

## Characterization of Wooden Surfaces treated by dielectric barrier Discharges at atmospheric Pressure. The Estimation of activated surface groups by contact angle measurements and UV/VIS-Spectrometry

Henrik Schulz\* and Anita Horn, Archäomertrie-Labor der HAWK Hildesheim  
Kaiserstr. 19, D-31134 Hildesheim, Germany

### Abstract

A simple model of determining the change of the surface groups onto beech and spruce wood after a treatment by dielectric barrier discharge at atmospheric pressure has been developed, based on the measurement of the contact angle of aqueous test liquids under *n*-hexane as the outer fluid. The relationship between the cosines of the contact angles of the untreated and plasma treated wooden surfaces is linear but strongly sensitive to the interaction parameter  $\phi$  of the adsorption. The slope of this simple linear relation is unit and the interception is equal to the change in the spreading pressure  $\Delta\pi$ . The interceptions provide the values of  $\Delta\pi$  between 1 to 7 mNm<sup>-1</sup> for spruce wood and 8 to 14 mNm<sup>-1</sup> for beech wood. These results were combined with the displacement of the absorption maximum of the staining of the plasma treated wooden surface with toluidine blue as metachromatic dye. Hereby it is possible to estimate the change in the surface concentration  $\Delta N$  of the activated functional groups onto the wooden surface after the plasma treatment. The predicted values of  $\Delta N$  are 7.1 10<sup>12</sup> to 5.0 10<sup>13</sup> cm<sup>-2</sup> for spruce wood and 1.3 to 2.3 10<sup>14</sup> cm<sup>-2</sup> for beech wood. The magnitude of these values are suitable and comparable with those known from inorganic isolators like silicon dioxide and aluminium oxide.

**Keywords:** wooden surface, dielectric barrier discharge, spreading pressure, surface concentration, staining, plasma

### INTRODUCTION

Long before we have called it a sustainable growing material, wood was one of the oldest stuff and trading material that human societies worked with. Nowadays wood gets an increasing importance as traditional engineering material [1-4].

A major problem in wood technology is the long term stability and reliability of any kind of bonds and their adhesiveness. Wood is obviously such an extreme complex material. Also the wooden surface is different and depends upon the origin of the tree, its density and water content, the extent of seasoning, the direction of the cut, and many other factors [5]. Therefore it is valuable to pay more attention to the structure, grain and seasoning of wood.

---

\* correspondence should addressed to:

e-mail: [henrik.schulz@archaeometrielabor.com](mailto:henrik.schulz@archaeometrielabor.com) or fax: (+49)-(5121)-881-371

Additionally to the three main wood components cellulose, lignin and hemi cellulose wood contains small amounts of extractives that are characteristic for each special wooden specimen. But these minor constituents have great influence onto the properties of the industrial made wooden products. Reasons enough to find a technique that equalize the wooden surface and create good conditions for coating and adhesion in general. We have chosen a treatment by dielectric barrier discharge (DBD) under normal atmosphere, i.e. in the presence of air. Figure 1 illustrates the principle of the DBD technique.

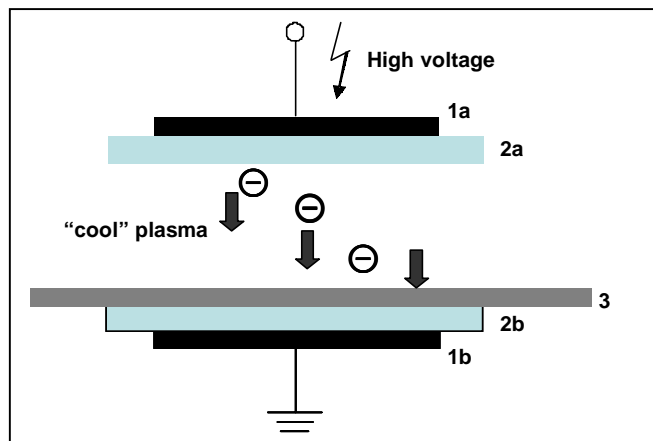


Figure 1 Scheme of the low electric current plasma chamber and the *DBD* technique (*Dielectric Barrier Discharge*, [6,7]), 1a and 1b: electrodes, 2a and 2b: dielectrics, 3: wooden surface

The DBD technique used a radio frequency inductor to produce an electrostatic field under a high voltage potential between the electrodes. In addition the electrostatic field is attenuated by the dielectric material that surrounded the electrodes, e.g. boron nitride that barrier the counter electrode. This barrier discharge of short pulse durations and repetitions results in only low energetic impacts by discharging onto the surface of the material between the two electrodes. This is important because chemical reactions at the wooden surface are strongly diminished and practically negligible.

It is known that water and other hydrophilic liquids spread more effectively on the wooden surface after the electric discharge procedure than before. But there is also known that these increase in spreading is not a long-term effect. It is diminished few days after the treatment and has disappeared total at the end. The explanation of the higher hydrophilic activity of the wooden surface immediately after treatment with plasma seems to be clear because of a higher surface free energy, but what is the meaning of the time relaxation and the delay

process of the activated surface energy? At first we will consider the situation of a real wooden surface under normal atmosphere of moist air. A certain number of water molecules from the gaseous phase will be adsorbed at the surface and be stabilized by mediation of the hydrogen bonding via the ubiquitous hydroxy groups of the cellulose but as well of the lignin and other resinous compounds. The situation of the adsorption layer at the wooden surface will be changed vigorously by the impacts of the electrical charged particles of the plasma. One of the main topics is questioned about the number of adsorbed molecules at the interfacial region and the change of that quantity after the plasma treatment. A change in adsorption is always accompanied by a change of energy, in particular the change of the surface free energy  $\Delta G$  or in relation to the change of a specific area  $\Delta A$  the interfacial tension  $\gamma$ :

$$\gamma = \frac{\Delta G}{\Delta A} \quad (1)$$

An easy way to study such changes at the surface of solids by experiments is the so-called wetting procedure. The wetting of a surface by a liquid and their final extent of spreading is very simple but covers a lot of information about the real surface. Figure 2 exhibits the classical three-phase situation of two immiscible fluids 1 and 2 in contact with a plane surface of the solid S. Furthermore the fluid 1 is called the “inner fluid” and fluid 2 the “outer fluid”.

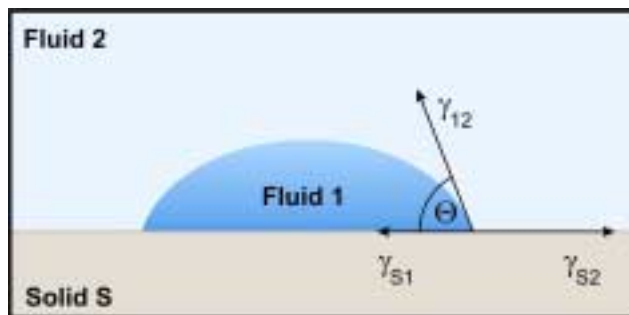


Figure 2 The force equilibrium at the point of the coexistence of the three phases to derive the classical YOUNG’S equation (2) [8]

In the classical way the three depicted arrows symbolise the three forces related to  $\gamma_{12}$ ,  $\gamma_{S1}$  and  $\gamma_{S2}$ . All three forces start at the triple point, i.e. where all of the phases co-exist simultaneously in equilibrium. The directions of  $\gamma_{S1}$  and  $\gamma_{S2}$  are opposite but parallel to the surface of the solid.  $\gamma_{12}$  and  $\gamma_{S1}$  encircle the so-called contact angle  $\Theta$ . If we consider the force balance the YOUNG’S equation (2) straight follows as:

$$\gamma_{12} \cdot \cos \Theta + \gamma_{S1} = \gamma_{S2} \quad (2)$$

Finally we take into account pre-adsorbed molecules onto the surface of the solid S which are belonging to the outer fluid 2 (index: “S2”). Additionally to that pre-adsorption also co-adsorption of other molecules out of the inner fluid 1 is possible. These adsorption phenomena are summarized by the so-called *spreading pressure*  $\pi$ . For the situation as mentioned above (pre-adsorption and co-adsorption) we could formulate:

$$\pi = \pi_{S2,1}$$

The real but just adsorbed molecules decrease the interfacial tension  $\gamma_s$  of the ideal “bare” surface (nothing at all is adsorbed) and can be written to:

$$\gamma_{S2} = \gamma_s - \pi_{S2,1} \quad (3)$$

The combination of the equations (2) and (3) results in equation (4) that we shall use in the following discussion:

$$\gamma_s - \pi_{S2,1} = \gamma_{S1} + \gamma_{12} \cdot \cos \Theta \quad (4)$$

In Table 1 several situations of adsorption at the interfacial molecular level are summarized schematically. The sophisticated real situation is strongly simplified and reduced onto the main topic: distribution and spreading of the adsorbed molecules at the interfacial region.

Table 1 also presents the schedule of the following experiments and investigations.

To compare the different experiments that are summarized in Table 1 we make the following assumptions and postulate:

#### Case 1:

The wooden surface is still untreated by plasma (index “zero”, 0) and is handled under normal atmosphere of moisten air (index “V”, symbolized in Table 1 as circles). The part of pre-adsorption of water molecules (index “V”) is expressed by  $\pi_{0,V}$  as:

$$\gamma_{SV,0} = \gamma_{S,0} - \pi_{0,V} \quad (3.1)$$

After a drop of the test liquid contacts the wooden surface (index “L”) the measured contact angle  $\Theta = \Theta_{0,LV} = \Theta_{0,V}$  describes the YOUNG’s equation (2) in that manner:

$$\gamma_{SV,0} = \gamma_{SL,0} + \gamma_{LV} \cdot \cos \Theta_{0,LV} \quad (2.1)$$

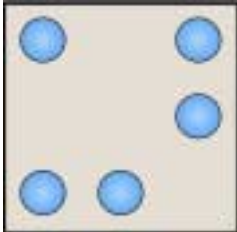
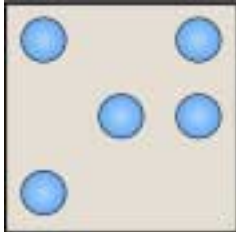
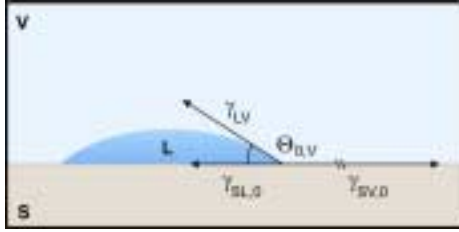

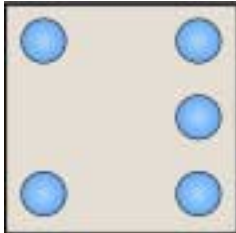
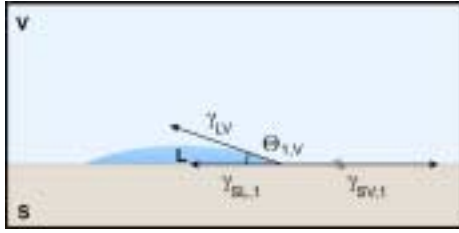
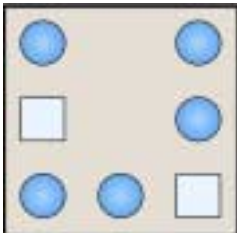
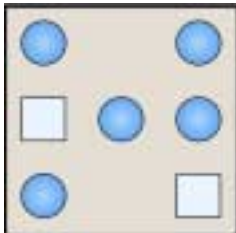
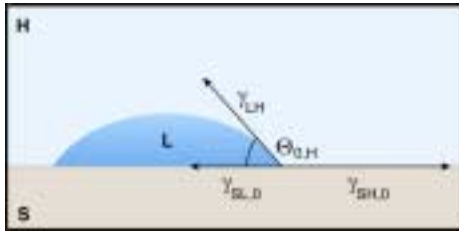
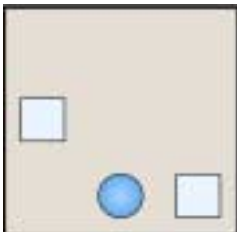
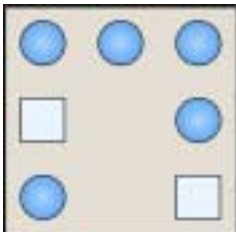
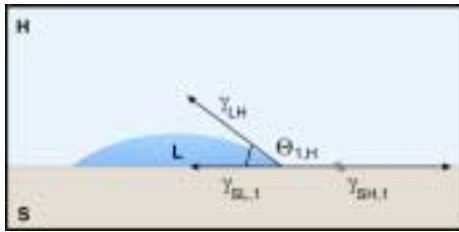
The combination of both terms as given above results in:

$$\gamma_{S,0} - \pi_{0,V} = \gamma_{SL,0} + \gamma_{LV} \cdot \cos \Theta_{0,V} \quad (4.1)$$

Because the statistically number of primary places of specific adsorption of water molecules onto the wooden surface before ( $\pi_{0,V}$ ) and after wetting ( $\pi_{0,LV}$ ) with the test liquid (based on water as solvent) remains fairly constant, we expect:

$$\pi_{0,V} = \pi_{0,LV}$$

**Table 1** Scheme of the molecular distribution at the wood/air interface respectively the wood/outer liquid interface before and after the plasma treatment. (The symbols mean: circles: adsorbed water; squares: co-adsorbed *n*-hexane.)

condition of the wooden surface (S)	before wetting with the test liquid (L)	after wetting with the test liquid (L)	three-phase situation with contact angle $\Theta$
<p>Case 1:</p> <p>The wooden surface is still untreated by plasma (index “zero”, 0) and is handled under normal atmosphere of moisten air (index “V”).</p>	 <p style="text-align: center;"><math>\pi_{0,V}</math></p>	 <p style="text-align: center;"><math>\pi_{0,LV}</math></p>	 <p style="text-align: center;"><math>\gamma_{S,0} - \pi_{0,V} = \gamma_{SL,0} + \gamma_{LV} \cdot \cos \Theta_{0,V}</math></p>
<p>Case 2:</p> <p>The same situation like case 1, but now the wooden surface is just treated by plasma (index “one”, 1).</p>	 <p style="text-align: center;"><math>\pi_{1,V}</math></p>	 <p style="text-align: center;"><math>\pi_{1,LV}</math></p>	 <p style="text-align: center;"><math>\gamma_{S,1} - \pi_{1,V} = \gamma_{SL,1} + \gamma_{LV} \cdot \cos \Theta_{1,V}</math></p>
<p>Case 3:</p> <p>This case is vary similar to case 1, but the initially presence of normal atmosphere (moisten air) is even replaced by <i>n</i>-hexane as outer fluid (index “H”).</p>	 <p style="text-align: center;"><math>\pi_{0,V} + \pi_{0,H}</math></p>	 <p style="text-align: center;"><math>\pi_{0,LV} + \pi_{0,LH}</math></p>	 <p style="text-align: center;"><math>\gamma_{S,0} - (\pi_{0,V} + \pi_{0,H}) = \gamma_{SL,0} + \gamma_{LH} \cdot \cos \Theta_{0,H}</math></p>
<p>Case 4:</p> <p>The situation is like that in case 3, but now the wooden surface is just treated by plasma, was in contact with moisten air and finally the air is replaced by <i>n</i>-hexane as outer fluid.</p>	 <p style="text-align: center;"><math>\pi_{1,V} + \pi_{1,H}</math></p>	 <p style="text-align: center;"><math>\pi_{1,LV} + \pi_{1,LH}</math></p>	 <p style="text-align: center;"><math>\gamma_{S,1} - (\pi_{1,V} + \pi_{1,H}) = \gamma_{SL,1} + \gamma_{LH} \cdot \cos \Theta_{1,H}</math></p>

Case 2:

The same situation like case 1, but now the wooden surface is just treated by plasma (index “one”, 1). The part of pre-adsorption of water molecules before ( $\pi_{0,V}$ ) and after ( $\pi_{1,V}$ ) the treatment is different:

$$\pi_{0,V} > \pi_{1,V}$$

but after wetting the surface with the aqueous test liquid (index “L”) the coverage of water molecules is the same like that before, i.e. the initial situation stated out in case 1:

$$\pi_{1,LV} = \pi_{0,V}$$

With the measured contact angle  $\Theta_{1,V}$  the YOUNG’s equation (4) is actually:

$$\begin{aligned} \gamma_{SV,1} &= \gamma_{S,1} - \pi_{1,V} \quad \text{and} \\ \gamma_{S,1} - \pi_{1,V} &= \gamma_{SL,1} + \gamma_{LV} \cdot \cos \Theta_{1,V} \end{aligned} \quad (4.2)$$

Case 3:

This case is very similar to case 1, but the initially presence of normal atmosphere (moisten air, index “V”) is even replaced by *n*-hexane as outer fluid (index “H”). Both spreading pressures  $\pi_{0,V}$  and  $\pi_{0,H}$  have an effect on the coverage of fluids onto the surface. But the situation of adsorption before and after contact the wooden surface under *n*-hexane with the aqueous test liquids remains unchanged and the same:

$$\pi_{0,V} + \pi_{0,H} = \pi_{0,LV} + \pi_{0,LH}$$

and

$$\pi_{0,H} = \pi_{0,LH}$$

because of

$$\pi_{0,V} = \pi_{0,LV} \quad (\text{see case 1}).$$

Considering the strong polar surface of wood (hydroxy groups) we can expect

$$\pi_{0,V} > \pi_{0,H}$$

The YOUNG term is very similar to case 1:

$$\gamma_{SH,0} = \gamma_{S,0} - (\pi_{0,V} + \pi_{0,H})$$

and

$$\gamma_{S,0} - (\pi_{0,V} + \pi_{0,H}) = \gamma_{SL,0} + \gamma_{LH} \cdot \cos \Theta_{0,H} \quad (4.3)$$

Case 4:

The situation is like that in case 3, but now the wooden surface is just treated by plasma, was in contact with moisten air and finally the air is replaced by n-hexane as outer fluid. The coverage of n-hexane onto the wooden surface before and after the contact with the test liquids remains constant:

$$\pi_{1,H} = \pi_{1,LH}$$

and also unchanged in relation to the untreated situation (see case 3):

$$\pi_{1,H} = \pi_{0,H}$$

Analogous to eq. (4.3) the YOUNG expression is the following:

$$\gamma_{SH,1} = \gamma_{S,1} - (\pi_{1,V} + \pi_{1,H})$$

and

$$\gamma_{S,1} - (\pi_{1,V} + \pi_{1,H}) = \gamma_{SL,1} + \gamma_{LH} \cdot \cos \Theta_{1,H} \quad (4.4)$$

If we consider the ideal situation, where no adsorption at all takes place, we can write:

$$\gamma_{S,0} = \gamma_{S,1}$$

And furthermore is valid:

$$\gamma_{SL,0} = \gamma_{SL,1}$$

because the strength of interaction between the surface groups and the molecules of the test liquids only depends on the kind of intermolecular bonding, and not on the absolute number of places of adsorption onto the surface.

In an easy combination of the equations (4.1) to (4.4) using the simplifications given above we can calculate the change of adsorption  $\Delta\pi = \pi_{0,V} - \pi_{1,V}$  by simple contact angle measurements. Finally we can estimate the absolute number of the activated surface groups immediately after the treatment by dielectric discharges.

To make all these surface phenomena visible we have stained the untreated and plasma treated wooden surfaces with a metachromatic dye. Metachromatism is a phenomenon of the change of the light absorption of dyes which is caused by aggregation and specific adsorption of the dye molecules onto a solid surface. Obviously one of the best investigated staining reaction is the *toluidine blue reaction* [9-11]. Chemically *Toluidine Blue O* is the ionic form (the ammonium and thionium chloride) of 3-Amino-7-(dimethylamino)-2-methyl-phenothiazine. If one extract the ionic form of the toluidine blue out of an aqueous alkaline solution into an aprotic solvent like n-hexane the colour changes to a yellowish orange.

This form is called the *imino base*. Figure 3 summarizes the chemical reactions:

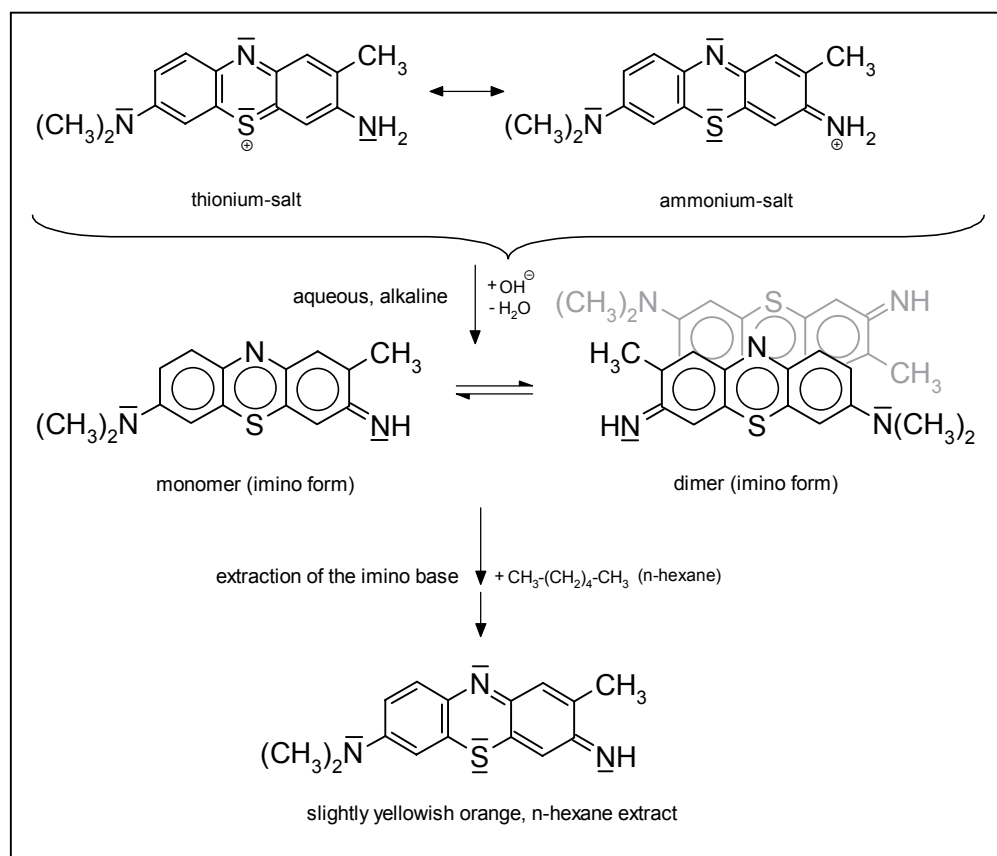


Figure 3 Change of the ionic form of *Toluidine Blue O* into the non-ionic *imino base* and the following transfer of the imino base into n-hexane by extraction

If we dip untreated wood into an imino base extraction of n-hexane the wooden surface coloured bluish, but the plasma treated wood gets purple. In Figure 4 this displacement of the wavelength is illustrated for a piece of spruce.

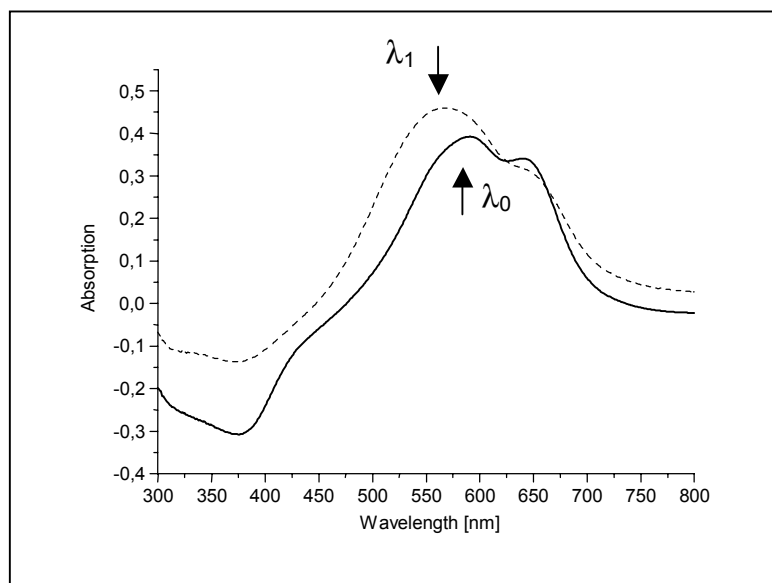


Figure 4 Metachromatic shift  $\Delta\lambda = \lambda_0 - \lambda_1$  of the shorter wavelength of the adsorbed toluidine blue before (full line) and after the plasma treatment (dashed line) of a test piece of spruce

There are several explanations [10,11] for the displacement of the light absorption of the free dye and the adsorbed dye onto the surface of a macromolecule like cellulose or protein. Aggregation (monomer and dimer forms) [9] and orientation [11] of the dye via hydrogen bonds with solvent molecules and the functional groups at the surface of macromolecules are discussed.

We interpret the colour change of the dye onto the untreated wooden surface by interacting with the adsorbed water molecules, that results in the bluish hue. Further we assume that one molecule of toluidine blue takes up a surface area of about  $6 - 7 \text{ \AA}$  in diameter [12] but then it is similar to the dimension of glucose as part of the macromolecule cellulose [13]. So that in the case of a plasma treated surface the dye interacts directly with the “bare” wooden surface (without any adsorbed water molecules).

The molecules of the dye are flattening onto the wooden surface arranged e.g. by alcoholic hydroxy groups of the cellulose. The situation is schematically explained in Figure 5. The relations between the case studies in Table 1 and the dye/surface interaction that shown in Figure 5 are clearly seen.

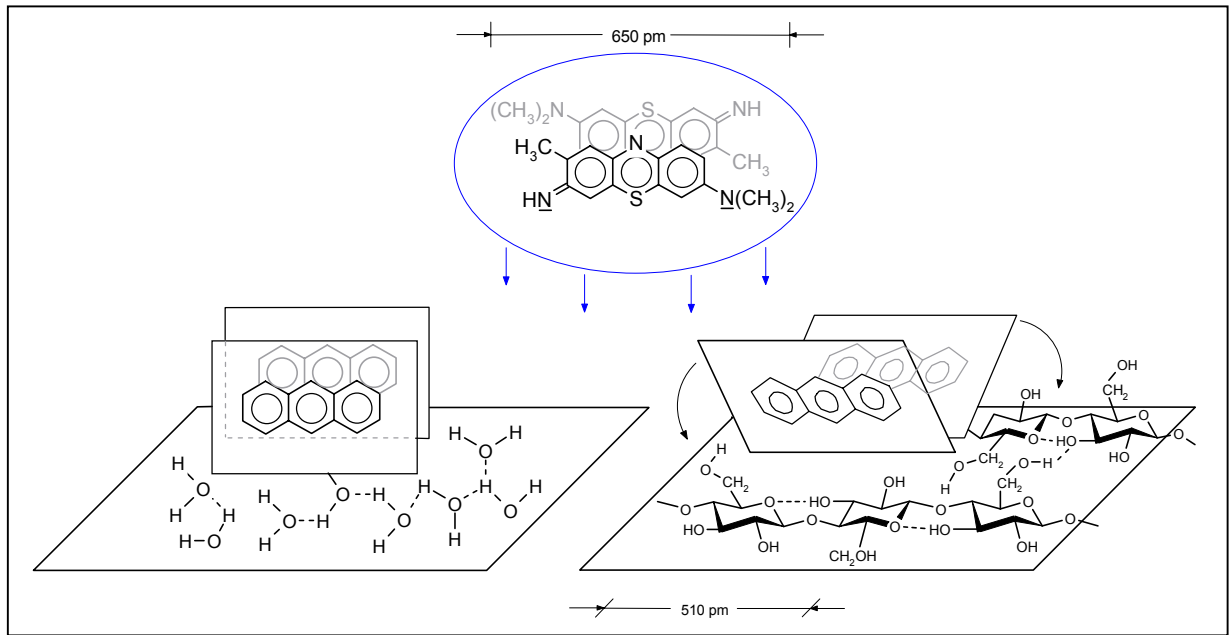


Figure 5 Two situations of adsorption of the uncharged imino form of the toluidine blue onto a wooden surface. Left side: Untreated wooden surface; unspecific adsorption by interaction with pre-adsorbed water molecules and re-reaction into the charged ammonium form. Right side: Plasma treated wooden surface; specific adsorption by hydrogen bonding between the alcoholic hydroxy groups onto the wooden surface and the imino form of the dye.

We postulate a simple correlation between the metachromatic shift  $\Delta\lambda = \lambda_0 - \lambda_1$  (indices as given above) of the shorter absorption band (around 600 nm) and the number  $\Delta N$  of activated surface groups onto the plasma treated wooden surface. In this manner we connect the change in adsorption (energy)  $\Delta\pi = \pi_{0,v} - \pi_{1,v}$ , the metachromatic shift  $\Delta\lambda$  and the number of surface groups  $\Delta N$  by means of the well-known PLANCK relation  $\Delta E = h \cdot \Delta\nu$  in which the quantum energy  $\Delta E$  respects the energy which is necessary to orientate just one molecule of the dye that adsorbes at one activated surface group.  $\Delta\nu$  is the frequency shift,  $h$  is the PLANCK constant and  $c$  the velocity of light.

Straight forward we can write:

$$\Delta E \cdot \Delta N = \Delta\pi \quad (5)$$

and recalculate the number  $\Delta N$  as follows:

$$\Delta N = \left( \frac{1}{hc} \right) \left( \frac{\Delta\pi}{\Delta\lambda} \right) \lambda_0 \cdot \lambda_1 \quad (6)$$

## EXPERIMENTAL

### **Sample Preparation**

Beech (hardwood) and spruce (softwood) were chosen because of the very common use as timber. Because of the important influence of the wood anatomical structure on the following measurements the cut of the raw material was the crucial moment. We used test samples with a fairly radial-tangential. If possible we have measured the contact angles only on areas of early wood regions.

The test samples were cut mechanically using a circular saw and smoothed by a planing machine. The dimensions of the final test samples: 5 x 15 x 75 (high x broad x long; in millimetre). The storage of the test samples was in extra boxes in darkness under room condition.

### **Plasma Treatment**

The scheme of the discharge chamber are given in Figure 1 in the introduction. The construction of the chamber is non-commercial [6,7]. The material of the dielectric barrier is boron nitride (BN) which jackets the copper electrode. An alternating high voltage with separate high voltage pulses of 30 kV, a pulse duration of 2  $\mu$ s and a pulse repetition rate of 15 kHz is applied to the electrode, in order to cause a discharge between the electrode and the wooden surface at atmospheric pressure. The distance between the electrodes was 20 mm and that between the boron nitride electrode and the wooden surface of the test samples was 5 mm. The air atmosphere was unconditioned, i.e. under normal pressure and room temperature, but blown by a ventilator through the discharge gap with a rate of around 3 m/s. Immediately after the treatment the test samples were collected in boxes mentioned above. The activated surfaces should not be in direct contact with holders or other materials. The time between the plasma treatment and the following contact angles measurements and the staining procedure should be as short as possible.

## Contact Angle Measurements

Contact angle measurement occurs by the Sessile Drop Method with a video-based optical contact angle meter, equipped with an electronic syringe unit (OCA 15plus, DataPhysics Instruments GmbH, Germany). The measurement is carried out at room conditions. SCA 20 software, Version 1.6, is used to operate the instrument and to calculate contact angles as well as free surface energy of the solid samples.

Settings : Syringe type: Hamilton 1750 TLL (500  $\mu$ l) used with a replaceable dosing needle with a inner diameter of 0.1 mm (Art.-No. 5132-1/4-B, GLT mbH, Germany).

Drop type: normal, drop volume: 5  $\mu$ l, dosing rate: 4  $\mu$ l/s

Frame grabbing time 20 s (25 images/s).

Calculation method for the sessile drop: circle fitting (neglects gravity).

Test Liquids: Water, water/ethylene glycol mixtures and aqueous solutions of CaCl<sub>2</sub> (see table 2).

## Colorimetric Measurements by UV/VIS-Spectroscopy

Dye: Tolidineblue O, Chloride salt, dye content ~ 80%, Sigma-Aldrich Chemie, Steinheim

Dye processing: Sodium hydroxide was added to a 10<sup>-4</sup> molar aqueous solution, to convert the dye salt into the dye base. The solution was covered with *n*-Hexane and shaken out for 15 min. using a ultrasonic bath. Later on the mixture was transferred to a separation funnel and the upper *n*-hexane phase with the imino form of the dye was separated.

Procedure of dyeing: the samples were dyed by immersion using a Chromatogram Immersion device (CAMAG), two samples at a time. Time of dyeing: 10 min.

Method of Measuring : UV/VIS-Spectroscopy, Tidas diode array spectrometer, J&M GmbH, Aalen, Germany; diffuse reflection, 45° optics,  $\varnothing$  of measuring spot approx. 1,5 mm

Settings: Absorbance, scan parameters: 300-800 nm, Step 1 nm, time of integration: 50 ms, time between two scans (time interval): 10 s, accumulation of scans: 10.

Settings for spot and scanning measurements: The means out of 170 spot measurements of the treated samples and 30 spots of the reference for each species of wood.

## RESULTS

According to an earlier investigation of wooden surfaces by contact angle measurements [14] we have always chosen ethylene glycol/water mixtures and aqueous calcium chloride solutions as test liquids. Because of a better reproduction of our results we have measured the surface tensions  $\gamma_{LV}$  resp. the interfacial tensions  $\gamma_{LH}$  versus air resp. n-hexane by ourself. The values are summarized in Table 2:

Table 2: Surface and interfacial tensions  $\gamma_{LV}$  resp.  $\gamma_{LH}$  in [mN/m] of the used test liquids, aqueous solutions, measured under room condition (25 °C, 60 % RH))

No. #	test liquid	$\gamma_{LV}$ (versus air)	$\gamma_{LH}$ (versus. hexane)
1	CaCl <sub>2</sub> , 10%	78,1 ±0,40	46,7 ±0,16
2	CaCl <sub>2</sub> , 5%	73,4 ±0,07	47,5 ±0,05
3	water	70,3 ±0,12	46,6 ±0,07
4	ethylene glycol, 10%	69,2 ±0,07	41,2 ±0,06
5	ethylene glycol, 20%	63,7 ±0,02	35,3 ±0,12
6	ethylene glycol, 30%	59,8 ±0,22	33,1 ±0,02
7	ethylene glycol, 40%	61,6 ±0,29	30,8 ±0,06
8	ethylene glycol, 50%	55,0 ±0,05	27,4 ±0,03
9	ethylene glycol, 60%	51,4 ±0,14	25,5 ±0,05

We notify that our own values verify with those reported by literature [14,15,16] and are in a good agreement.

In strong contrast to the very precise measurements of the surface tensions of liquids by the *pendent drop* method which are given above (Table 2) stands the determination of the solid surface free energy using the *contact angle* method. Not only the well known but general effects of the surface roughness and especially the chemical heterogeneity of the wooden surface make it very difficult to measure a reliable and representative contact angle of the wetting and spreading test liquid onto the solid surface [17,18]. Unfortunately the measured contact angles of so-called *high energy surfaces* like wood exhibit hysteresis and cannot be defined unambiguously by experiment. The results compiled in the tables 3 and 4 compare badly with the conciseness of Table 2. Nevertheless these data should be practicable for the further discussions. Considering the dynamic process of wetting and spreading of the test

liquid after the application onto the wooden surface the contact angle was measured two seconds later. Finally the mean of the contact angles  $\Theta$  were calculated out of five reliable measurements for each test liquid onto the same piece of wood (without consideration of the standard deviation). The results for two wooden surfaces (spruce and beech wood) are summarized in Table 3 and 4. For the indices and the case studies see also Table 1 as given in the introduction.

Table 3: Means of the contact angles  $\Theta$  [in degree] onto even spruce wood surfaces, calculated out of five reliable measurements for each test liquid onto the same piece of wood, two seconds after the application of the test liquid (without consideration of the standard deviation)

test liquid	case 1	case 2	case 3	case 4
	$\Theta_{0,v}$	$\Theta_{1,v}$	$\Theta_{0,H}$	$\Theta_{1,H}$
CaCl <sub>2</sub> , 10%	53,2	11,4	70,5	42,9
CaCl <sub>2</sub> , 5%	56	12,7	74,8	50,6
water	44	10,9	61,1	53,5
ethylene glycol, 10%	40,2	11,2	65,1	51,2
ethylene glycol, 20%	29,5	11,4	62,1	49,3
ethylene glycol, 30%	30,7	8,5	63,2	62,1
ethylene glycol, 40%	24,7	8,9	64,1	54,7
ethylene glycol, 50%	15,1	9,9	58,3	53,9
ethylene glycol, 60%	16,5	7,8	57,7	44,6

Table 4: Means of the contact angles  $\Theta$  [in degree] for several test liquids onto beech wood surfaces (calculations as given in table 3.)

test liquid	case 1	case 2	case 3	case 4
	$\Theta_{0,v}$	$\Theta_{1,v}$	$\Theta_{0,H}$	$\Theta_{1,H}$
CaCl <sub>2</sub> , 10%	40,5	19,6	80,6	43,4
CaCl <sub>2</sub> , 5%	23,4	8,2	78,1	37,4
water	23,6	5,2	66,9	44,9
ethylene glycol, 10%	26,4	8,4	64,2	39,3
ethylene glycol, 20%	15,8	7,8	61,1	42,7
ethylene glycol, 30%	11,6	6,6	58,3	39,2
ethylene glycol, 40%	12,2	5,8	60,7	38
ethylene glycol, 50%	10	7,6	55,4	36,2
ethylene glycol, 60%	8,7	5,2	55,6	36,3

The estimated contact angles under normal atmosphere (moisten air) are concerned about the reliability of the measured values onto the untreated as well as the plasma treated wooden surfaces. Low energy materials tend to adsorb strongly onto high-energy surfaces, as this will decrease the surface energy of the system. The plasma treatment of wooden surfaces leads to a borderline case: The surface energy of the solid surface and the surface energies of the test liquids are very similar. The contact angle is small. Contact angles below  $10^\circ$  are poor, unreliable and cause of errors. Therefore we have changed the outer fluid by n-hexane and received much better results of the contact angles (see table 4.).

Also the differences in the surface activity of the two kinds of wood before and after the plasma treatment can be realized by staining. The metachromatic shifts  $\Delta\lambda = \lambda_0 - \lambda_1$  of the adsorbed toluidine blue onto both wood (untreated and plasma treated beech and spruce) is given in table 5.

Table 5: The metachromatic shift  $\Delta\lambda = \lambda_0 - \lambda_1$  of untreated (reference) and plasma treated wood samples (means out of 170 spot measurements of the treated samples and 30 spots of the reference for each kind wood), discharge condition: normal atmosphere of air, pulse duration of 2  $\mu\text{s}$  and a pulse repletion rate of 15 kHz, total time 10 s, duration of staining (imino base extraction by n-hexane) 10 minutes

wood	$\lambda_0$ [nm]	$\lambda_1$ [nm]	$\Delta\lambda$ [nm]
beech	$599\pm 1$	$588\pm 1$	11
spruce	$591\pm 1$	$567\pm 1$	24

Obviously the increase of the shift  $\Delta\lambda$  is accompanied by the decrease of the contact angle  $\Theta$ . But there are more hidden details that pointed out the specific adsorption of the dye molecules onto the activated wooden surface, especially about the role of the number of surface groups  $N_0$ . In the following discussion the energetic aspect of adsorption shall consider in detail.

## DISCUSSION

Low-energy materials (organic compounds but also water) tend to adsorb strongly onto high-energy surfaces and decrease the total surface energy of the system. High-energy materials like metals, metal oxides and inorganic compounds (silica, sapphire, graphite) have surface tensions  $\gamma_s$  in the range of 200 – 5000 mN/m. On the other hand, the order of  $\gamma_s$  of low-energy

materials ranged below 100 mN/m. Wood as a highly functional surface (for example by the hydroxy group of the cellulose molecules, see also Figure 5) stands between the low- and high-energy materials, especially after plasma treatment. Thus, a freshly treated wooden surface that exposed to an ordinary environment (e.g. moisten air) tends rapidly to be covered with a film of adsorbed water. Therefore we should expect a remarkable value of the *spreading pressure*  $\pi$  [18a]. All these phenomena are summarized in Table 1. Let us compile the essentials of the given models of adsorption again:

- 1). The total number  $N_0$  of surface groups are fairly constant and not influenced by the plasma treatment of the surface:

$$\pi_{0,V} \approx \pi_{0,LV} \approx \pi_{1,LV}$$

- 2.) *n*-hexane is accepted to adsorb only statistically, because there are no polar functional groups in the outer fluid that could arrange interaction with the polar surface of the wood; so no specific adsorption take place:

$$\pi_{0,H} \approx \pi_{0,LH} \approx \pi_{1,H} \approx \pi_{1,LH}$$

- 3). The plasma treatment strongly increases the number  $\Delta N$  of activated functional groups onto the wooden surface,  $\Delta N = N_0 - N$ , wherein  $N$  is the number of remaining inactive and saturated surface groups by adsorption.

- 4.) The number of activated functional groups  $\Delta N$  is proportional to the change of the spreading pressure,  $\Delta\pi = \pi_{0,V} - \pi_{1,V}$ :

$$\Delta\pi \sim \Delta N$$

- 5).  $\gamma_{S,0} = \gamma_{S,1}$

In both cases (per definition) the surface is “bare” (total empty), there is no adsorption at all.

- 6). Although the interaction between the surface (functional groups) and the wetting liquid is very sensitive to the polar and hydrogen bonding forces the change in  $\gamma_{SL}$  before and after the plasma treatment is negligible because of the nearly constant surface concentration of functional groups at all (no additional new kind of surface groups will be created by the plasma treatment and the absolute number of them remain constant): In other words: If the *interaction parameter*  $\phi$  for a series of test liquid is constant, the change in  $\gamma_{SL}$  disappears:

$$\Delta\gamma_{SL} = \gamma_{SL,0} - \gamma_{SL,1} = 0$$

The latter circumstance can be explained by the theory of GOOD and GIRIFALCO [18a, 19]. In combination of the YOUNG equation and the theory of GOOD and GIRIFALCO the exact but striking simple relation:

$$\gamma_c = \frac{1}{4}(1 + \cos \theta)^2 \gamma_{LH} \quad (7)$$

terms out, wherein  $\gamma_c$  is the critical surface tension:

$$\gamma_c = \lim_{\Theta \rightarrow 0} \gamma_{LH} \quad (7.1)$$

For a series of test liquids with almost the same interaction parameter ( $\phi = \text{const.}$ ) the plot of  $\gamma_c$  against  $\gamma_{LH}$  is a function with a maximum at  $\gamma_{c,\text{max}}$ . Figure 6. shows such a plot of a sample of spruce wood before and after treated by plasma.

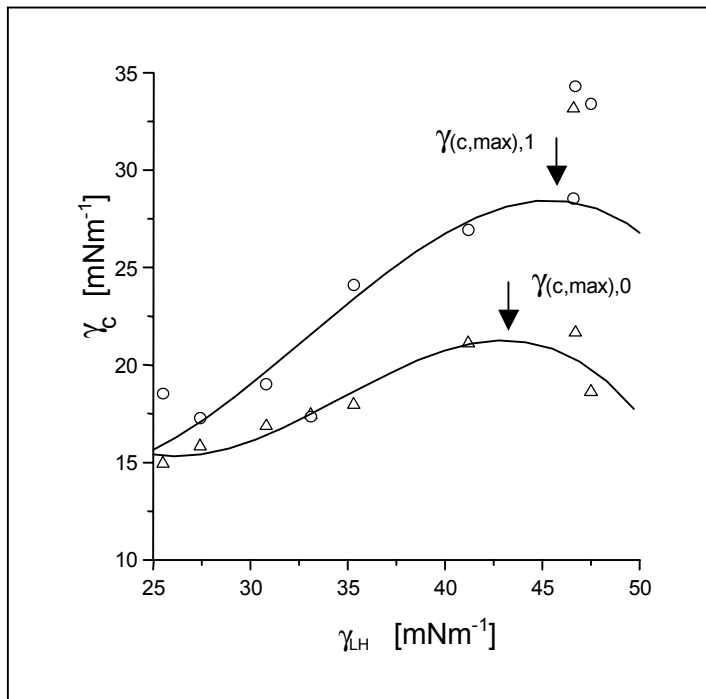


Figure 6. Equation of state plots (eq. (7)) of untreated ( $\Delta$ ) and plasma treated (O) spruce under *n*-hexane as outer fluid

In table 6. the values of  $\gamma_{(c,\text{max}),0}$ ,  $\gamma_{(c,\text{max}),1}$  and  $\Delta\gamma_{c,\text{max}}$  of both wood species under air and *n*-hexane as outer liquid are summarized.

Table 6: The values of  $\gamma_{(c,max),0}$ ,  $\gamma_{(c,max),1}$  and  $\Delta\gamma_{c,max}$  (in [mNm<sup>-1</sup>]) of both wood species under air resp. *n*-hexane as outer liquid (indices “V” resp. “H”)

	under moisten air (index “V”)			under <i>n</i> -hexane (index “H”)			
	$\gamma_{(c,max),0}$	$\gamma_{(c,max),1}$	$\Delta\gamma_{c,max}$	$\gamma_{(c,max),0}$	$\gamma_{(c,max),1}$	$\Delta\gamma_{c,max}$	$\Delta\pi$
beech	60,7	-	-	19,8	29,7	9,9	8 to 14
spruce	54,1	-	-	20,6	26,3	5,7	1 to 7

If we consider that the change in the interfacial energy of the wooden surface after the plasma treatment is only effected by the change of the spreading pressure  $\Delta\pi = \pi_{0,V} - \pi_{1,V}$  this value is easy to calculate in making the difference between eq. (4.3) minus eq. (4.4):

$$\gamma_{LH} \cdot \cos \Theta_{1,H} = (\pi_{0,V} - \pi_{1,V}) + \gamma_{LH} \cdot \cos \Theta_{0,H} \quad (8)$$

The very simple linear relation with the slope of unit one, the abscisse  $\gamma_{LH} \cdot \cos \Theta_{0,H}$  and the ordinate  $\gamma_{LH} \cdot \cos \Theta_{1,H}$  has the interception of  $\Delta\pi$ . In Figure 7. a scratch of four values of  $\Delta\pi$  is illustrated for spruce wood under *n*-hexane.

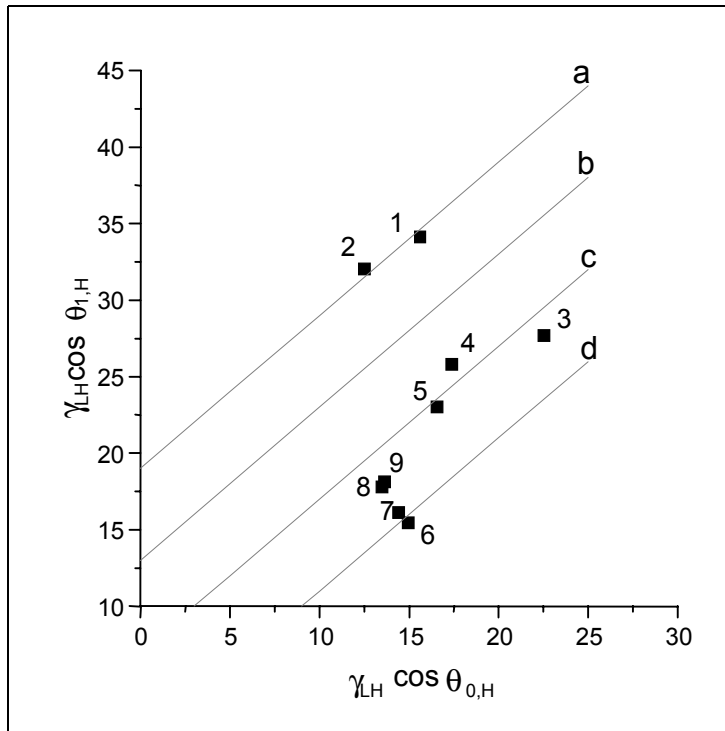


Figure 7. Graphs for the interpretation of eq. (8) by a series of test liquids (numbers as are given in table 2.), surface of spruce wood.

a)  $\Delta\pi = 19$  mNm<sup>-1</sup>; b)  $\Delta\pi = 13$  mNm<sup>-1</sup>; c)  $\Delta\pi = 7$  mNm<sup>-1</sup> and d)  $\Delta\pi = 1$  mNm<sup>-1</sup>

This plot gives a good impression of the sensitive influence of the interaction parameter  $\phi$  which is causing by the different test liquids. The test liquids No. 1 and No. 2 are strongly ionic ( $\text{CaCl}_2/\text{H}_2\text{O}$ ) rather than the more polar and hydrogen bonding liquids No. 3 – 9 (water/ethylene glycol mixtures). If we consider only the latter series we receive an expected value of  $\Delta\pi$  between 1 and 7  $\text{mNm}^{-1}$  for the sample of spruce wood. In the same way we have estimated the value for the sample of beech wood:  $\Delta\pi$  between 8 and 14  $\text{mNm}^{-1}$ . These two value are compiled into the table 6 (last right column). If we compare the values of  $\Delta\pi$  with those of  $\Delta\gamma_{c,\max}$  they correspond in good agreement for both wood species. The reliability of the equation of state (eq. (7)) and the adsorption therm (eq. (8)) is given in practice an we set  $\Delta\gamma_{c,\max} = \Delta\pi$ . If we do so, finally we can estimate the number  $\Delta N$  of activated functional groups onto the wooden surface that are created by the plasma treatment. We use eq. (6):

$$\Delta N = \left( \frac{1}{hc} \right) \left( \frac{\Delta\pi}{\Delta\lambda} \right) \lambda_0 \cdot \lambda_1 \quad (6)$$

With the data given in the tables 5. and 6. the following values of  $\Delta N$  were calculated and are summarized in table 7.

Table 7: Summary of the experimental data (see table 5 and 6) for the estimation of the increase of the number of activated surface groups  $\Delta N$  by plasma treatment (beech and spruce wood)

wood	$\lambda_0$ [nm]	$\lambda_1$ [nm]	$\Delta\lambda$ [nm]	$\Delta\pi$ [ $\text{mNm}^{-1}$ ]	$\Delta N$ [ $\text{cm}^{-2}$ ]
beech	599	588	11	8	$1,3 \cdot 10^{14}$
				14	$2,3 \cdot 10^{14}$
spruce	591	567	24	1	$7,1 \cdot 10^{12}$
				7	$5,0 \cdot 10^{13}$

The magnitude of the estimated  $\Delta N$  is of reasonable order for surface groups of isolators [20]. Unfortunately no details about the number of hydroxy groups onto the surface of cellulose or wood were given or found in literature resp. We found in the literature for the number of hydroxy groups onto surfaces of  $\text{SiO}_2$   $5 \cdot 10^{14} \text{ cm}^{-2}$  and  $\text{Al}_2\text{O}_3$   $8 \cdot 10^{14} \text{ cm}^{-2}$  [21].

## CONCLUSIONS

The reasonable results in assessing the contribution of adsorption to the interfacial energy and the prediction of the extent in change of activated surface groups after plasma treatment justified some simplifying assumptions in order to apply theories to much more complex practical systems like wood.

With the help of a rather simple model it is possible to characterize the change of a wooden surface after the treatment by electric discharge with a series of measurements of the contact angles and the light absorption of suitable dyes (e.g. toluidine blue). The practical advantage of both methods is there more summarized than in detail working procedure of the measurement. The determination of the interfacial energy by contact angle measurements and also the absorption of light onto and their reflectance from a surface are integral and collective methods. It means that most of the microscopic small inhomogeneities and artefacts onto the real wooden surface would scaled down by the huge number of the regular surface groups. Therefore the fuzzy set potential of both methods is remarkable and useful in further investigations of surface phenomena. The simple model given above can help to recognize good treatment for technological practising like to glue, to paste, to cover or to coat. The number of activated surface groups  $\Delta N$  could be a kind of quality mark as part of the control of the technical process in production and manufacturing. In contrast to the very easy and rapid staining procedure the measurements of contact angles are time consuming and often disturbed by the environment. Therefore the relation between  $\Delta N$  and  $\Delta\lambda$  is in particular of interest. The predicted values of  $\Delta N$  are  $7.1 \cdot 10^{12}$  to  $5.0 \cdot 10^{13} \text{ cm}^{-2}$  for spruce wood and  $1.3$  to  $2.3 \cdot 10^{14} \text{ cm}^{-2}$  for beech wood. The magnitude of these values are suitable and comparable with those known from inorganic isolators like silicon dioxide and aluminium oxide [20,21]. The model that is given here could be used to verify several wood species and there surfaces to improve and optimise the procedure of dielectric barrier discharges at atmospheric pressure in the technological advance.

## ACKNOWLEDGMENTS

This work was supported by research grants from the Volkswagenstiftung. The authors are indebted to their colleagues, Andreas Buder, Peter Rehn and Dr. W. Viöl for their help in the preparation of the manuscript. Special thanks to Mr. P. Rehn for carrying out the DBD experiments.

## REFERENCES

- [1] Zeppenfeld, G., Klebstoffe in der Holz- und Möbelindustrie, Leipzig, 1991
- [2] Fengel, D. and Wegener, G., Wood – Chemistry, Ultrastructure, Reactions, de Gruyter, Berlin, 1989
- [3] Wagenführ, R. and Scheiber, Ch., Holzatlas, Leipzig, 1989
- [4] Sjöström, E., Wood chemistry, Fundamentals and Applications, Academic Press, New York, 1981
- [5] Richardson, P., Timbers of the World, Harlow, Longman, 1979
- [6] Rehn, P., Wolkenhauer, A., Bente, B., Förster, S. and Viöl, W., Wood surface modification in dielectric barrier discharges at atmospheric pressure, *Surface and Coating Technol.*, 174-175, p. 515-518 (2003)
- [7] Avramidis, G., Leck, M., Meiners, A., Rehn, P., Viöl, W., and Wolkenhauer, A., Improvement of adhesion of wood coatings by plasma-pre-treatment, *holztechnologie*, 46(2005)40-47
- [8] Myers, D., Surfaces, Interfaces and Colloids, Principles and Applications, 2<sup>nd</sup>. ed., Wiley-VCH, 1999
- [9] Harms, H., Handbuch der Farbstoffe für die Mikroskopie, Staufen Verlag, 1965
- [10] Toepfer, K., Die Thiazinfarbstoffe. – Progress in Histochemistry and Cytochemistry, Stuttgart, 1(1970) 277-354
- [11] Hutschenreiter, J. and Scheuner, G., Das Auftreten von Metachromasie, Doppelbrechung und Dichroismus durch die Toluidinblaureaktion. – Progress in Histochemistry and Cytochemistry, Stuttgart, 7(1975), 73 p.
- [12] Fautrez, J., and Lison, L., *Protoplasma*, 27, 183 (1937); cited in [11], p. 7
- [13] Volhardt, J., Lehrbuch der Organischen Chemie, VCH, Weinheim, 1998
- [14] Nguyen, T. and Johns, W. E., The Effects of Aging and Extraction on the Surface Free Energy of Douglas Fir and Redwood, *Wood Sci. Technol.*, 13, 29-40 (1979)
- [15] DataPhysics, Software Package for the system OCA 15plus, DataPhysics Instruments GmbH, Germany, [www.dataphysics.de](http://www.dataphysics.de)
- [16] Jasper, J. J., The Surface Tension of Pure Liquid Compounds, *J. Phys. Chem. Ref. Data*, Vol. 1, No. 4, NSDRS, 1972, p. 859
- [17] Myers, D., Surfaces, Interfaces and Colloids, Wiley-VCH, 2<sup>nd</sup>. ed., 1999
- [18] Wu, S., Polymer Interface and Adhesion, Dekker, 1982
- [18a] *ibid.*, p. 215
- [19] Girifalco, L.A. and Good, R. J., *J. Phys. Chem.*, 61, 904(1957)
- [20] Schulz, H., Investigations of the electrical potential at electrolyte/polymer interfaces, thesis, Berlin, 1986
- [21] Davis, J.A., James, R.D. and Leckie, J.O., *J. Colloid Interface Sci.*, 63, 480(1978)