ISSN 1311-0829

ГОДИШНИК НА ТЕХНИЧЕСКИ УНИВЕРСИТЕТ-СОФИЯ

Том 65, книга 2, 2015

Юбилей "70 ГОДИНИ ТЕХНИЧЕСКИ УНИВЕРСИТЕТ - СОФИЯ"

PROCEEDINGS OF TECHNICAL UNIVERSITY OF SOFIA

Volume 65, Issue 2, 2015

Anniversary "70 YEARS TECHNICAL UNIVERSITY OF SOFIA"

Технически университет-София
София 1000, бул."Кл. Охридски" 8
България http://tu-sofia.bg

Technical University of Sofia
Sofia, 1000, boul. Kliment Ohridski 8
Bulgaria http://tu-sofia.bg

ISSN 1311-0829

СЪДЪРЖАНИЕ том 65, книга 2

CONTENTS volume 65, Issue 2

Author's Index - Volume 65, Issue 2

Volume 65 Issue 2		
pages	**articles**	**authors**
262	**30**	**33**

Годишник на Технически Университет - София, т. 65, кн. 2, 2015
Proceedings of the Technical University of Sofia, v. 65, book 2, 2015

ФОСФОРНИ ЗАБАВИТЕЛИ НА ГОРЕНЕТО КАТО СРЕДСТВО ЗА ИЗУЧАВАНЕ НА ПЛАЗМЕНО-ПОДПОМОГНАТАТА ПОВЪРХНОСТНА ИМПРЕГНАЦИЯ

Ивайло Иванов, Диляна Господинова, Петър Динев

Резюме: *Фосфорните забавители на горенето (антипирени) бързо изместват халоген съдържащите забавители на горенето в областта на огнезащитата на горими материали и изделия. Тяхното действие се основава върху формирането на защитно въгленово покритие, което спира пламъчното горене и разпространяването на огъня в дълбочина. Овъгляването на повърхностния слой, съдържащ забавителя на горене, под действие на топлината при температури от порядъка на 190÷250 °C прави видимо проникването на импрегнационния разтвор, съдържащ забавителя на горене. Този подход позволява да бъде измерена дълбочината на проникване през повърхността на пробното тяло по направление на капилярите и напречно на тях.*

Ключови думи: *диелектричен бариерен разряд, защитно покритие от въглен, забавители на горенето, пламъчно горене, плазмено-подпомогната повърхностна импрегнация, фосфорни забавители на горенето.*

PHOSPHOROUS FLAME RETARDANTS AS TOOLS TO STUDY PLASMA-AIDED SURFACE IMPREGNATION OF WOOD

Ivaylo Ivanov, Dilyana Gospodinova, Peter Dineff

Abstract: *Phosphorous flame retardants (PFRs) quickly displace halogen containing flame retardants in flame retardancy of flammable wood materials and products. Their retardant action is based on the formation of charcoal protective coating that stops the flame spreading. Charcoal formation in the surface layer containing phosphorous flame retardant under heat impact at temperature of 190÷250 °C makes visible the penetration of the transparent flame retardant solution trough wood surface. This approach allows measuring the wicking depth through the surface of the wood specimen in the direction of capillary movement and transverse direction thereof.*

Keywords: *atmospheric dielectric barrier discharge (DBD), charcoal protective coating, phosphorous flame retardant (PFR), flaming, penetration, plasma-aided surface impregnation, spreading, wicking.*

ISSN 1311-0829

1. INTRODUCTION

Flame retardants (*FRs*) are used since the 1960s as chemicals which are added to materials both to render them more resistant to ignition and to delay the spreading of fire after ignition. They are designed to minimize the risk of a fire starting in case of contact with a small heat source such as a cigarette, candle or an electrical fault. If the flame retarded material or an adjacent material has ignited the flame retardant will slow down the combustion and often it will prevent the fire from spreading to other items (*EFRA*, 2007).

What are flame retardants?

Since the term "*flame retardant*" describes a function and not a chemical class, there is a wide range of different chemicals which are used for this purpose. *FRs* may have different compositions: they may contain halogens (bromine and chlorine), ***phosphorus***, nitrogen, metals, minerals based on aluminum and magnesium, or they may be based on borax, antimony trioxide, molybdenum, or the *FR* may be a nanocomposite (*EFRA*, 2007).

Flame retardants have become a class of chemicals which receive more and more scientific and public attention. The discussions about flame retardants started when brominated flame retardants (*BFRs*) became a topic of environmental concern in the early 1990s, when it was discovered that some *BFRs* could form halogenated dioxins and furans under severe thermal stress or when they were burnt in accidental fires or uncontrolled combustion. Findings in the environment and biota and the suspicion that some flame retardants bioaccumulate in organisms have added to these concerns. Meanwhile, the environmental and health properties of not only *BFRs* but also other types of flame retardants have been studied extensively. The most widely used *FRs* have become the subject of official risk assessments in Europe (*PINFA*, 2009).

What are halogen-free flame retardants?

Phosphorus (non-halogenated), ***I****norganic* and ***N****itrogen* flame retardants (*PIN FRs*) are halogen-free additives that can be added to or applied as a treatment to organic materials such as wood, plastics and textiles to impart fire protection to these materials. The group of *PIN FRs* covers a diverse range of chemicals which are commonly classified as: *i*) *Inorganic FRs*: This category comprises mainly metal hydroxides like aluminum hydroxide and magnesium hydroxide. Other compounds like e. g. zinc borate are used to a much lesser extent; *ii) Phosphorus* based or phosphorous flame retardants (*PFRs*) include organic and inorganic phosphates, phosphonates and phosphinates as well as red phosphorus, thus covering a wide range of phosphorus compounds with different oxidation states; *iii) Nitrogen* based flame retardants (*NFRs*) are typically melamine and melamine derivatives (e. g., melamine cyanurate, melamine polyphosphate, melem, melon), and they are often used in combination with phosphorus based flame retardants.

Phosphorous flame retardants

According to the *European Flame Retardants Association* (*EFRA*, 2007), the total consumption of *FRs* in Europe in 2006 was 465,000 tons, of which 10 % were *brominated flame retardants* (*BFRs*). Many halogenated chemicals, such as some *BFRs* and *polychlorinated biphenyls* (*PCBs*), have proven to be persistent, bioaccumulative, and/or toxic in the environment, and to animals and humans. Nowadays the production and use of *BFRs* are restricted more and more by the *European Union* (*EU*) and they have been voluntary phased out in the *USA*. These developments have urged the use of alternatives for *BFRs*, (*Bromine science and environmental forum*, *BSEF*, 2011), [1].

Since the ban on some *BFRs*, *phosphorus flame retardants* (*PFRs*), which were responsible for 20 % of the flame retardant consumption in 2006 in Europe, are often proposed as alternatives for *BFRs*. *PFRs*, which have already been used for over 150 years (*Andrae*, 2007), are considered as suitable alternatives for *BFRs*. Because of the need for vapor-phase activity, a number of volatile *PFRs*, *tributyl phosphate* (*TBP*), *triphenyl phosphate* (*TPhP*), and *triphenylphosphine oxide* (*TPPO*), have been identified as possible substitutes for bromine-containing formulations (*Horrocks et al.*, 2007). Not only several *BFRs* are being replaced by *PFRs*, but also the halogen containing *PFRs* may need to be substituted by non-halogenated *PFRs*. The *German Federal Environmental Agency* (*GFEA*) carried out a research project on substitution of hazardous *FRs*, [1].

PFRs can be divided in three main groups: *inorganic*, organic and halogen containing *PFRs*. The first group contains the inorganic *PFRs*, including frequently used *Red phosphor* (*RP*), *Phosphoric acid* (*PA*), *Di-ammonium hydrogen phosphate* (*DAP*), *Ammonium di-hydrogen phosphate* (*ADP*), and *Ammonium polyphosphate* (*APP*). The second group consists of the organic *PFRs*. Three different general structures of these *PFRs* can be recognized: the organophosphate esters (*OPEs*), the phosphonates, and the phosphinates. The third group is the widely used group of halogenated *PFRs*. These combine the properties of halogen and phosphorus components. Some *PFRs* are *reactive FRs*, which means they are chemically bound to a polymer, whereas others are *additive* and mixed into the polymer, [1].

Flame retarding mechanisms of PFRs

Most of the *PFRs* have a mechanism of action in the solid phase of burning materials (char formation), but some may also be active in the gas phase. In case of fire the solid materials are decomposed by heat into flammable gases, which will be on fire. There are several *FR*-mechanisms to prevent fire, of which the most effective ones are reactions in the solid phase and reactions in the gas phase (*EFRA*, 2007).

Halogenated *FRs* act in the gas phase, whereas non-halogenated *PFRs* mainly act *in the solid phase* of burning materials. In the gas phase halogenated *FRs* remove H^+ and OH^- radicals from the flammable gasses, by reaction with the Br and Cl atoms.

The removal of the H^+ and OH^- radicals results in a slowdown of the burning process, and reduces the spreading of the fire. Another mechanism of action of *PFRs* is offering a partial gas phase contribution to the flame extinguishing effect, which is comparable to bromine or chlorine containing *FRs*. When halogens and phosphorus are both present in polymer systems, they act independently and therefore additively (*EFRA*, 2007), [1 and 2].

When phosphorus is heated it will react, and form a polymeric form of phosphoric acid. This acid causes a charcoal layer on material's surface, which shields the material from oxygen and heat, in that way preventing the formation of flammable gasses. The content of phosphorus in *PFRs* varies from 8.2 % for bis (4-carboxyphenyl) phenylphosphine oxide (*BCPPO*) to almost 100 % for *RP*. A minimum amount of PFR is needed to form a char layer. Once the layer was formed there is no need for more *FR*, [1, 2, 3, and 4].

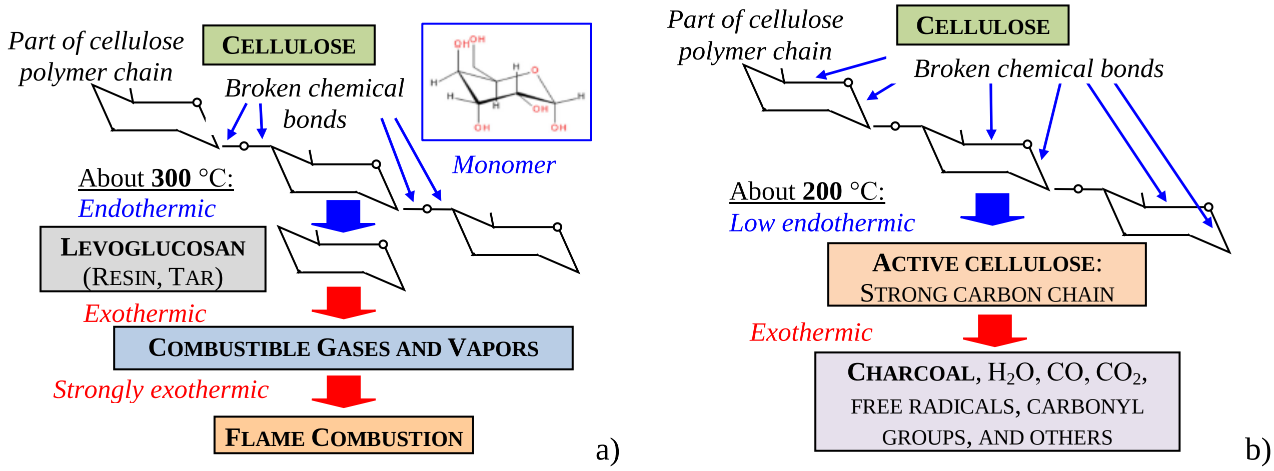


Fig.1. Two main mechanisms of thermal decomposition of the cellulose molecule in the wood pyrolysis: ***a*** – cellulose decomposition in flame combustion – resin and tar as residue; ***b*** – formation of charcoal shield as residue. The decomposition is often regarded as the superposition of the individual constituent's decomposition mechanisms: hemicellulose decomposes first [180÷350 °C] followed by cellulose [275÷350 °C], and lignin [250÷500 °C], (*Kim et al.* 2006).

Plasma-aided flame retardation of wood and wooden products

The *plasma-aided flame retardation* of wood and wooden products has been developed successively as a result of creating a functional layer (coating) containing phosphorus flame retardants. The flame retarded layer was built by new *plasma-aided surface finishing process* of surface (capillary) impregnation. This process comprises: *i* – cold plasma (*DBD-*) surface pre-treatment for increasing the wood surface energy and altering its chemical, electrical (ionic) and capillary activities; *ii-* surfactant enhanced impregnation to change the ionic activity and surface tension of *FR* impregnating solution by *surface-active agents* (surfactants), and in general to improve some characteristics of the capillary impregnation process such as solution spreading on the surface and wicking in the depth of porous media, as well as the amount of the penetrated (sorbed) flame retardant in the surface *FR*-layer. In this way the plasma pretreatment improves the flame retardation of wood and wooden products, [1, 2, and 3].

Wood cell wall is thought to be a composite material made of cellulose microfibrils embedded in a water-reactive matrix of hemicellulose and lignin. The ability of the matrix to adsorb water is thus of critical importance in the water solution surface (and capillary) impregnation of wood (*N. Barber* 1968). As a result of such plasma-aided impregnation a functional coating containing *FRs* in decreasing concentration in depth occurs. Flame suppressing effect depends on the uniformity, faultless (free of defects) and thickness of the charcoal coating. This coating is most commonly colorless, and does not allow to be studied directly (visually). The non-halogenated *PFRs* that act in solid phase of burning wood materials as charcoal top coating (against the spread of fire) gave us the idea to use a new approach to study directly the plasma-aided surface impregnation. After heat development and *PFR* wood transformation of cellulose according to char mechanism of thermal decomposition, Fig.1, a charcoal coating occurs at the place of the *FR*-functional coating. Thus, the colorless coating acquires color (black) and becomes visible. The charcoal path of wood pyrolysis develops and makes visible the results of plasma-aided impregnation finishing.

The objective of this paper is to study the effect of plasma pre-treatment on *European white* or *Scots pine* (*Pinus Sylvestris*, Bulgaria) wood surface functionalization as well as the effect of surfactant enhanced impregnation on the wicking phenomena, both aiming to improve the surface impregnation process.

This study has been developed as part of a large research on plasma-chemically activated wood surface and flame retarded constructive wood. The aim was to verify possibility of measuring the penetration (wicking) depth values after plasma-aided impregnation using well known *PFRs*.

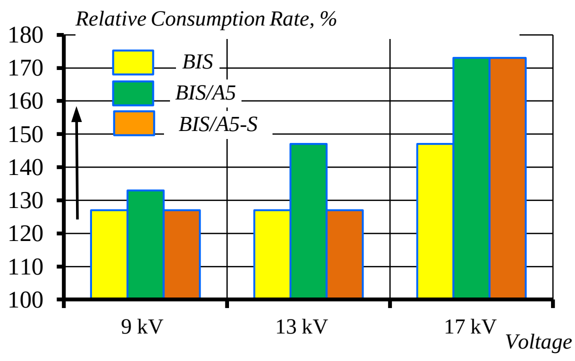
Studies of *cold plasma functionalization phenomena,* i.e. interactions of oxidative cold plasma with wood surface may add valuable information about the surface (and capillary) impregnation, printing, gluing and coating properties of wood. Such information is essential in the development of efficient processing methods and for the prediction of the functionality and durability of wood products.

1. Experimental Investigation

The plasma-aided *FR*-process involves two tools which are used for exerting direct impact on the thermal degradation of *FR*-woods: *the first one* consists in impregnating *European white pine* (*Pinus sylvestis*, Bulgaria) wood samples with three *PFR* water solutions - a basic impregnation solution of *PFR* (*BIS*); *BIS* with 5 vol. % of anionic phosphate surfactant (*BIS-A5*); and *BIS-A5* with 0.1 vol. % of siloxane surfactant (*BIS/A5-S*), Fig.2; *the second one* consists in performing cold plasma surface pre-treatment for 60 sec in the plasma of *DBD* before impregnating.

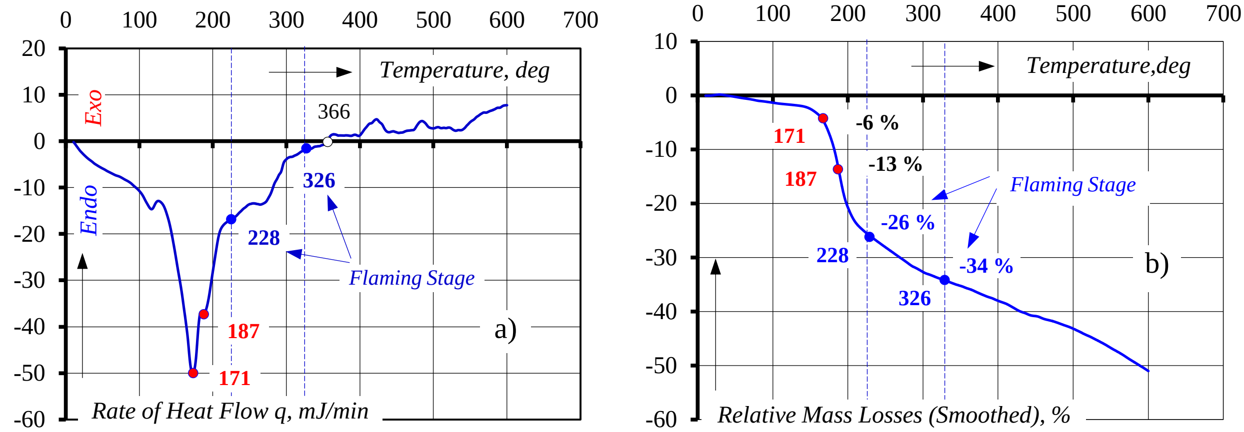
On the basis of prior art, as well as on our own former experience in plasma-aided surface (capillary) impregnation of wood, [5÷11], an oxidative (nitrogen oxides, NO_x) surface plasma pre-treatment has been applied on both sides of the test samples for 60 sec in *DBD* at industrial frequency (50 Hz) and 9, 13 and 17 kV (*RMS*), [6÷12].


a)



b)

Fig.2. General view (a) of a wood sample after the formation of new charcoal finish layer. The sample has dimensions of length/width/thickness: 150x30x5 mm. Maximum relative quantity of the three test impregnating solutions or *relative consumption rate* after plasma surface pre-treatment at different voltage – 9, 13, and 17 kV (RMS) and industrial frequency (50 Hz), is given (b). The relative consumption rate of bare or non-treated wood sample is 1.5 ml (cm^3) per sample or the consumption rate is 0.139 l/m^2 (dm^3/m^2).



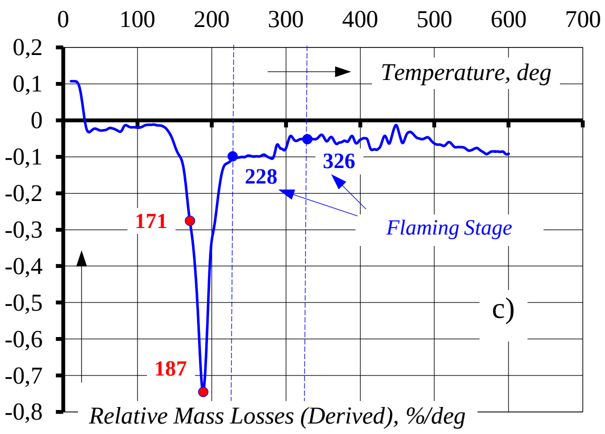


Fig.3. Thermal analysis – *TGA* (a), *DSC* (b) and *DTA* (c) -spectra of *phosphor flame retardant* (*PFR*) in air (heating rate: 10 °C per minute). It is shown the flaming stage of *European White Pine* (*Pinus Sylvestrus*, Bulgaria) – from 228 to 326 °C.

Anionic phosphate surfactant ("*Aniticrystallin A*", Chimatech, Ltd., Bulgaria) in quantity of 5 vol. %, and *siloxane surfactant* (super spreader: Y-17113, *Momentive Performance Materials* GmbH & Co. KG, Germany) in quantity of 0.1 vol. % have been used to control the ion activity of the *FR*-impregnation solution and its surface tension. The used anionic surfactants, alone and in combination with siloxane surfactant, lower the surface tension of the impregnating solution and thus allowing it to wet and penetrate solids, [6÷11].

3. Experimental Results and Discussion

The results from the thermal analysis of the used *PFR*– rate of heat flow, relative mass losses, and derived mass losses are presented on Fig.3, [11].

The stage of flaming (228÷326 °C) of *European white pine* characterized by the release of flammable gases and vapors is shifted towards higher temperature so that the *PFR* has undergone necessary chemical transformation (peak at 187 °C; 26 % relative loos of masses) and prepared the charcoal decomposition of cellulose, Fig.3.

The flame retardation effect of plasma-aided *PFR* (*BIS*) impregnated *European white pine* was shown by *DSC* and *TGA*-thermal analysis spectra in the flaming stage of temperature interval - 228÷236 °C, Fig.4.

On this basis it was revealed the heath development of *European white pine* samples impregnated with *BIS* at different temperature prior to the temperature range of flaming stage: 190, 210, 230, 250, and 270 °C, Fig.5.

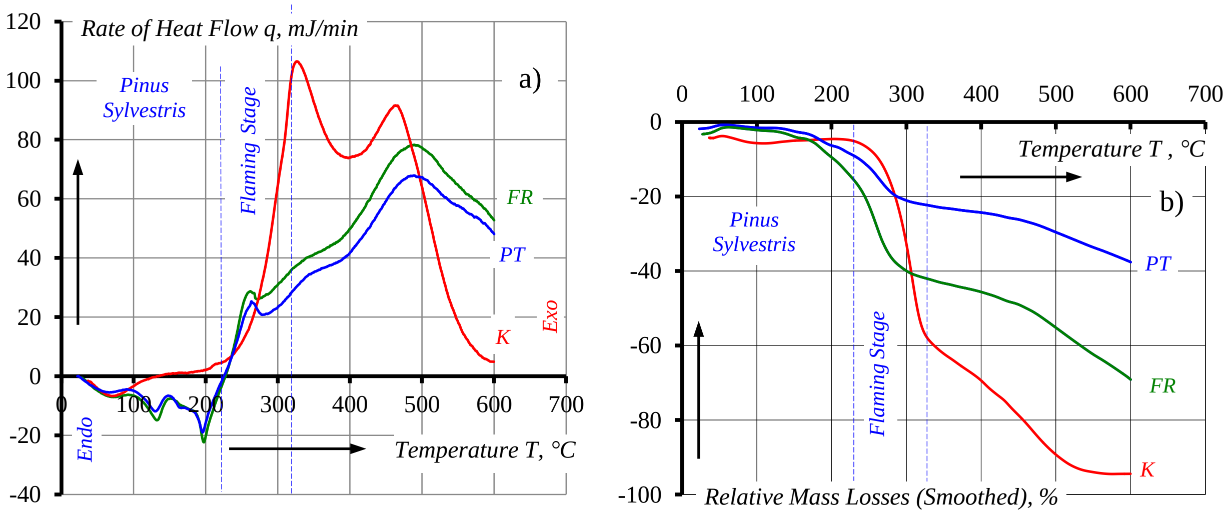


Fig.4. Thermal analysis – *DSC* (a) and *TGA* (b) -spectra of *European white pine* (*Pinus Sylvestris*) bare wood (*K*); *BIS*-impregnated wood (*FR*); plasma-aided *BIS*-impregnated wood.

Some cross-sectional visualization of surface charcoal coatings in the direction of the wood capillaries and transverse to them after capillary and surface impregnation (without plasma pre-treatment) by the used test *FR*-solutions at consumption rate of 0.139 l/m^2 (dm^3/m^2) and charcoal coating formation are shown on Fig.6.

The analysis of the produced visualizations, Fig.6, shows that the main problem for the wood sample flame retardation is the presence of many defects that violate the integrity of the coating. These concerns most closely to the sample impregnated with the *BIS*, Fig. 6. The number of defects and malformations decreases in samples with surfactants assisted impregnation (*BIS/A5* and *BIS/A5-S*).

The experimental study for plasma-aided impregnation has been conducted with three modes of plasma pre-treatment (at 9, 13 and 17 kV (RMS) and 50 Hz; air gap of 6 mm and alkali glass dielectric barrier thick 3 mm) and three test *PFR* impregnating solutions. The study was carried out for two different consumption rates: the first one is the maximum consumption rate of bare wood sample – 1.5 cm^3 per sample or 0.139 dm^3/m^2 for each of the impregnation solutions, Fig.8a; the second one is the maximum consumption rate (after Fig.2b) for each sample and solution, Fig.8b.

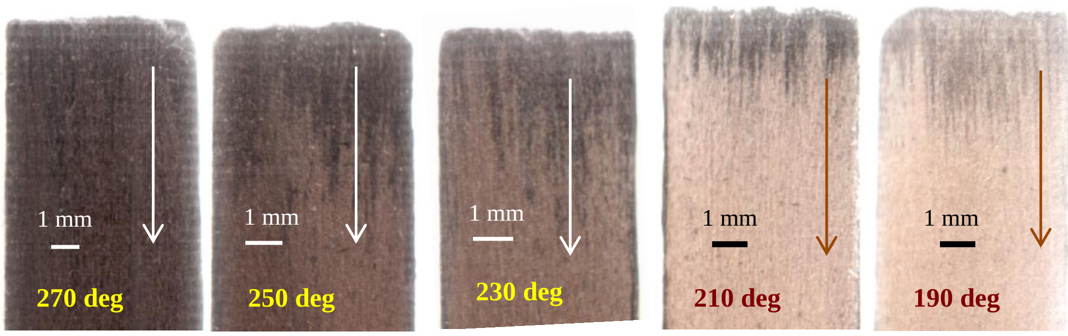


Fig.5. Cross-sectional view of the wood sanding finished samples (very fine sandpaper ISO/FEPA Grit size, ISO 6344: **P280**; average grain size: 52.2 μm), which displays the charcoal coatings along the capillaries (in the arrow direction) and transversely of them at different temperatures of heat development (from 190 to 270 °C). A wood sample surface prior to sanding is also shown. Obviously, the best charcoal coating visualization in the area of capillary impregnation (in the direction of the arrow) has been obtained at 230 and 250 °C. This is the area of the best heat *PFR* development (decomposition) process of hemicellulose (180÷350 °C).

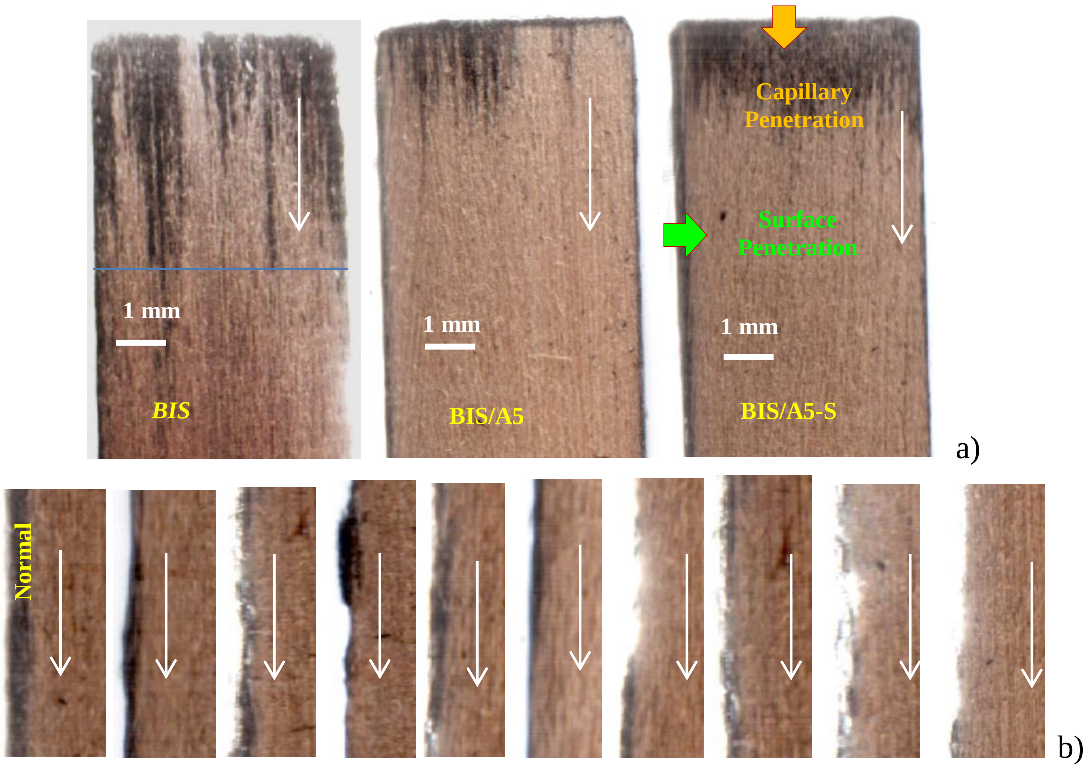


Fig 6. Cross-sectional visualization of charcoal surface coatings (a) in the direction of the wood capillaries (arrow's direction) and transverse to them after capillary and surface impregnation with three test *FR*-solutions at consumption rate of 0.139 l/m^2 (dm^3/m^2), and formation of charcoal layers. Different charcoal coating defects and malformations (b) occurred on the surface of a single sample (*BIS*).

Some very important conclusions can be drawn: *i* – two different kinds of solution (liquid) penetration in the depth of wood were manifested: the first one in the direction of the capillaries – capillary transfer or impregnation, and the second across the capillary – wicking (surface) transfer or penetration; *ii* – the depth of penetration in these two cases differs substantially - almost ten times, Fig.7; *iii* – the mode of plasma pre-treatment, the use of different surfactants and different amount (consumption rate) of *PFR* don't increase the thickness of charcoal coating – it remains within the range of 1.0÷3.5 mm for *capillary impregnation*, and 0.10÷0.45 mm for *surface impregnation*, Fig.7.

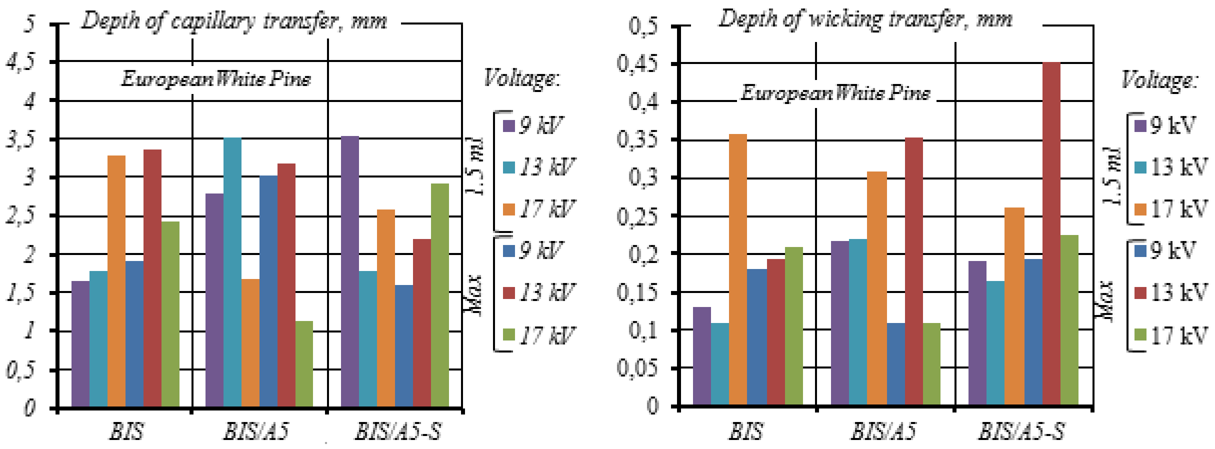


Fig.7. Effect of plasma pre-treatment mode (voltage), used impregnation *FR*-solution (surfactants), and consumption rate (maximum, Fig. 2; 1.5 cm^3 per sample or 0.139 dm^3/m^2) on the penetration depth: on capillary spreading (a) in the direction of wood capillaries, and on wicking (b) in the transversal direction of them.

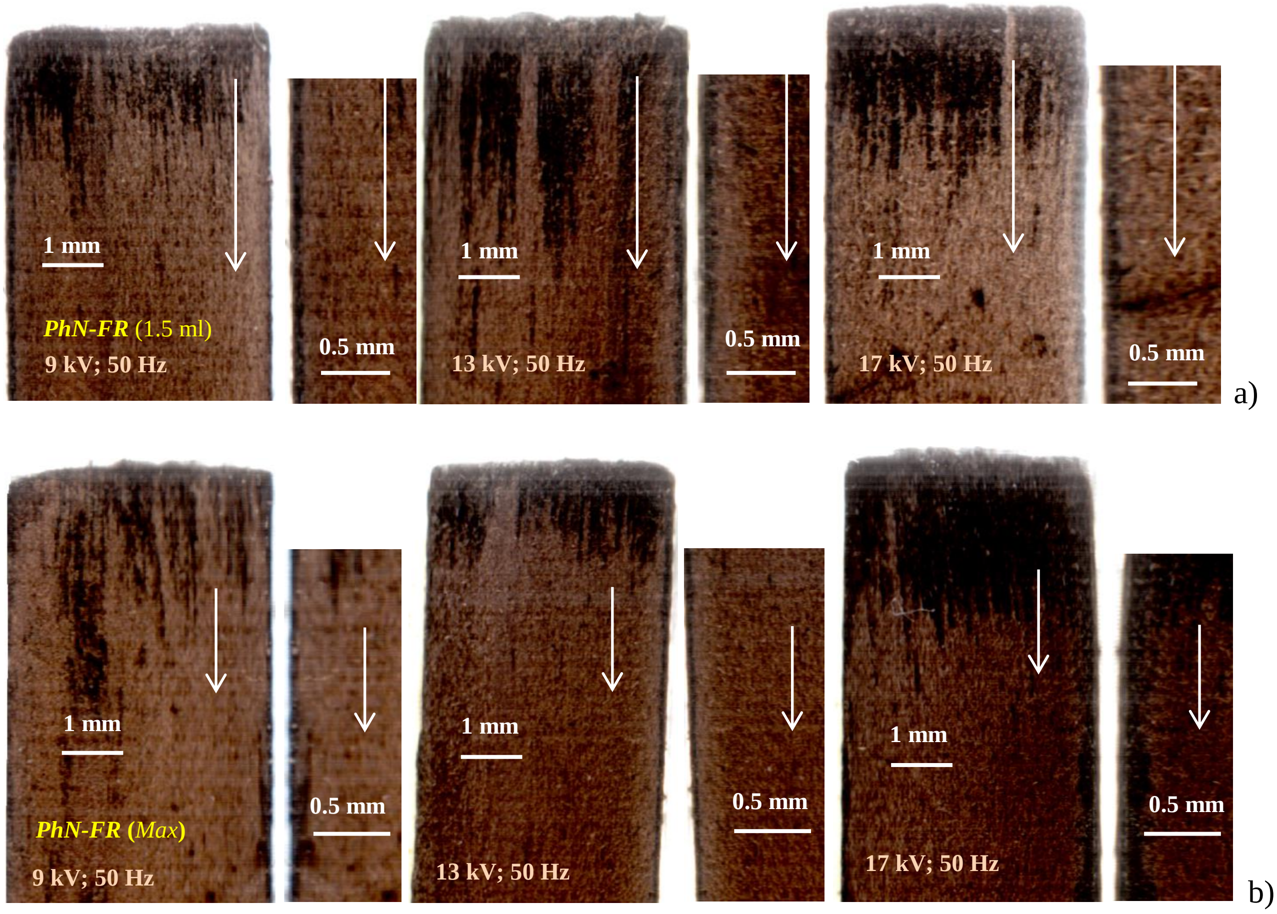


Fig.8. Cross-sectional visualization of charcoal surface layers (a) in the direction (at left) of the wood capillaries (in the arrow direction) and transverse to them (at right) after plasma-aided surface impregnation with three test *FR*-solutions at consumption rate of 1.5 cm^3 per sample (a) or 0.139 l/m^2 (dm^3/m^2) and different maximum consumption rate (b), and charcoal layers formation at 230 °C.

4. CONCLUSION

The used *PFR* allows to visualize the penetration of *FR*-solutions in the depth of the wood surface and to measure the two depths of penetration – the depth of capillary and surface (wicking) penetration. The effect of plasma pre-treatment can be successively assessed in a quantitatively and qualitatively manner.

All this enables us to say that not the thickness of the charcoal coating but its quality determines the flame retardation of the produced charcoal finish. By choosing plasma pre-treatment mode, adding surfactants to *BIS*-impregnating solution and increasing the *PFR* solution consumption rate we mainly reduced the defects and malformations in the charcoal layer.

REFERENCES

[1] Van der Veen I., De Boer J. (2012), *Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis;* Elsevier Ltd., Chemosphere, Vol.: 88, pp. 1119÷1153; *http://dx.doi.org/10.1016/j.chemosphere.2012.03.067.*

[2] Schartel B. (2010), *Phosphorus-based Flame Retardancy Mechanisms—Old Hat or a Starting Point for Future Development?* Materials, 2010, Vol.:3, pp. 4710÷4745; doi: 10.3390/ma3104710; *www.mdpi.com/journal/materials*.

[3] Lowden L., Richard T., *Flammability behavior of wood and a review of the methods for its reduction;* Fire Science Reviews, Springer Open Journal, 2013, 2:4, p. 19; *http://www.firesciencereviews.com/content/2/1/4*.

[4] Morgan, A. - Guest Editor (2015), *Innovative and Sustainable Flame Retardants in Building and Construction: Non-halogenated phosphorus, inorganic and nitrogen flame retardants;* PINFA Publisher, pp. 1÷51; *http://pinfa.org*.

[5] Dineff P., Kostova L. (2005), *Method for Plasma Chemical Surface Modification*, H05H 1/24, International Patent Publication No.: WO Patent 2006/133524 A2; International Patent Application No.: PCT/BG2006/000012; Priority Date: 14.06.2005 (109189); Publication Date: 21.12. 2006.

[6] Dineff P., Gospodinova D. (2007), *Plasma Aided Capillary Impregnation of Hardwood with Ionic Water Solution*, XV International Symposium on Electrical Apparatus and Technologies "SIELA'07", Plovdiv, Bulgaria, 31 May÷01 June, 2007; Proceedings of papers, Vol.: 1, 2007, pp. 33÷40

[7] Dineff P., Gospodinova D. (2007), *Plasma Aided Capillary Impregnation of Softwood and Wood Products with Ionic Water Solution*, XV. International Symposium on Electrical Apparatus and Technologies "SIELA'07", Plovdiv, Bulgaria, May 31÷June 01, 2007; Proceedings of papers, 2007, Vol.: 1, pp. 41÷48

[8] Dineff P., Gospodinova D., Kostova L. (2007), *Ion-Activated Water Solution Containing Flame Retardant for Plasma Aided Technology of Fire Protection and Safety*, IX. Scientific-Professional Symposium on Cooperation of Researches of Different Branches in the Field of Material Protection "YUCORR'07"; Tara, Serbia, May 21÷24, 2007. Proceedings of Papers, 2007, pp. 297÷301

[9] Dineff P., Gospodinova D. (2008), *Plasma aided impregnation technology for flame retarded wood producing*, VI-th International Conference on Challenges in Higher Education and Research in the 21-st Century "CHER-21'08". Sozopol, Bulgaria, June 04÷07, 2008; Proceedings of full papers, 2008, pp. 286÷290

[10] Dineff P., Gospodinova D., Kostova L., Vladkova T., Erfan C. (2008), *New attempt at plasma aided flame retardation in wood and cellulosic fibrous materials,* XX-th Congress of The Society of Chemist and Technologist of Macedonia "BICONGRESS'08", Ohrid, Macedonia, September 17÷20, 2008; Proceedings of papers, 2008, PPM-11-E: pp. 1÷4

[11] Dineff P., Gospodinova D., Kostova L., Vladkova T., Erfan C. (2008), *Plasma aided surface technology for modification of materials referred to fire protection;* Problems of Atomic Science and Technology, 2008, Issue: 6; Series Plasma Physics (14), pp. 198÷200

[12] Dineff P. (2009), *Plasma aided impregnation technology for flame retardancy of porous materials*; VI-th International Congress "Machines, Technologies, Materials - MTM 2009", February 18÷20, 2009; Sofia, Bulgaria; Scientific Proceedings of The Scientific Technical Union of Mechanical Engineering, Year: XVI, Vol.:6/109, 2009, Industrial Management, Vol.: 2, pp. 26÷31 (on Bulgarian)

Authors: Ivaylo Ivanov, Assist. prof.; Dilyana Gospodinova, Assoc. Prof., Ph.D; Peter Dineff, Prof. D.Sc.; Department of Electrical Apparatus, Faculty of Electrical Engineering, Technical University; E-mail address: *igi@tu-sofia.bg; dilianang@abv.bg*; *dineff_pd@abv.bg*

Received 30 September 2015 **Reviewer:** Prof. Ph.D. Margarita Neznakomova