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PLASMA AIDED CAPILLARY IMPREGNATION OF HARDWOOD WITH IONIC WATER SOLUTION

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Abstract. The positive results of plasma aided capillary impregnation (*PACI*) are determined by the plasma-chemical activation and plasma polarization of the wood surface, which are accompanied by important change in its ion activity. Correcting the wood-impregnating solution in accordance with the changed ion activity by introducing ionic surfactants allows a considerable improvement of the impregnation process efficiency. This new technology has been admitted to industrial implementation after confirming its efficiency before an accredited state laboratory for fire protection of wood and wooden constructional structures.

Keywords: anionic, cationic and amphoteric surfactants, capillary impregnation, drop capillary test, flammability, ignitability, plasma activation, rate of capillary adsorption, water solution containing flame retardant.

INTRODUCTION

Wood inactivation

A wood surface, which is exposed to a high temperature condition, can experience surface inactivation. An inactivated wood surface does not bond well with adhesive and impregnating agent, because the inactivation process, such as drying or mechanical machining, reduces the ability of an adhesive or impregnating agent to properly wet, flow, penetrate, and be chemically bonded. Thus, the ability to establish a close contact between surface wood molecules and adhesive or impregnating agent is diminished.

Wood (chemical) *inactivation* is a surface phenomenon affecting just a thin outer layer of wood. Initially, *Northcott* (1959) designated inactivation as "casehardening" of a wood surface. Later, *Hancock* (1963) introduced the term "inactivated" to denote the apparent adverse effect of this type of wood surface on the reactivity of phenolic adhesive. *Troudhton and Chow* (1971) defined a surface inactivation phenomenon as a heat-induced change in the wood veneer surface resulting in loss of bonding ability, [1].

Inactivation reflects physical and chemical modifications of the wood surface. These modifications create hydrophobic and weak boundary layers, which reduce wettability and cause poor adhesion. Some wood species are more susceptible to surface inactivation than other. Industrial gluing problems, which originate from wood surface inactivation, became apparent because plywood production expanded drastically, (*Christiansen*, 1990).

Different wood

Wood is commonly classified as either softwood or hardwood. The wood from conifers (e.g. pine) is called softwood, and the wood from broad-leaved trees (e.g. oak) is called hardwood.

Table 1. Heart hardwood investigated samples.

Species of hard wood (seasoned & dry)	Small pore			Large pore	
	Cherry	Beech	Maple	Ash	Oak
DENSITY (dry), kg/m^3	534÷425	552÷717	620÷755	540÷670	590÷930
DENSITY (measured), kg/m^3	620	656	665	692	743

The structure of the hardwoods is more complex. They are more or less filled with pores: in some cases (oak, chestnut, ash) quite large and distinct, in others (beech, poplar, cherry) too small to be seen plainly without a small hand lens. In discussing such woods it is customary to divide them into two large classes, ring- or large porous and diffuse- or small porous.

Wood is a high porous material (porosity 65 ÷ 75 %), the capillary activity of which depends too much on the size of pores, and on the chemical inactivity of the wood surface. The chemical inactivity is also accompanied by certain (stable) ionic balance of the wood surface. The wood surface activation should be invariably accompanied by a change in the wood surface ion activity, which is very important for processes such as capillary impregnation with flame retardants.

Plasma aided capillary impregnation

Impregnation is a contemporary process that is widely used for the modification of porous materials, including the fire protection of wood and wood products as well. The capillary impregnation with water solutions containing flame retardants represents a successful technological approach to the fire protection of flammable materials, [2].

Plasma aided capillary impregnation (*PACI*) is a new method which not only makes use of the cold plasma of a atmospheric dielectric barrier discharge for chemically activating the wood surface, but also takes into account the changed ionic and capillary activity after plasma treatment in order to coordinate this change with the ionic activity of impregnating solutions. For that purpose, three correcting ionic solutions are used, which contain various ionic surfactant systems: anionic, cationic, and amphoteric (anionic & cationic), [3].

The TASK of the present work consists in illustrating the basic principle of plasma aided capillary impregnation of hardwood – the principle of coordinating the ionic activity of the wood surface, which is its own and/or acquired after plasma activation, with the ion activity of wood-impregnating water solutions.

EXPERIMENTAL INVESTIGATION

The basic wood-impregnating water solution with the trade name *CSE-96* of *Interiorprotect, Ltd.* (Sofia, Bulgaria) is used, and its ion activity is corrected by adding various quantities of ionic surfactant corrective solutions – 2, 5, and 10 vol. %. *CSE-96* is a 30 mass % water solution of phosphorus and nitrogen-containing flame retardants, representing a colorless solution of density 1.14 ÷ 1.17 g/cm^3, with controlled contents of phosphorous (P_2O_5) 11 ÷ 13 mass % at pH = 7 ÷ 8 (for a one-percent solution).

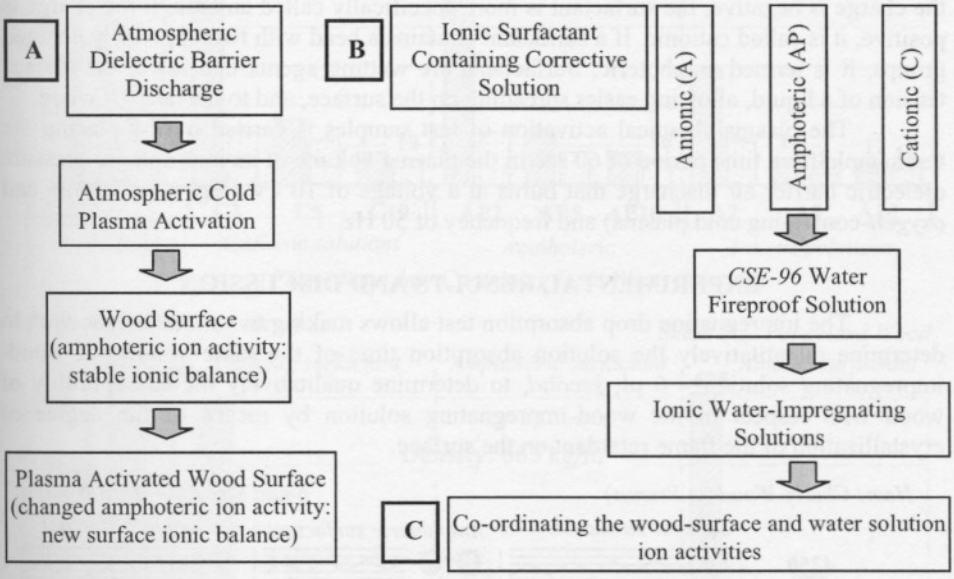


Figure 1. Plasma aided capillary impregnation technology with ionic water solutions: **A** – plasma-chemical surface activation – changing the wood-surface chemistry and ionic surface activity; **B** – ionic surfactant corrected water-impregnating solution; **C** – co-ordination of wood-surface and water ion activities.

Initially, this experiment has permitted the analysis of the capillary activity of five species of small and large pores species of hard wood. Test samples of wood of size 5 × 30 × 150 mm have been manufactured. Heart wood has been used for their fabrication. Wood materials of various structures and densities have been selected, Table 1, which should ensure the necessary representativeness of the results obtained.

The capillary activity of surface wood layer is measured by the time needed for absorbing a microdrop from the solution examined. The drop has a volume of 6 μl, which ensures that its own weight will not affect its spherical shape and the process of absorbing. This drop is produced by means of an automatic pipette, the volume of which can be regulated from 1 μl to 20 μl, [1].

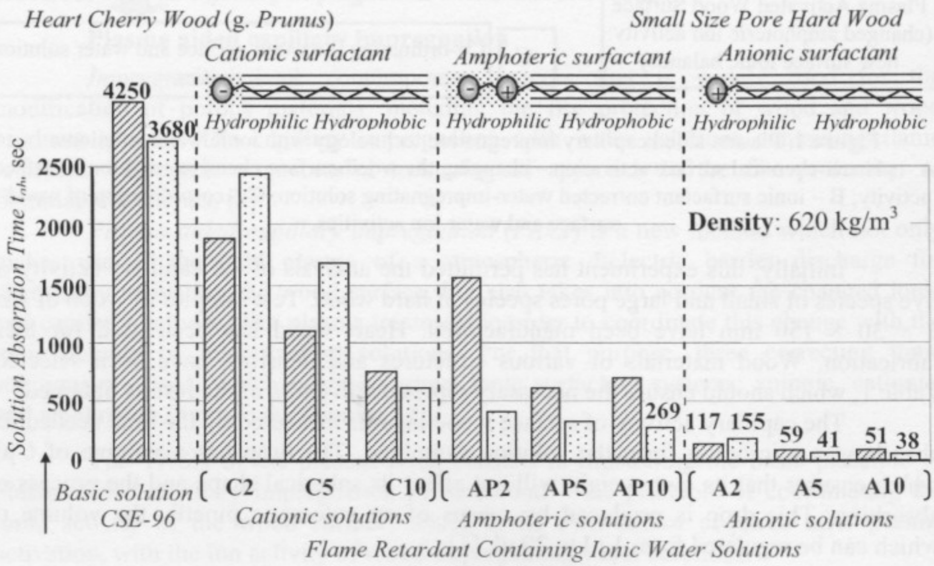
Plasma aided impregnation technology with ionic water solutions containing flame retardant is based on both the cold plasma chemical and ionic surface activation, and the ion activity correction of wood-impregnating water solutions. Surfactants are usually compounds that are amphihilic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads"), Fig. 1. A surfactant can be classified by the presence of formally charged groups in its head.

A surfactant which dissociates in water and releases cation and anion (or the both) is termed ionic surfactant. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed amphoteric. Surfactants are wetting agents that lower the surface tension of a liquid, allowing easier spreading on the surface, and to the deep of wood.

The plasma-chemical activation of test samples is carried out by placing the test sample for a time period of 60 sec in the plasma volume of an atmospheric-pressure dielectric barrier air discharge that burns at a voltage of 10 kV (regime of *ozone*- and *oxygen*-containing cold plasma) and frequency of 50 Hz.

EXPERIMENTAL RESULTS AND DISCUSSION

The impregnation drop absorption test allows making two assessments: *first*, to determine quantitatively the solution absorption time of the same volume of wood-impregnating solution – 6 μl; *second*, to determine qualitatively the susceptibility of wood with respect to the wood-impregnating solution by means of the degree of crystallization of the flame retardant on the surface.



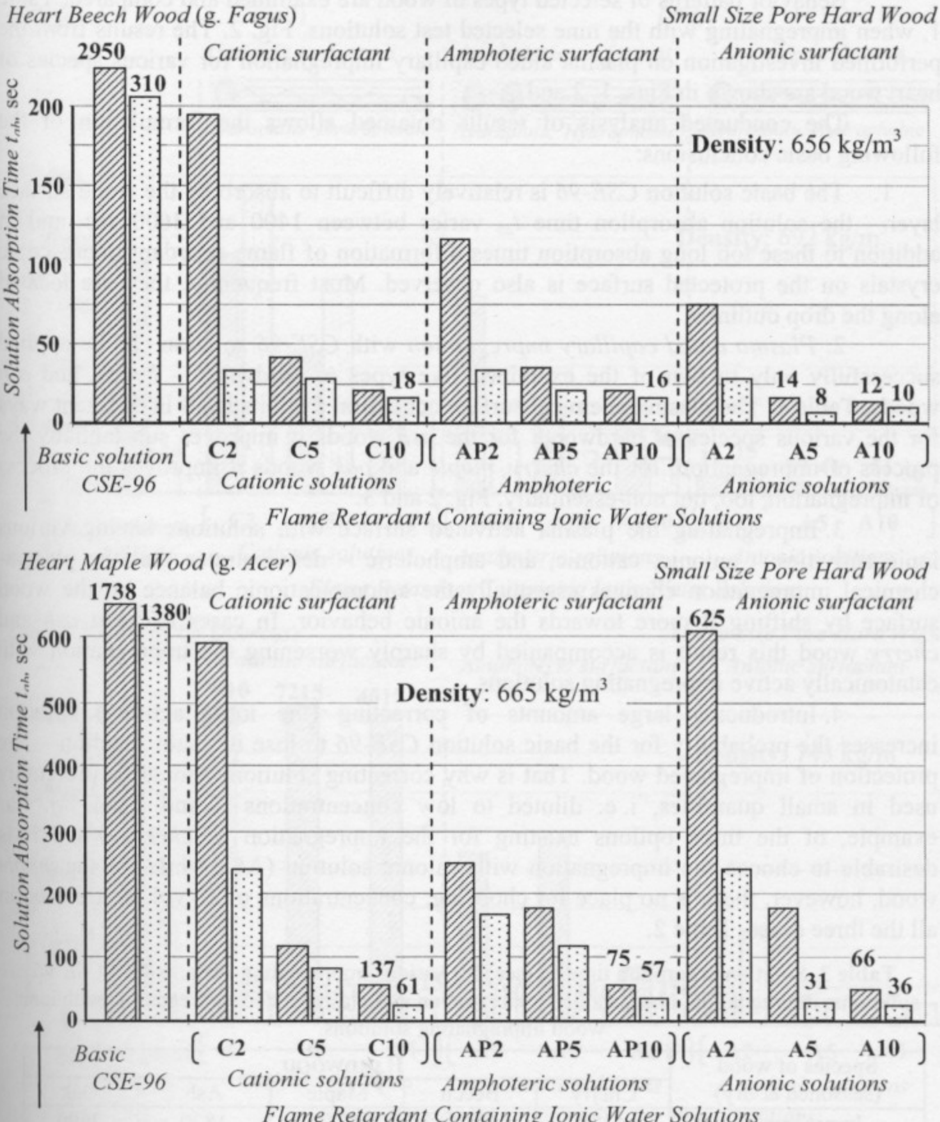


Figure 2. Results of impregnation drop absorption (vol.: 6 μl) test for investigated small pore hardwood samples:

C2, C5, C10 – cationic water-impregnating solutions with 2, 5, and 10 vol. % of surfactant; *AP2, AP5, AP10* – anionic water-impregnating solutions with 2, 5, and 10 vol. % of surfactant; **A2, A5**, *A10* – amphoteric water -impregnating solutions with 2, 5, and 10 vol. % of surfactant.

Behavior patterns of selected types of wood are examined and compared, Table 1, when impregnating with the nine selected test solutions, Fig. 2. The results from the performed investigation on plasma aided capillary impregnation for various species of heart wood are shown in Figs. 1, 2 and 3.

The conducted analysis of results obtained allows the formulation of the following basic conclusions:

1. The basic solution *CSE-96* is relatively difficult to absorb by the wood surface layer - the solution absorption time t_{ab} varies between 1400 and 3600 sec, and in addition to these too long absorption times a formation of flame retardant microscopic crystals on the protected surface is also observed. Most frequently, they are located along the drop outline.

2. *Plasma aided capillary impregnation* with *CSE-96* solution can be applied successfully only to two of the examined five types of hardwood – *beech*, and *ash* woods, Table 1. The plasma-chemical surface activation exhibits itself in different ways for the various species of hardwood: for the *ash* woods it improves substantially the process of impregnation; for the *cherry*, *maple* and *oak* woods it improves the process of impregnation, too, but non-essentially, Fig. 2 and 3.

3. Impregnating the plasma activated surface with solutions having various ionic activities – anionic, cationic, and amphoteric – demonstrates that the plasma-chemical impregnation changes essentially the anionic-cationic balance on the wood surface by shifting it more towards the anionic behavior. In cases of heart *ash* and *cherry* wood this result is accompanied by sharply worsening the impregnation with catatonically active impregnating solutions.

4. Introducing large amounts of correcting (the ionic activity) solution increases the probability for the basic solution *CSE-96* to lose its main function – fire protection of impregnated wood. That is why correcting solutions should be preferably used in small quantities, i. e. diluted to low concentrations (2 and 5 vol. %). For example, of the three options existing for the impregnation of *cherry* wood it is desirable to choose the impregnation with anionic solution (A5), while for the *maple* wood, however, there is no place for choosing: concentrations of 10 vol. % are used in all the three cases, Table 2.

Table 3. Solution absorption time t_{ab} (sec) for various impregnating variants with *CSE-96* solutions: impregnation, plasma aided impregnation and plasma aided impregnation with ionic wood impregnating solutions.

Species of wood (seasoned & dry)		HARDWOOD				
		Cherry	Beech	Maple	Ash	Oak
Impregnation		4250	2950	1738	1820	3600
Plasma	CSE-96	3680	310	1380	150	1300
Plasma	CSE-96+A	41/A5	26/A2	36/A10	41/A5	68/A5
Plasma	CSE-96+C	650/C10	18/C10	45/C10	600/C10	147/C5
Plasma	CSE-96+AP	269/AP10	35/AP2	57/AP10	269/AP10	190/AP2

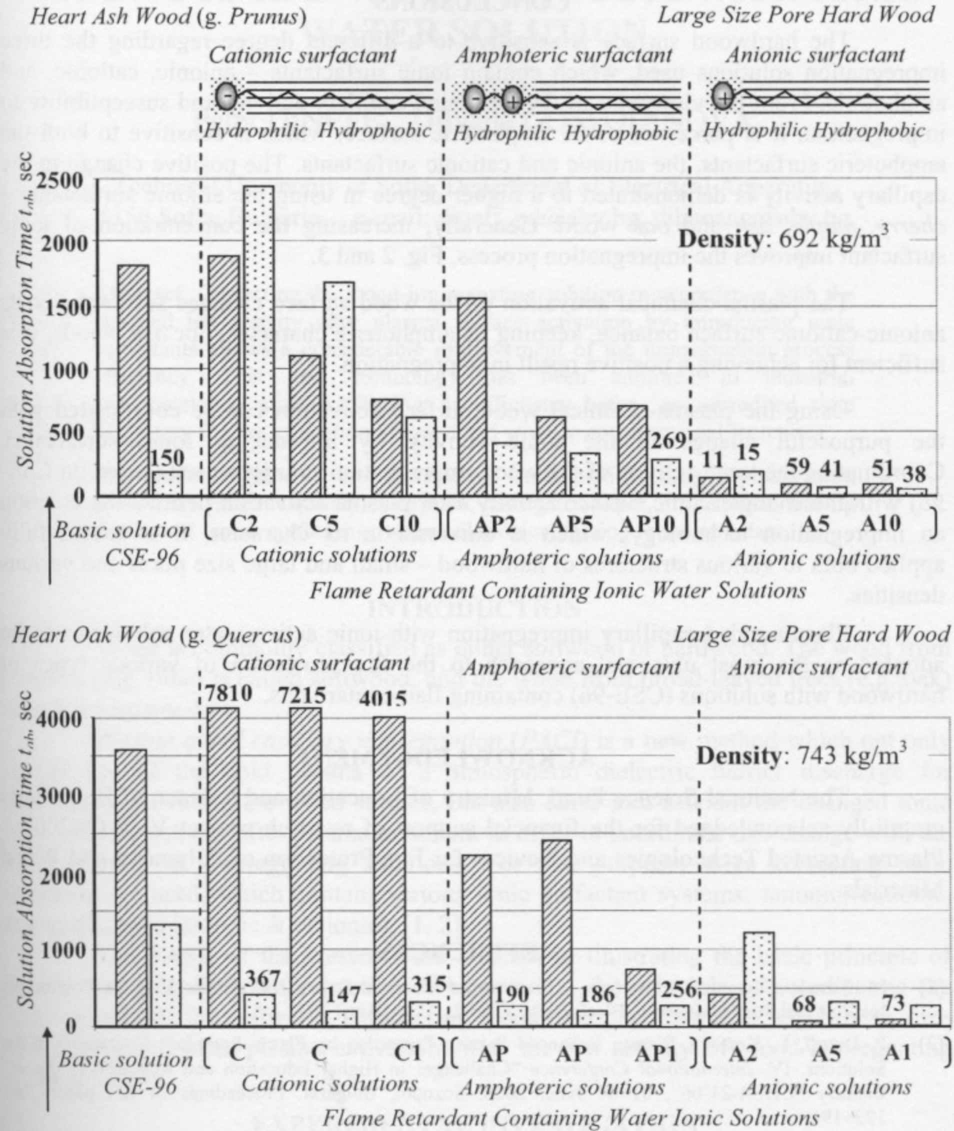


Figure 3. Results of impregnation drop absorption (vol.: 6 μl) test for large size pore hardwood samples:

C2, C5, C10 – cationic water-impregnating solutions with 2, 5, and 10 vol. % of surfactant; *AP2, AP5, AP10* – anionic water-impregnating solutions with 2, 5, and 10 vol. % of surfactant; **A2, A5,** *A10* – amphoteric water- impregnating solutions with 2, 5, and 10 vol. % of surfactant.

CONCLUSIONS

The hardwood surface is sensitive to a different degree regarding the three impregnation solutions used, which contain ionic surfactants – anionic, cationic, and amphoteric. From the viewpoint of demonstrated capillary activity and susceptibility to impregnation, it is perceived as an amphoteric surface, which is sensitive to both the amphoteric surfactants, the anionic and cationic surfactants. The positive change in the capillary activity is demonstrated to a higher degree in using the anionic surfactants – *cherry*, *maple*, *ash* and *oak* wood. Generally, increasing the concentration of ionic surfactant improves the impregnation process, Fig. 2 and 3.

The plasma-chemical activation of the wood surface changes substantially its anionic-cationic surface balance, keeping its amphoteric character. For *ash* woods, it is sufficient for achieving a positive result in impregnation.

Using the plasma-chemical wood surface activation can be coordinated with the purposeful change in the ionic activity by introducing ionic surfactants. Coordinating the ionic activity of the wood-impregnation solutions used (based on *CSE-96*) with the changed ionic surface activity after plasma activation permits the creation an impregnation technology, which is universal in its character. It is successfully applied both to various structures of hardwood – small and large size pores and various densities.

Plasma aided capillary impregnation with ionic active water solutions can be adopted as the most universal approach to the fire protection of various types of hardwood with solutions (CSE-96) containing flame retardants.

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