A study of the ferromagnetic microwires retention in cellulose matrix in the security papers

Mirela Maria CODESCU[1,a], Wilhelm KAPPEL[1,b], Eugen MANTA[1,c,*], Eros PATROI[1,d], Delia PATROI[1,e], Remus ERDEI[1,f], Valentin MIDONI[2,g], Ion ZĂPODEANU[3], Marilena BURLACU[3,h]

[1] Research & Development National Institute for Electrical Engineering ICPE-CA 313 Splaiul Unirii, Bucharest - 3, Romania

[2] SC MEDAPTEH PLUS CERT SA, 27 Selimber St, Magurele, Romania

[3] SC CEPROHART SA Braila, 3 Al. I. Cuza Blvd, Braila, Romania

[a]mirela.codescu@icpe-ca.ro;[b]wilhelm.kappel@icpe-ca.ro; [c]eugen.manta@icpe-ca.ro; [d]eros.patroi@icpe-ca.ro; [e]delia.patroi@icpe-ca.ro; [f]remus.erdei@icpe-ca.ro; [g]medapteh@mail.ru; [h]marilena_burlacu@yahoo.com

Keywords: Security papers, Ferromagnetic microwires, Retention, Cellulose matrix

Abstract. Prepared by the Taylor – Ulitovsky technique, the glass-coated microwires are formed from a metallic core, with the diameter 3 to 50 μm, surrounded by an insulating layer from glass, with the thickness of 1 to 20 μm. Embedded in the cellulose matrix, the ferromagnetic glass-coated microwires allow their use as security element for the authentication of valuable papers in the electronic validation process. The authentication of the security paper is realised with a special detector, by “YES” or “NO” answer. This paper can be used as anti-shoplifting or validating elements to identify the counterfeit products. The paper presents the experimental results related to the retention of ferromagnetic microwires in the cellulose matrix, a complex process characterised by specific features, primarily due to the shape and diameter/length ratio of the microwires. The ferromagnetic retention yield was $\eta = 65 – 90\%$, for the prepared papers with basis weight more than 50 g/m^2.

Introduction

Faced with increasing of goods counterfeiting, a wide range of methods are currently used to protect consumer goods, bank, state and commercial documents. Thanks to impossibility to produce security elements without proper equipment and under special conditions imposed by the very high degree of accuracy, the advanced technologies offer the solution, ensuring a high degree of protection against falsification. Investment and research efforts are being made to diversify the field of high security elements. The moment of launching the technology for glass-coated microwires (GMW) fabrication [1,2] has become revolutionary on the high-tech technology market, opening up the gates of a large variety of technological benefits for the existing applications and also setting the foundation for new applications [3-9]. The advantages of ferromagnetic GMWs securing [10] were: possibility of identifying at distance; stable magnetic properties even at high temperatures and corrosive media; wide range of functional temperatures; stability at shielding – the codes shielded by metallic panels can be read; stability at the mechanical action; small sizes and low consumption and, for the microfibbers from the last generation, with special properties, allowing the possibility to the information magnetic encoding): very large amount of the generated codes; the information can be read both from a stationary source and from a source in motion; the encoding is impossible to destroy, both in the continuously and in variable magnetic field, (reliable encoding); possibility to read the information from any code randomly oriented in space.

The structure of the paper consists of vegetable fibers (wood or non-wood), in which auxiliary materials, such as fillers, gluing agents, pigments, additives etc. are incorporated. Depending on the application field of paper, some structural features are imposed to the network: number of fiber-fiber contacts and of sizes of interfibrillar spaces, density and roughness of the surfaces. These properties are depending on the fibbers nature, on their processing degree, on the amount and properties of the auxiliary, and also on the processing technique used for forming and finishing of network. The term of filler defines any non-fibrous material added to the paper pulp to improve the optical properties of the paper, but also other features such as porosity, smoothness, printing ability etc. By incorporating of pigments into the paper pulp, the papers optical inhomogeneity increases, the amount of reflected and refracted light in the paper sheet increases, and the whiteness and opacity is improved. At the same time, the pigment particles retained in the sheet structure increase the interfibrillar spaces and reduce the possibility to set-up interfibrillar bonds having negative effects on the paper resistance indices. The fillers retention into the paper sheet is realised mainly by filtration for the particles with large sizes and by colloidal phenomena for fine particles. The introduction of filling is primarily determined by technical considerations, since certain characteristics of the paper, particularly optical indices and printing ability, are limited if only fibrous materials are used. Currently fillers can also serve as partial substitutes for fibrous materials in some cases, thereby helping to reduce the production costs.

Developed by the Taylor-Ulitovsky process, the GMWs consist of a cylindrical metal core that is covered with a glass-insulating layer, the diameter of the metal core is 3 - 50 μm, and the thickness of the glass insulation is 1 - 20 μm. The length of such microwires, under laboratory conditions, reaches approx. 1 km. The ferromagnetic glass-coated microwires, cut at ca. 7 mm lengths, is included in the paper composition also as filling material, but in the paper pulp and in the paper sheet structure, the microwire segments have a certain behaviour that differentiates them from the classical materials of filling. Unlike these materials, the ferromagnetic microwires introduced into the paper in very small amounts do not significantly influence the rheological characteristics of the paste and the paper resistance characteristics. The appearance of wires, the diameter, length and the microwires density are also specific characteristics that differentiate the materials currently used to fill the paper. The importance of retention efficiency in the case of ferromagnetic microwires is primarily due to the need to achieve a certain microwires density in the paper sheet, in order to ensure its security without affecting the paper quality and functionality.

2. Experimentals

The Taylor-Ulitovsky technique for GMWs preparation consists in placing in a high-frequency inductor of a glass tube with a metallic rod inside (Fig. 1). Under the influence of the generated electromagnetic field, the metal melts, forming a drop. In contact with the molten metal, a part of the glass tube softens and a coating is formed from the glass covering the drop. For a particular working regime [11], this glass soaked by pulling also trains the metal, leading to microwires formation, which is collected on the spool. Different metal core structures can be obtained: polycrystalline crystals of different sizes (microcrystalline, nanocrystalline) or amorphous. For experimental research were used $Fe_{77}B_{13}Si_{10}$ GMWs, which are structurally, by X-ray diffraction and magnetically, by vibrating sample magnetometry, characterized.

Achieving certain density of GMW in the paper sheet structure, as in the fillers case, depends on the action of factors with a particular influence on intelligent material retention in the papermaking process. Knowing and controlling these influences will ultimately allow finally reaching the density that is sufficient for paper securing. In this respect, have been experimented several programs in which the basic recipe for realisation of the GMWs secured paper has been supplemented with several variables specific to each influenced factor studied.

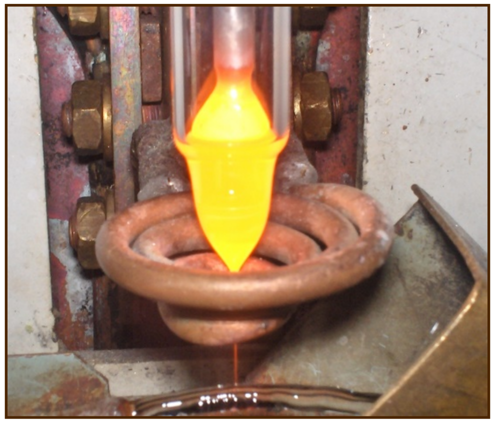


Fig. 1. Aspect during the $Fe_{77}B_{13}Si_{10}$ ferromagnetic glass-coated microwires drawing.

Table 1. The studied parameters and the experimented recipes used to for paper preparation

Parameter	S/H ratio, [wt. %]	S/H Schopper – Riegler degree, [°SR]	Microwires amount, [g]	Retentor amount, [%]	Paper weight, [g/m^2]
Nature of the fibrous materials	100 S or 100 H	30	0.005; 0.007; 0.009		
Schopper – Riegler degree °SR of the cellulosic material	60/40	30/20; 40/30; 50/40; 60/50	0.009		
GMWs amount	60/40	30/20; 40/30; 50/40; 60/50	0,005; 0,007; 0,009; 0,011		
Softwood / hardwood cellulosic pulp ratio from the fibrous composition of paper	20/80; 30/70; 40/60; 50/50	45/30	0.007		
Amount of retention emulsion, dosed in the paper manufacturing receipts	60/40	30/20		0; 0.2; 0.4; 0.6; 0.8	
Paper weight	60/40	30/20			50; 70; 90; 110

The GMWs with 7 mm lengths are embedded as filler into the cellulose matrix (the pulp), the main receipt of the mixture, in wt.%, being: bleached cellulose sulphate from softwood (S) pulp (different amounts: 30 - 100%; Schopper – Riegler degree: 30 - 60 °SR); bleached cellulose sulphate from hardwood (H) pulp (different amounts: 30 - 100%; Schopper – Riegler degree 20 - 50 °SR); paper filling material: 15% calcium carbonate; gluing emulsion: 1,5% alkyl–dimercetene (AKD); retention additive: 0,5% polyamide–amine and different amounts of GMW (for 10 sheets with paper weight q = 75 g/m^2) – 0.005g; 0.007g; 0.009g and 0.011g. The particularities of the experimented recipes for paper sheets preparation are chosen to highlight the influence of different process parameters (Table 1). The Schopper-Riegler test provides a measure of the rate at which a dilute suspension of pulp may be dewatered. It has been shown that the drainability is correlated to the surface conditions and swelling of the fibbers, and constitutes a useful index of the amount of mechanical treatment to which the pulp has been subjected. The retention efficiency (η) was expressed as the ratio of the amount of GMW initially used to prepare the cellulosic paste and the remaining GMW amount in the laboratory prepared sheet (in each experiment, the retention yield was determined for 10 sheets of paper).

3. Results and discussions

3.1 Structural characterization for $Fe_{77}B_{13}Si_{10}$ ferromagnetic glass-coated microwires

After preparation, the GMWs were structurally characterized by X-ray diffraction investigations. The glass-coating was eliminated using as etchant a solution of 50% hydrogen fluoride (HF) in water. As expected, the ferromagnetic microwires are quasi-amorphous. The samples show a crystalline structure of Fe_3Si in the cubic system, the structure that is very similar to that of α-Fe, but with a lower cell parameter, in this case the network parameter being a = 2.837 Å compared to a = 2.866 Å in the case α-Fe. It is considered that the effect is due to the ultra-rapid solidification phenomenon of the alloy, but a small contribution to this reduction can also be brought about by the induction of a local stress factor by the preparation conditions, due to the presence of glass covering the metallic core. Other phase present in the $Fe_{77}B_{13}Si_{10}$ GMW is Fe_8B, which crystallizes in a tetragonal system. The mean crystallite size, determined for the Fe_3Si phase using the Debye-Scherrer formula is D = 19 nm. The calculated crystallinity of the analysed sample is around 74,4%.

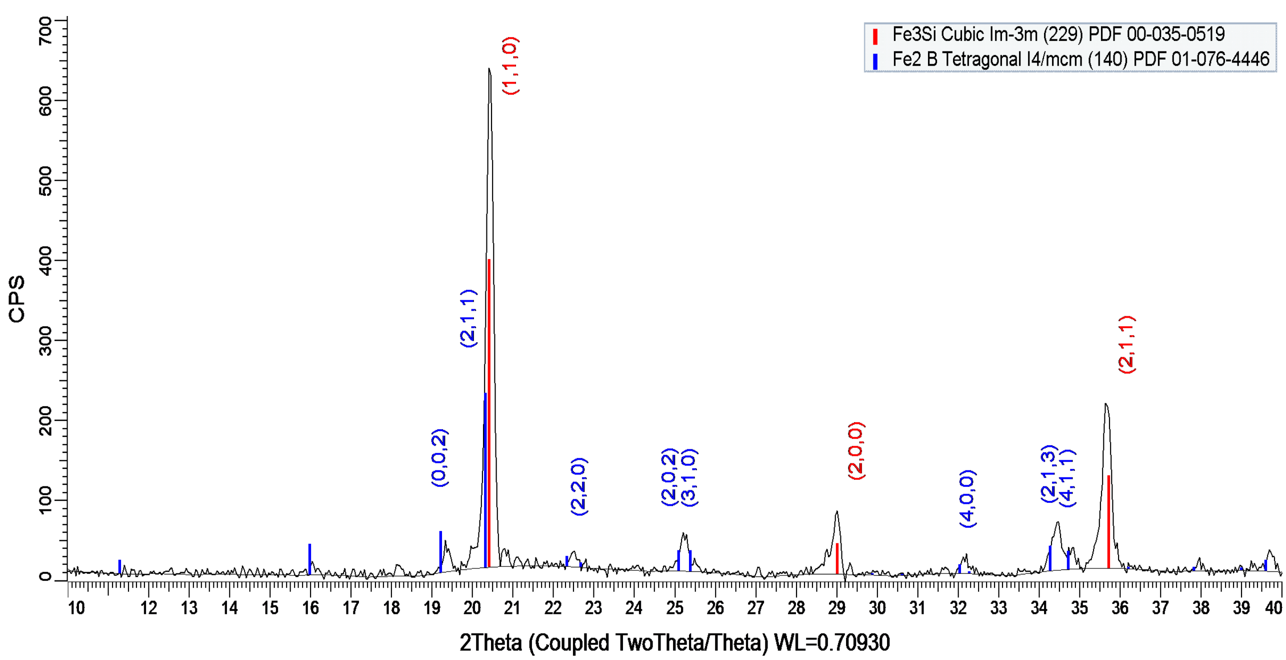


Fig. 2. X-ray diffraction diffractogram of the $Fe_{77}B_{13}Si_{10}$ ferromagnetic GMWs.

3.2 Magnetic characterization for $Fe_{77}B_{13}Si_{10}$ ferromagnetic microwires

The shape of hysteresis curve (Fig. 3), plotted for the $Fe_{77}B_{13}Si_{10}$ GMWs confirms that the microwire metallic core is ferromagnetic. The magnetic values, obtained by evaluating the magnetic core volume, were compared with data obtained on bulk material. From the point of view of the magnetic properties, the structure of the ferromagnetic material (evidenced by the X-ray diffractogram in Fig. 2) favours the magnetic properties suitable for application as soft magnetic material, i.e. high magnetization (1,2 T) and low coercivity H_c = 17.73 (A/m).

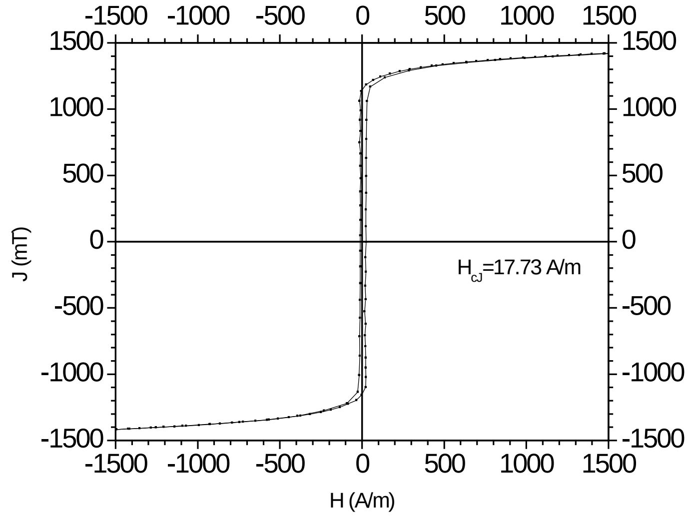


Fig. 3. Hysteresis curve of the $Fe_{77}B_{13}Si_{10}$ ferromagnetic GMWs.

3.3 Influence of fibrous material nature

The results obtained during this experiment show that both for softwood pulp and hardwood pulp, the number of microwires retained in the paper sheets increases with the ferromagnetic GMWs amount (Table 2).

Table 2. Number of ferromagnetic microwires retained in paper sheets at various additions of ferromagnetic microwires (paper weight q = 75 g/m^2).

Specification	Microwires addition for 10 sheets, [g]		
	0,005	0,007	0,009
The number of microwires retained in paper sheets obtained from 100% softwood cellulose	258	366	472
The number of microwires retained in paper sheets obtained from 100% hardwood pulp	239	330	424

When the retention efficiency is determined, it can be seen that the increase of the initial GMWs addition, occur differences of 4 – 9% between the two types of cellulose, both having the same Schopper-Riegler degree: 30 ^{o}SR, the lower values being obtained in the case of the hardwood cellulose. Depending on the GMWs amount added to the pulp, in the case of the softwood cellulose, the retention efficiency increases slightly, whereas for the hardwood cellulose, this efficiency decreases (Fig. 4). For the same type of cellulose, the decrease or the increase of the efficiency based on the ferromagnetic GMWs addition is ca. 2% (in the studied range, for addition of 0.005 – 0.009 g GMWs / 10 sheets).

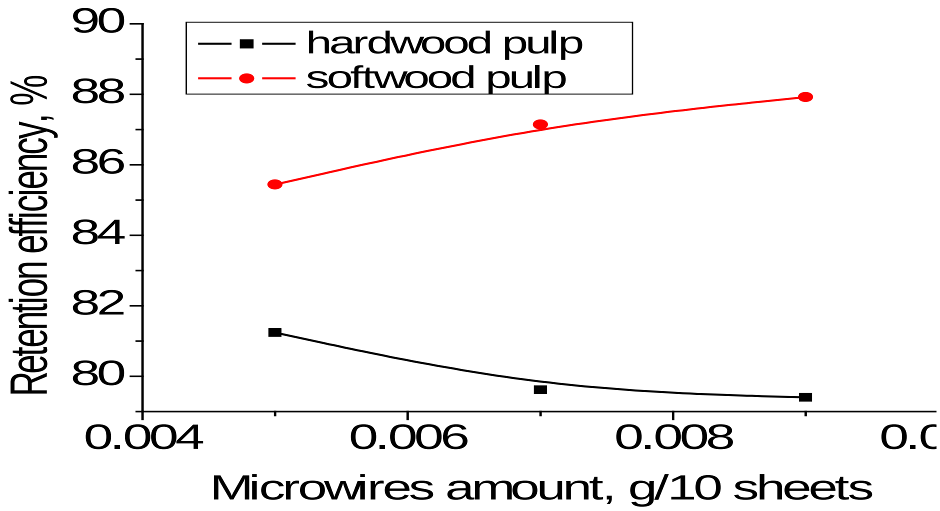


Fig. 4. Dependence of retention efficiency on the nature of the fibbers material, for various amounts of ferromagnetic microwires.

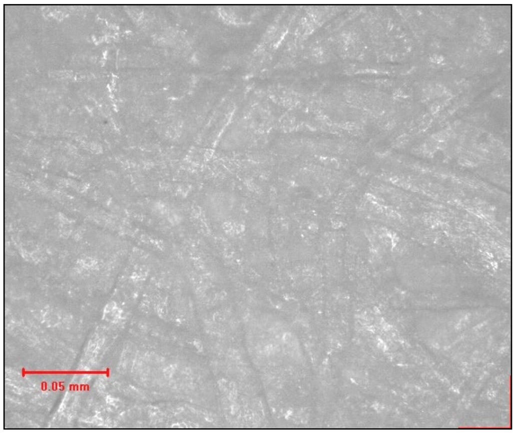
The ferromagnetic GMWs, having an average length of ca. 7 mm and a much higher density than the cellulose fibbers, are better retained by the greater fibber (in diameter and length) of softwood pulp than those of hardwood pulp. Also, the softwood pulp fibbers, with 30 °SR, already exhibit a certain degree of fibre-lisation, and the structure of paper, at stage of network formation, retains better the ferromagnetic GMWs. In the case of the hardwood cellulosic fibbers, due to their smaller sizes, the GMWS retention efficiency is lower, these ones “penetrating” easily at filtering the fibrous network of the paper sheets.

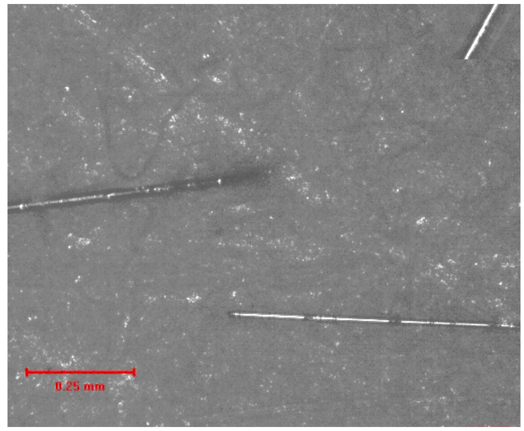
3.4 Influence of sizes of the ferromagnetic microwires and cellulosic fibbers

In order to estimate the compatibility of the ferromagnetic GMWs with the cellulose matrix in which they will be embedded, were prepared samples showing that the microwires sizes are compatible with the dimensions of the cellulose fibbers of the matrix. The comparison was always done with a blank sample, i.e. a sample without filler, prepared from cellulose only. The micrographs of these samples are shown in Fig 5a) and b).

3.5 Influence of the Schopper-Riegler degree of the cellulosic material

By increasing of the milling degree, the fibbers specific surface increased and their ability to be felt is improved. Consequently, the amount of filler material retained in the paper sheet by adsorption and filtration should increase proportionally to the increasing of the milling degree. Additionally, it should be added that the dehydration rate of the paste on the forming screen decreases with the advance of milling process, which also has a positive effect on the retention rate. Figure 7 shows the variation of GMWs retention efficiency (at an addition of 0.009 g/10 sheets), depending on the increase of the milling degree of the cellulose used in the production of the laboratory paper sheets (for softwood cellulose, with 30; 40; 50 and 60 °SR and hardwood cellulose, with 20; 30; 40 and 50 °SR).



a)


b)

Fig. 5. Optical micrographs of the cellulose matrix without a) and with randomly inserted $Fe_{77}B_{13}Si_{10}$ microwires filler b).

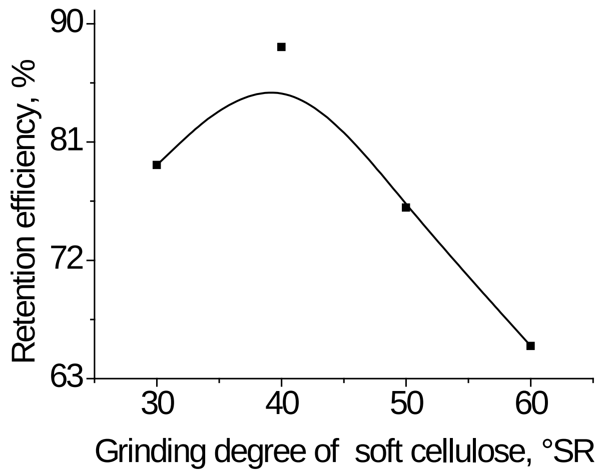


Fig. 7. Microwires retention efficiency *versus* milling rate of the paper pulp.

The ferromagnetic GMWs behaviour is the same to that of the classic filler up to a certain milling degree, after which it begins to decrease rather abruptly. The highest value was obtained on paper sheets in which softwood pulp had a milling degree of 40 °SR, and the hardwood pulp 30 °SR. Considering the specific characteristics of the ferromagnetic GMWs (shape, dimensions and specific weight), it may be possible, that starting from a certain milling degree, the under developing paper fibrous network to be more easily traversed thereby resulting a decreased retention efficiency. The same evolution of retention efficiency was found for other values of the GMWs amount.

3.6 Influence of the amount of ferromagnetic microwires

The data reported in literature shows that the retention efficiency of the classical fillers used in the paper manufacturing process is influenced both by the properties of the filler material, in particular the shape and size of the particles and by the amount of filler material used in the preparation of paper pastes. It has a growing trend, with the increase of the amount of filler up to a certain value, then the retention efficiency decreases. The retention efficiency dependence on the GMWs amount was studied so far only separately, for the two types of cellulose, namely S pulp and H pulp. Using a certain combination of these two types of celluloses, the results presented in Fig. 8 show that indeed the retention efficiency is depending on the ferromagnetic GMWs amount. The retention efficiency increases with the increase of the GMWs amount (in the range of 0.005 – 0.011 g/10 sheets), even when the milling degree of fibrous material was modified (30 - 60 °SR for the S cellulose and 20 - 50 °SR for the H cellulose). The growth trend is not substantial, ranging from 1 to 4%.

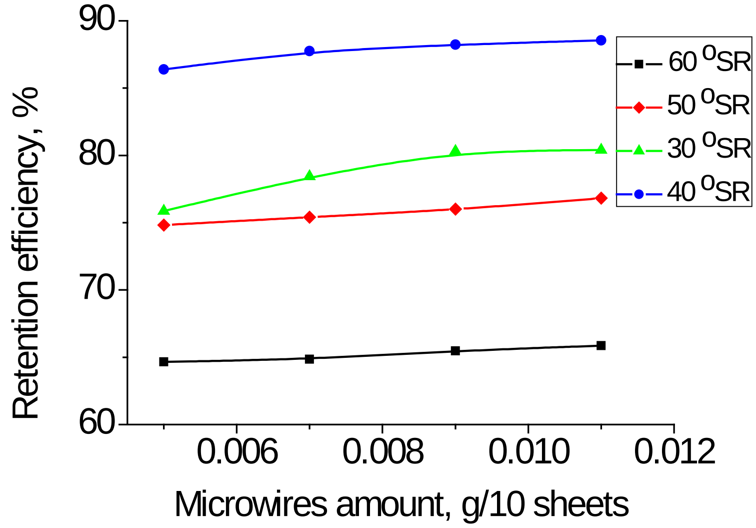


Fig. 8. Dependence of retention efficiency on the amount of microwires, for various milling degrees of the cellulose pulp.

3.7 Influence of the hardwood and softwood celluloses ratio in the paper composition

It is known that each assortment of paper must be realised with a certain fibrous composition that will provide the desired quality characteristics, be the cheapest and to require the simplest manufacturing technology. In this regard, the paper fibrous composition will usually consist on two types of cellulose, usually hardwood and softwood pulps. Table 3 shows the GMWs retention efficiency, resulted in the case of paper sheets whose fibrous compositions were obtained from H and S celluloses, combined in various ratios. In the case of the paper sheets having a higher content of softwood pulp (from 20% to 50%), should increase the GMWs retention efficiency. On the other hand, the softwood pulp has a high milling degree, much higher than that of hardwood pulp, which makes that the fibrous material mixture to present an increased milling degree from ca. 30 °SR to 40 °SR.

Table 3. The GMWs retention efficiency for fibrous composition consisting of different ratios of H and S celluloses

Specification	Cellulosic ratio H/S, [%]			
	80/20	70/30	60/40	50/50
Retention efficiency, [%]	78,38	76,28	74,00	72,48

In these conditions, the values determined for the retention efficiency decrease slightly as the softwood pulp amount increases in the paper pulp composition.

3.8 Influence of the retentor amount dosed in the manufacturing prescriptions

From the data presented in Fig. 9, results that the retention efficiency of the GMWs depends on the retentor amount used to prepare the paper paste, and in this case the increase of efficiency is proportional with the retentor content. If the investigation field of experiment had been extended to larger retentor contents, it was probable that the retention performance would not have significantly increased. In practice, a retentor overdose is not recommended, to avoid the formation of very large flocks that disturb the process of paper formation. The increase in retention efficiency with the retentor amount indicates that the behaviour of microwires from the paper pulp aligns to the main behaviour of the fillers and of the cellulosic fibbers. It means that microwires retention is achieved by both mechanisms, namely mechanical retention and colloidal adsorption. The results show also that in the overall retention the greatest share is the mechanical retention. Without retentor addition, the retention efficiency already has an appreciable value (60.86%), although the cellulosic milling degrees used in the experimental recipes are quite low (30 °SR for the softwood pulp, respectively 20 ^{o}SR for hardwood pulp).

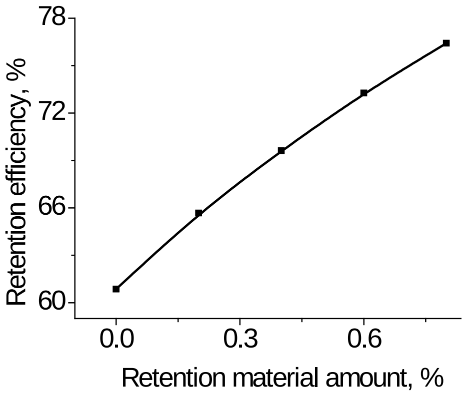


Fig. 9. Variation of retention efficiency [η] on the retentor content.

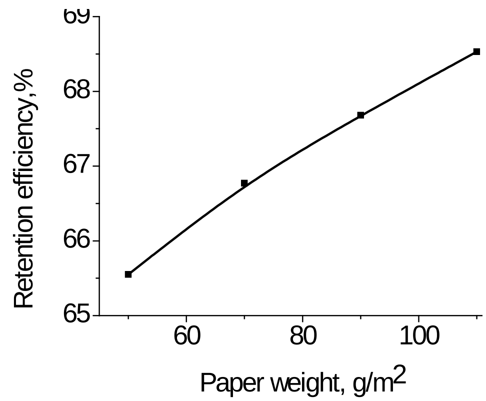


Fig. 10. Influence of paper weight on retention efficiency [η] of ferromagnetic GMWs.

3.9 Influence of the paper weight

Another factor that significantly influences the retention efficiency is the paper weight. With the increase of the weight and the thickness of the filter layer, it is also expected to increase the cross-sectional strength of the filler material, in this case of the microwires. At higher pass resistance, the amount of microwires remaining in the paper sheet will increase, which means an increase of the retention efficiency. The retention efficiency determined under these conditions is presented in Fig. 10. By increasing of the paper weight from 50 to 110 g/m^2, the retention efficiency increased with ca. 3%, from 65.55% to 68.53%. The values determined for the retention efficiency include both mechanical retention and colloidal retention, since on the paper sheets realisation was used also retentor.

Summary

The embedding of GMWs in the cellulosic matrix of the paper aims to develop a new type of paper, with a novel securing element – the ferromagnetic GMW - as a field sensor, for applications in the field of electronic detection of valuable documents validation. The retention of GMWs in the paper sheet, unlike the usual filler materials, has a certain specificity given mainly by the shape and size of the microwires (6 to 8 mm long and diameter smaller or comparable with the cellulose fibbers diameter), of their density (over 3 kg/m^3 versus 1,300 kg/m^3 per paper and 2,500-2,700 kg/m^3 for calcium carbonate) and the possibility of superficial loading. In order to be used as security paper, depending on its destination, a certain density of FM microwires must be achieved in the paper. To the achievement of this density acts the retention efficiency of the ferromagnetic GMWs, influenced by technological factors as well as factors specific to the paper manufacturing equipment. The paper analyzes the main technological factors involved in ferromagnetic GMWs retention, such as: fibbers nature, grinding degree of the cellulosic pulp, GMWs amount, the hardwood and the softwood cellulose ratio in the fibrous paper composition, the amount of retention emulsion dosed in the paper manufacturing receipts, the paper weight. Through the performed experimental work was realised the experimental model for the retention of

Materials Research Proceedings **8** (2018) 1-10 doi: http://dx.doi.org/10.21741/9781945291999-1

ferromagnetic GMWs in the cellulosic paper structure, defined by the following manufacturing receipt: 30-70% softwood bleached cellulose, with Schopper-Riegler degree: 35-65 ^{o}SR; 30-70% hardwood bleached cellulose, with Schopper-Riegler degree: 30-50 ^{o}SR; calcium carbonate: 10 - 30%, as filling material; 0.3-0.5% polyamide-amine, as retention emulsion; 1-1.5% alkyl – dimercetines, as gluing agent; 0.02 - 0.05% GMWs. Under these conditions, the retention yield of the GMWs for a paper with a weight greater than 50 g/m^2 will be: η = 65 - 90%. Taking into account the variation limits of the indicated parameters, this model contains practically several experimental versions of the GMWs secured paper.

References

[1] G. F. Taylor, A method of drawing metallic filaments and discussion of their properties and uses, Phys. Rev. 23 (1924) 665-60. https://doi.org/10.1103/PhysRev.23.655

[2] A. Zhukov, J. Gonzalez, J. M. Blanco, M. Vazquez, V. Larin, Microwires coated by glass: a new family of soft and hard magnetic materials, J. Mat. Res 15 (2000) 2107-2113. https://doi.org/10.1557/JMR.2000.0303

[3] A. Talaat, J. Alonso, V. Zhukova, E. Garaio, J. A. García, H. Srikanth, M. H. Phan, A. Zhukov, Ferromagnetic glass-coated microwires with good heating properties for magnetic hyperthermia, Scie. Rep. 6 39300 (2016) 1-6. https://doi.org/10.1038/srep39300

[4] A. Zhukov, Glass-coated magnetic microwires for technical applications, *J. Magn. Magn. Mater. 242 – 245 (2002) 216-223. https://doi.org/10.1016/S0304-8853(01)01258-6*

[5] Jing-Shun Liu, Xiao-Dong Wang, Fa-Xiang Qin, Fu-Yang Cao, Da-Wei Xing, Hua-Xin Peng, Xiang Xue, Jian-Fei Sun, GMI Output stability of glass-coated co-based microwires for sensor application, Piers online, 7 7 (2011) 661-665.

[6] R. Hudak, I. Polacek, P. Klein, R. Sabol, E. Varga, J. Zivcak, M. Vazquez, Nanocrystalline Magnetic Glass-Coated Microwires Using the effect of superparamagnetism are usable as temperature sensors in biomedical applications, IEEE Trans. on Magn. 53 4 (2017) 5300305.

[7] J. Nabias, A. Asfour, J-P Yonnet, Temperature dependence of giant magnetoimpedance in amorphous microwires for sensor application, IEEE Trans. on Magn. 53 4 (2017) 4001005.

[8] M. Karimov, M. Gruzdev, Method and device for protecting products against counterfeiting, US 20070291988 A1, 2007.

[9] E. Manta, M. M. Codescu, M. Petrescu, Ferromagnetic glass-coated microwires and their applications, U.P.B. Sci. Bull. Series B 74 4 (2012) 177-184.

[10] M. M. Codescu, E. Manta, E. A. Pătroi, W. Kappel, I. Zăpodeanu, M. Burlacu, P. Nechita, V. Midoni, Securing elements with ferromagnetic microwires, Optoel. & Adv. Mat. – Rapid Comm. 4 10 (2010) 1361-1365.

[11] S. A. Baranov, O. V. Yaltychenko, E. Yu. Kanarovskii, M. M. Codescu, Preparation of the cast glass-coated amorphous magnetic microwires, Proc. SPIE 10010, Advanced Topics in Nanoelectronics, Microelectronics and Nanotechnologies VIII, 1001016 (2016) 117-123.