popa, "Gheorghe Asachi" Technical University of Iasi, Romania

Prof. Patrick Martin, Université d'Artois, IUT Béthune, France

In the context of biorefinery and complex valorification of raw biomass the main objective of this thesis is the extraction, isolation and characterization of natural polyphenols from different raw materials. Known for their health benefits and the high antioxidant activity, these compounds have been extensively studied and are still an active area of research. The first part of this work is dedicated to an extensive bibliographic study concerning the classification of polyphenols, natural sources of bioactive compounds and different analytical techniques widely used for the extraction, separation and characterization of phenolics, all these aspects leading to the establishment of the research objectives and activities.

The second part presents the experimental results and the original contributions in this field. Four different vegetal materials were used in this study. *Asclepias syriaca* and *Crataegus monogyna* are two different plant species both being

known for the complex chemical composition and potential health benefits. The other two materials are represented by grape seeds and spruce bark because a special attention is focused on the extraction from inexpensive or residual sources from agricultural industries and it is well known that by-products, remaining after industrial processes, still contain high amounts of phenolic compounds. The raw material was first degreased using hexane as solvent and the lipophilic fraction obtained was analysed by GC-MS in order to establish the main fatty acids. The extraction of phenolic compounds (Soxhlet) was carried out on the defatted samples using ethanol, methanol and water as extraction agents. Supercritical fluids extraction was also used for the recovery of natural polyphenols from the vegetal samples. The vegetal residue resulted after the solvents extraction was subjected to an alkaline hydrolysis in order to liberate the compounds that exist as insoluble bound

complexes, which are coupled to cell wall polymers through ester and glycosidic links and are not extractable by organic solvents. A first step in the characterization of the polyphenolic extracts was the determination of different classes of phenolic compounds using colorimetric methods. Thereby the total phenolic content, total tannins, flavonoids and flavonols content and also anthocyanins content were determined. FTIR and NMR (^1H -NMR, ^{31}P -NMR) spectroscopy were used as additional tools to screen vegetal samples for their content of phenolic compounds. The spectras of the samples were obtained and the effective peaks and the functional groups were compared with those of the standards and according to literature. Furthermore, the ^{31}P -NMR technique allowed both the quantitative and the qualitative characterization of all labile OH groups present in polyphenols structure and provided valuable information on the polymerization degree. Identification and quantification of individual phenolic compounds from the extracts was achieved using HPLC and GC-MS. The concentrations of phenolics identified in the vegetal samples were

calculated according to the calibration curves for the standard compounds (hydroxycinnamic acids, hydroxybenzoic acids, flavanols and flavonoids).

The last part of this thesis involves the approach of different experiments concerning the stability and properties of polyphenols. Even though phenolic compounds are known to be highly instable and very susceptible to degradation so far the aspects regarding their stability and degradation in various conditions has not been studied. So, taking into account the potential use of bioactive compounds in food industry the evaluation of the degradation of standard phenolic compounds and vegetal extracts under high temperature and UV irradiation was studied. The stability under UV irradiation was evaluated also in the presence of some usual additives (NaCl, citric acid, ascorbic acid, sodium nitrate) often used in industry. On the other hand, the antioxidant and antibacterial properties of the natural polyphenolic extracts were determined along with the application of vegetal extracts in biological systems as plant growth modulators.

**CONTRIBUTIONS REGARDING THE ROLE OF
POLYPHENOLIC COMPOUNDS ON PHYSIOLOGICAL
PROCEESS FROM PLANT IN DIFFERENT STRESS
CONDITIONS**

Candidate: Alina Petronela STINGU, Chem. Eng

Supervisors:

Prof. Valentin I. POPA, "Gheorghe Asachi" Technical University of Iasi, Romania
Prof. Patrick Martin, Université d'Artois, IUT Béthune, France

The main objective of this Ph.D. thesis was the evaluation of the morpho-physiological responses of plants in the presence of different natural bioactive compounds and heavy metal ions excess. It was evaluated the possibilities of using natural bioactive compounds, obtained from different raw materials (spruce bark, chestnuts shell, grape seeds and *Asclepias syriaca* plant), as natural plant growth regulators, plant development, natural amendment in phytoremediation process, respectively. First of all it was realized a preliminary study to analyze the influence of polyphenolic compounds in combination with different concentrations of copper/ cadmium ions on different plant species (oat, bean, rape, tomatoes, spinach, radish, maize) growth and development, bioaccumulation capacity and translocation of heavy metals. Maize plant (*Zea mays*) was chosen for the following stage of the experimental procedure because maize plant represents an important nutritional plant, which can easily transport heavy metal ions to the superior trophic level.

At the same time, maize plant presents higher heavy metal bioaccumulation capacity, being suitable for phytoremediation / phytoattenuation process with multiple direction for an efficiently valorization. Germination test and vegetative pots experiments of maize plant were performed in a heavy metal contaminated growth medium supplemented with different polyphenolic aqueous extracts obtained from spruce bark, chestnuts shell, grape seeds and *Asclepias syriaca* plant. The evaluation of germination capacity, vegetative plants elongation, vegetal biomass accumulation, assimilatory pigments concentrations (chlorophyll a+b, carotene) was carried out in the presence of three different concentrations of natural polyphenolic extracts and the main characteristic phenolic compounds of those extracts (catechine, ferulic acid, gallic acid, vanillic acid, p-coumaric acid, cinnamic acid) identified using HPLC technique. The results shown that the polyphenolic extracts, characterized by different phenolic compounds, act as a natural regulators on

maize plants growth and development, depending the nature and the concentrations of the tested extract. The identification of the phenolic characteristics compounds of the natural polyphenolic extracts allow to initiate a comparative study between those on the effects registered on maize plant growth and development, pigments assimilation, heavy metal (copper/ cadmium) bioaccumulation and recovery capacity. Those parameters were followed in the case of aqueous extract growth medium addition comparing with the case when the contaminated environment was supplemented with four different concentrations (1, 10, 50, 100 μM) of phenolic compounds (catechine, gallic acid, vanillic acid, p-coumaric acid). The influence of polyphenolic compounds/ heavy metals on metabolic process, associated to germination and post-germination process was studied by quantification of the activity of the most important enzyme (POD, SOD, CAT) responsible for oxidative stress reduction. Anatomic cross section, FTIR and SEM-EDX analysis for roots and primary leaves of maize plants were also used to evaluate the influence of spruce bark and grape seeds extract, comparing with catechine, vanillic, gallic and p-coumaric acid (100 μM) on maize plant responses to copper excess (100 μg Cu (II)/ g sandy soil). It could be concluded that the polyphenolic compounds which supplemented the contaminated soils with copper ions, have had an important role in improving plant protection system and

allowed a normal growth and development of the maize plant. Polyphenolic compounds actively participate in plant metabolic process, promoting the intensification of the principal enzymes activity which are responsible for plant protection under oxidative stress, generated by heavy metals ions. The presence of spruce bark and grape seeds extracts in the growth medium induced similar effects on maize plant growth and development as those registered in the presence of catechine and gallic acid. The most important stimulation effects on plant growth and development in a copper contaminated environment were observed in the presence of polyphenolic extracts, catechine and gallic acid. Histo-anatomical section realized for the roots and primary leaves of maize plant underline the significant role of polyphenolic compounds (catechine, gallic acid, aqueous extracts) in improving plant structure grown under heavy metal stress conditions. Polyphenolic compounds modulated the heavy metal bioaccumulation capacity of maize plant. Spruce bark and grape seeds polyphenolic extracts, catechine and gallic acid reduced the bioaccumulation capacity with 0-50% comparing with the results obtained in the presence of copper ions, meanwhile the vanillic acid promoted and improved the copper bioaccumulation capacity. The reduction of bioaccumulation capacity allowed concluding that the polyphenolic compounds are implicated in complexation process, blocking the metal ions

in the rootlets area of the plant, protecting the plant from the noxious effects of heavy metals. The recovery of metal ions by maize plant was improved with 0-50% in the presence of catechine, gallic and vanillic acids, with 50-100% in the presence of grape seeds extracts but reduced with 0-50% when the contaminated growth medium was supplemented with spruce bark aqueous extract. Experimental results and specific analysis techniques (atomic absorption spectrometry, FTIR, SEM-EDX, anatomic cross section) confirmed the modulator effects

of polyphenolic compounds on the growth and development process of maize plant in different stress conditions. The presence of polyphenolic compounds in a heavy metal polluted environment modified also the bioaccumulation capacity, the possibilities of metal ions to be recovered and the translocation of the heavy metals to the aerial parts of the plant, depending on the nature of the extract, the concentration of the specific polyphenolic compounds and on metal stress conditions.

INFRASTRUCTURE DEVELOPMENT OF QUALITY CONTROL FOR ENVIRONMENTAL FACTORS LABORATORY FOR THE ESTIMATION, CHARACTERIZATION AND RECOVERY OF RENEWABLE AND RECYCLED RESOURCES, THROUGH CHEMICAL AND BIOCHEMICAL PROCESSES

Acronym: MEDRES LAB
Research Grant no. 94 /2007 (PNCDI II)

This project aims at infrastructure development and capacity extension of a laboratory for the analysis and control performed in the field of environmental factors, being the first regional laboratory specialized in the characterization of the renewable resources to be processed by chemical and biotechnological processes.

The data provided by the Romanian Accreditation Association (www.renar.ro) evidence a deficiency existing at national level concerning a specialized laboratory equipped for complex characterization of such types of resources, to assuring their processing in the context of environmental protection. This project has two major objectives:

- **Modernization** of the Environmental Quality Control Laboratory, within the Chemical Engineering Faculty, already renown, in only 8 years of activity, for the numerous partnerships established with different universities, industry, research institutes and non-governmental organizations. Using all its available tools, the laboratory assures the logistics for the quality control of all environmental components (water, air, soil), as well as information and education for specialized staff.

- **Development** of new procedures to evaluate renewable and recycled resources. The application of new directions follows the current researches, the industrial requirements as well as the actual European trends. Currently, the renewable and recycled resources are used as raw material for chemical and energetic supplies, and the tendency is to substitute conventional materials. Based on such information, recycling of secondary products might meet the sustainable development conditions, thus becoming the centre of a close functional environmentally-compatible system. At the same time, such a laboratory will make use of

the present knowledge for upgrading by-products and for developing new methods for processing different resources or some special raw materials to obtain biopolymers, biofuels, proteins and

- natural bioactive compounds. Preservation of the environment will be assured by special recycling processes, closing the circuits and obtaining products which are designed based on life cycle analysis. All these problems will open new possibilities to develop fruitful cooperation relationships with industrial partners and research institutes, thus creating the necessary premises to approach competitive projects in different domains and for technological transfers, as well.

The laboratory endowments will concern the equipments acquisition which are needed for extending the available services and will contribute to the testing and certification of some special compounds obtained by application of biotechnological processes. The project will carry on **four stages**: *equipment acquisition*, materials, soft and computing technologies, applicative and pre-competitive (testing, verifications, measurements, analysis) *research activities*, *dissemination* and *project management activities*. It will also accomplish training activities, audit and certification of laboratory according to ISO 17025 and initiation of RENAR accreditation action.

The general objective of the project is represented by **the development of an equipments base for research in the field of sustainable and incorporated management of renewable resources**.

The specific objectives are:

- **Development of the existing infrastructure** of the Environmental Factors Quality Controls Regional Laboratory, by acquisition of performance

equipments for the development of public-private partnerships in the region.

- **Accomplishment of a equipments base** assuring new directions of research for renewable and recycled resources, using the existing structure.
- **Development of research capacities** employed as work packages or European programs (such as FP 7) coordinators.
- **Disseminations of relevant results** at the level of national and international scientific communities, governmental organizations specialized in renewable resources management (Agriculture and Forestry Departments, Environment Protection Agencies, local and regional authorities) and civil society.

Implementation of the MEDRES laboratory will lead to the following **estimated results**:

- Development of RDI activities and approach of new domains/sub-domains of scientific research, according to the European trends in renewable and recycled resources.
- Higher quality and diversification of the educational process, modernization of faculty laboratories for the master and PhD students.
- Extended involvement of Romanian researches in European programs RDI (such as the partnership proposal in FP 7)
- New research services at industrial level, especially for measurements, testing, trials and certifications.

As the **stipulated benefits**, based on the present tendencies and on the experience acquired by the research staff, it is highly possible that new opportunities to be developed for resources diversification and enlarged treatment possibilities, through biorefinery technologies. In this way, the renewable and recycled resources will be used for obtaining chemical products and with energetic value. In the North East development area of Romania, such activities will be **correlated with future programs**, following a better utilization of the existing agricultural areas and extension of the forestry zone necessary for providing additional renewable resources. The "Gheorghe Asachi" Technical University of Iasi will play an important role in the SUSTENPOL

INNOVATION (SUSTINOV) excellence centre which will be created in Piatra Neamt, aimed at promoting the concept of sustainable development. Apart from the excellence centre, the laboratory designed by this project will **promote new technologies and activities**, with a positive role in setting up **new working positions** in this area, characterized by a high rate of unemployment. The development of new research programs with the newly-created RDI base will permit an increase of the staff research capacities, such as a more active involvement of young researchers (PhD students and postdoctoral researches). The possible risks of this project could be related to the difficulties of finding partners and to the implementation of the newly developed technologies and products. However, such risks can be prevented and reduced by the involvement of the TECHNOLOGICAL PLATFORM FOR FOREST BASED SECTOR – FTP and of the existing excellence centre.

The estimated profit is the integration of excellence centers in international RDI networks, as well as the extension of the possible applications in various regions of Romania. The implementation of this project will open access to the RDI infrastructure, necessary to obtain new "green chemistry" products. Thus, the created infrastructure will permit specialized and certified services for the business medium and possibilities of financial support for PhD and postdoctoral fellowships.

Potential beneficiaries of this project will be other universities and research institutes, thanks to their integration in a RDI network on Resources Management, specialized organizations from MEDRES laboratory geographical areas, members of the national and international networks on Resources Management, researches, PhD students, the Romanian civil society, as a whole.

More information on the MEDRES Lab Project: http://medres_lab.cs.tuiasi.ro.

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BOOK REVIEW

New Release ... New Release ... New Release ... New Release ...



Polysaccharides in Medicinal and Pharmaceutical Applications

Edited by Valentin Popa

This book presents new and specific aspects in the field of polysaccharides and their derivatives recommended for use in medicine and pharmacy. At the same time the aspects developed in this book will be useful to design new systems for drugs delivery, immunomodulation, and new materials based on polysaccharides isolated from different sources and their derivatives.

The structure and properties of polysaccharides from different sources with potential applications in the fields of medicine and pharmacy are discussed. Thus, the structural aspects concerning hyaluronic acids, fungal extra cellular polysaccharides, celluloses, alginates, hemicelluloses, dextran, glycoconjugates and cyclodextrins are covered. The applications are described both for nonmodified and modified forms of polysaccharides for drug delivery, immunomodulation, tissue engineering and hydrogel preparation.

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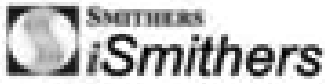
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