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WETTING PHENOMENA ON WOOD

Factors influencing measurements of wood wettability

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To Tina

"Newtons tredje rörelselag säger att varje kraft alstrar en motkraft som är av samma styrka." (ur Domens Dag, Kjell Höglund, Ormens År, Atlantis Grammofon AB, 1989).

ABSTRACT

Wetting phenomena refer to macroscopic manifestations of intermolecular forces acting across a solid-liquid interface. The purpose of this work is to achieve a better understanding of wetting phenomena on wood which also may guide us to improve the interaction between e.g. wood and adhesives.

A modified Wilhelmy method has been developed for the measurement of wetting forces on wood. In addition, wetting and surface characterization techniques based on column wicking and inverse gas chromatography (IGC), respectively, have been applied to spruce wood particles. The wetting measurements by the Wilhelmy method were performed on extracted and non-extracted, fresh and aged pine wood veneers. The results show that a severe contamination of the probe liquids may occur during the measurements. The contamination is caused by dissolution or by the presence of extractives at the wood-liquid interface, and it generally results in a distinct decrease in the liquid surface tension. It is also observed that wicking of the liquid occurs into voids of wood and along its irregular and rough surface. The Wilhelmy method may however provide an efficient means of recording and controlling such contamination and wicking effects.

The measured wetting forces permit an apparent contact angle to be estimated. Based on the van Oss-Chaudhury-Good approach, (Lewis) acid-base properties of the wood veneers were determined. The results indicate that the acid and base components of the surface free energy of the wood increase and decrease, respectively, with aging time, probably due to reorientation of functional groups, and due to oxidation, at the wood/extractives-air interface.

The surface characterization of spruce particles by IGC indicated that wood without extractives shows a greater Lewis acidic and less Lewis basic character than wood containing extractives. The wetting measurements on spruce particles by the column wicking were in general influenced by sorption of the probe liquids in the wood substance, i.e. bulk sorption. Temperature measurements during the wetting process also indicate that sorption of probe liquid vapor may occur in advance of the moving liquid front.

By more suitable methods for measurements of the wetting properties of wood, valuable technical information about the capacity of wood to interact with adhesives and coatings may be generated.

Keywords: Wood, wetting, wettability, apparent contact angles, work of adhesion, surface free energy, Lewis acid-base properties, Wilhelmy method, inverse gas chromatography (IGC), wicking, capillary rise, extractives, contamination, aging.

SAMMANFATTNING (IN SWEDISH)

Vättningsfenomen är makroskopiska manifestationer av intermolekylära krafter som uppträder mellan en vätska och en solid kropp i direkt kontakt via ett gränsskikt. Syftet med detta arbete är att få bättre insikt om träets vätningsegenskaper och att i förlängningen kunna uppnå förbättrad samverkan och adhesion mellan trä och lim eller ytbehandlingsmedel.

Centralt i arbetet är utvecklingen av en modifierad ”Wilhelmy-metod”, för mätning av vättningskrafter som verkar på ett träfanér vid neddoppning i olika väl-definierade provvätskor. Därutöver har även vättnings- och ytkarakteriseringsteknik baserad på ”inverse gas chromatography” (IGC) respektive ”column wicking” (kapillär stighöjdsmetod), tillämpats på granpulver.

Baserat på Wilhelmy-metoden har vättningsmätningar genomförts på extraherade och icke-extraherade, färsk och åldrade fanér av furu (*Pinus silvestris* L.). Resultat visar att Wilhelmy-metoden möjliggör en effektiv detektering av en eventuell kontaminering av använda provvätskor som sker genom upplösning av träets extraktivämnen vid gränsskiktet mellan trä och vätska. En sådan kontaminering sänker generellt sett den använda provvätskans ytspänning, vilket medför svårigheter vid utvärderingen av uppmätta vättningskrafter. En omorientering av funktionella grupper i gränsskiktet mellan trä/extraktivämnen och en vätska är också trolig.

Det är viktigt att slå fast att ett system, bestående av en vätska som är i kontakt med en träyta, generellt är i ett icke-jämviktstillstånd. Ett fenomen som uppstår i ett sådant system är kapillär väsketransport, vilket starkt påverkar en vättningsanalys. Resultat visar att Wilhelmy-metoden möjliggör en uppskattning och kontroll gällande både en initial och en kontinuerlig kapillär effekt vid vättningsmätningar på trä.

De uppmätta vättningskrafterna ger även en indikation på kontaktvinkeln mellan vätskan och träet. Denna kontaktvinkel på trä är dock en fenomenologisk parameter som starkt påverkas av en rad faktorer, t.ex. träets heterogenitet, ytråhet, porositet och sorptionsegenskaper.

Ett Lewis syra-bas-koncept för analys av vättningsfenomen utvecklades bl.a. av Fowkes på 70-talet, och senare av van Oss, Chaudhury och Good. Baserat på detta angreppssätt och kontaktvinklar som uppskattats genom Wilhelmy-metoden har träfanérens (Lewis) syra-bas-egenskaper beräknats. Resultat indikerar att syra- och baskomponenten av träets ytenergi ökar respektive minskar vid åldring, troligen genom en omorientering av extraktivämnenas funktionella grupper och genom oxidering, vid gränsskiktet mellan trä/extraktivämnen och luft.

Ytkarakteriseringen av granpulver (*Picea abies* Karst.) genom IGC indikerar att trä utan extraktivämnen har mer (Lewis) syra-karaktär och mindre (Lewis) bas-karaktär jämfört med trä innehållande extraktivämnen.

Vättningsmätningarna på granpulver med den kapillära stighöjdsmetoden påverkas i vissa fall starkt av sorption av vätskorna i träsubstansen, s.k. bulksorption, vilket försvårar vättningsanalysen. Temperaturmätningar under vättningsförloppet indikerar också att sorption av ånga från vissa provvätskor uppkommer framför den stigande vätskefronten.

Förbättrade analysmetoder för träets vätbarhet och adhesionsegenskaper kan generera värdefull teknisk information om träets potential för samverkan med lim och ytbehandlingsmedel. Därigenom skulle även nya avancerade limmer och ytbehandlingsmedel kunna utvecklas, med målet att förbättra beständigheten och egenskaperna hos olika trä- och träbaserade produkter, t.ex. i hårt fuktbelastade miljöer.

PREFACE

This work has been carried out at Kungliga Tekniska Högskolan, Avd. för Träteknologi (KTH – Royal Institute of Technology, Division of Wood Technology and Processing), and is a contribution to the R&D program called *Value Activation* (in Swedish: *Värdeaktivering*).

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Stockholm, December, 1999

Magnus Wålinder

LIST OF PAPERS

This doctoral thesis is based on the following papers referred to in the text by their Roman numerals:

- I. Wålinder, M.E.P. and I. Johansson
“Measurement of wood wettability by the Wilhelmy method. Part 1. Contamination of probe liquids by extractives”
Submitted to *Holzforschung*.
- II. Wålinder, M.E.P. and G. Ström
“Measurement of wood wettability by the Wilhelmy method. Part 2. Determination of apparent contact angles”
Submitted to *Holzforschung*.
- III. Wålinder, M.E.P. and D.J. Gardner
“Factors influencing contact angle measurements on wood particles by column wicking”
J. Adhesion Sci. Technol., Vol. 13, No. 12, pp. 1363–1374 (1999).
- IV. Wålinder, M.E.P. and D.J. Gardner
“Surface energetics of extracted and non-extracted spruce wood particles studied by inverse gas chromatography (IGC)”
Submitted to *Wood Fiber Sci.*
- V. Wålinder, M.E.P.
“Study of Lewis acid-base properties of wood by contact angle analysis”
Manuscript

OUTLINE OF THE THESIS

Chapter 1 presents the general context of the thesis, a short description of the wood material, a literature survey including basic concepts and definitions about wetting phenomena both in general and related to wood, and finally the formulation of objectives.

Chapter 2 presents an overview of the methodologies and materials used in the study. Chapter 3 summarizes and discusses the results of the five appended papers (I–V). In this chapter an effort is made to recognize important issues and factors influencing measurements of wood wettability. This also includes the formulation of some basic principles and recommendations when determining the wetting properties of wood. An attempt is also made to analyze obtained wetting parameters by determining so-called Lewis acid-base (AB) properties of wood. Chapter 4 presents concluding remarks and recommendations for potential future work in this field.

CONTENTS

ABSTRACT.....	v
SAMMANFATTNING (IN SWEDISH)	vii
PREFACE	ix
LIST OF PAPERS.....	xi
OUTLINE OF THE THESIS	xi
CONTENTS	xiii
1. INTRODUCTION.....	1
1.1 General context of the thesis	1
1.2 The wood material	2
1.3 Wetting phenomena. Basic concepts and definitions	6
1.4 Wetting studies on wood	15
1.5 Statement of objectives.....	18
2. METHODS	19
2.1 The Wilhelmy method	19
2.2 Wicking (capillary rise) method	22
2.3 Inverse gas chromatography (IGC).....	23
2.4 Materials	24
3. FACTORS INFLUENCING MEASUREMENTS OF WOOD WETTABILITY	27
3.1 Contamination of probe liquids by wood extractives	27
3.2 Wicking effects.....	32
3.3 Estimation of apparent contact angles on wood by the Wilhelmy method	35
3.4 Estimation of apparent contact angles on wood particles by the wicking method.....	38
3.5 Surface energetics of wood particles studied by inverse gas chromatography (IGC).....	41
3.6 Lewis acid-base properties of wood determined by contact angle analysis.....	44
4. CONCLUSIONS AND FUTURE WORK.....	49
5. REFERENCES.....	53
APPENDED PAPERS (I–V)	61

1. INTRODUCTION

1.1 GENERAL CONTEXT OF THE THESIS

Wood is a renewable resource which is available in vast quantities. These features are unusual compared to almost any other engineering and structural material. The wood tissue can be looked upon as a natural polymer, which is created with pronounced variation, exhibiting many extraordinary properties, such as high strength related to weight, easiness to shape and machine, and unique aesthetic and tactile values.

The primary functions of the stem and its wood tissue in its natural state are to carry the crown and branches and, simultaneously, to transport large quantities of water for the photosynthesis process in the needles and leaves. In the normal use of wood, however, the wood material is usually mechanically converted by sawing, milling and sanding, and also artificially dried to a low moisture content.

In order to enhance the utilization of wood and its inherent properties, a long-range Research and Development program, called *Value Activation*, has been formulated (Wiklund 1991 and 1993). This concept is focused on achieving a basic understanding of wood and those properties that are not fully exploited in conventional wood manufacturing systems to date. The strategy is to activate these inherent properties and thus add economic value to completed wood products. In order to achieve this, a better knowledge of the fundamental behavior of wood is required, together with new applied processing technology and the development of necessary manufacturing systems. Some recent studies within this program are e.g., Stehr (1999), Sandberg (1998), Holmberg (1998), Kifetew (1996), Wålinder (1996), and Seltman (1995).

One idea within this concept is the design of manufacturing systems for calculating and producing a mix of components which can give superior performance and higher value than each individual element. The components will be specified by requirements concerning, for instance, hardness, form stability, gluability, coatability, strength, durability, appearance and aesthetics. Subsequently, these components will be parts of *combined solid wood products* held together by adhesives, where each part contributes with its specific properties to the optimal function of the entire system. An example of this could be glued window sills combining basically three different wood elements. The outer element could be produced of pine heartwood with vertical annual rings to achieve high dimension stability and maximum natural durability without using preservatives; the central element of low-density spruce for maximum thermal insulation capacity; and the inner element of pine sapwood for maximum aesthetic value. In this situation, knowledge about the gluability and coatability of such wood elements is of particular importance. For example, it may be important to distinguish between the gluability of heartwood and sapwood to achieve a durable heartwood-sapwood glue-bond.

Studies of *wetting phenomena on wood*, i.e. interactions of liquids with wood, may add valuable information about the gluing and coating properties of wood. Such information is essential in the development of efficient processing

methods, and for the prediction of the durability and in-service performance of glued and coated wood products. It should also be mentioned here that a high percentage, maybe 80 % or more, of all wood products produced today are glued, and that about 70 % (by volume) of all the adhesives produced in the world today are for application to wood (Pizzi 1998).

The present thesis is focused on the measurement and determination of so-called wetting or surface thermodynamic parameters on wood, such as contact angles, surface free energy, and work of adhesion, i.e. parameters which provide an estimate of the wettability (wetting properties) of materials. In practice, especially when dealing with wood, it is important to bear in mind that such wetting parameters are indeed phenomenological parameters, influenced by e.g. surface roughness and heterogeneity, and do not exclusively represent surface thermodynamics. In this case, it is preferable to use the expression *apparent* wetting parameters, e.g. apparent contact angle instead of the contact angle, which is strictly defined for perfectly smooth and homogeneous surfaces.

The origins of wetting phenomena and surface thermodynamics can be traced to fundamental theories about molecular interactions. An important approach related to wetting phenomena is the *Lewis acid-base (AB) concept*, pioneered by Fowkes in the 70's (see e.g. Fowkes and Mostafa 1978). To obtain a durable wood-adhesive bond, especially when exposed to moisture variations, an acid-base interaction between wood and adhesive, equal to the interaction between wood and water should be achieved. A large amount of literature has recently been devoted both to fundamentals and to the practical aspects of acid-base concepts at solid-liquid interfaces (see e.g. Mittal and Andersen 1991; Jensen 1991; Berg 1993a; Good 1993; Lee 1993; van Oss 1994; Della Volpe and Siboni 1997; Dwight 1999; Chahimi 1999).

Knowledge of wetting phenomena on wood may not only be important for an understanding of the interaction between wood and e.g. adhesives or coatings, but may also add valuable fundamental information about the wood material itself and its complex nature. Wood is a natural composite consisting of cellulose, hemicellulose, lignin, and extractives. In other words, there are intermolecular forces between these constituents, which may contribute to some of the unique behavior of wood. It is evident that these intermolecular forces play a central role in the understanding of fundamental mechanisms involved in, for instance, fracture mechanics and rheology. Molecular interactions are also obviously involved in sorption, diffusion and shrinkage/swelling processes in wood. The understanding of wetting phenomena on wood may therefore be considered as an interdisciplinary search for fundamental knowledge in wood science.

1.2 THE WOOD MATERIAL

The term wood refers to the xylem, i.e. a water-conducting and strengthening cellular tissue, originating from photosynthesis in the leaves, and formed by cell division in the vascular cambium of the living tree¹. Thorough reviews of wood struc-

¹ From: Terminology of Forest science technology practise and products. Society of American Foresters. Second printing 1983. ISBN 0-939970-16-3.

ture and composition, together with its physical and mechanical properties, can be found in various textbooks such as Kollmann and Côté (1984), Panshin and de Zeeuw (1980), and Siau (1984). In addition, the chemistry of wood has also been reviewed by e.g. Rowell (1984) and Sjöström (1981).

The wood tissue can be considered as a natural composite material with great variation in structure and properties, whether viewed from a macroscopic, microscopic, or molecular perspective. These variations in wood are due mainly to its heterogeneous and complex composition.

Figure 1 shows a schematic illustration of the macroscopic structure of coniferous wood of the northern temperate zone. From a macroscopic view, such wood may be considered to be a composite of earlywood (lighter) and latewood (darker), which together form concentric annual rings. It is often also important to distinguish between juvenile wood, heartwood and sapwood, and other features such as pith, knots, texture and various anomalies. In the present work, so-called clear wood specimens have been studied, which excludes abnormal wood, e.g. juvenile and reaction wood. Figure 1 also shows the three principal directions and sections in wood: (*L*) the longitudinal direction, along the grain (the fiber direction); (*R*) the radial direction, across the grain and perpendicular to the annual rings; and (*T*) the tangential direction, across the grain and tangential to the annual rings. The corresponding sections are: the cross section; the radial section; and the tangential section.

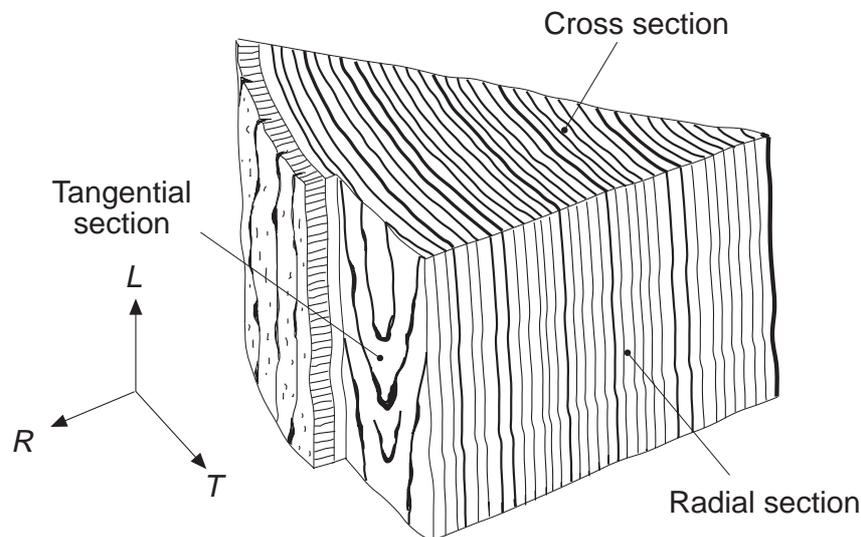


Figure 1. Schematic illustration of the macroscopic structure of coniferous wood.

Microscopically, wood may be considered to be composed of elongated cellular elements (with their length axis oriented in the longitudinal direction) arranged like a honeycomb, i.e. a porous and varying structure. Figure 2 shows photomicrographs of the typical microstructure of a pinewood cross section and radial section. The cellular structure in wood, as shown in Figure 2a, is created through division

and expansion of cells in the cambium layer inside the bark. The main cellular element in softwoods such as pine and spruce is called a tracheid, and is about 2–5 mm in length, 10–50 μm in diameter, with a cell-wall thickness of 3–6 μm (Ilvessalo-Pfäffli 1995; Timell 1986). In Scandinavia, a normal growth period lasts in general from May to early September, and there is a significant difference between the wood cells formed early and those formed late in a growing season.

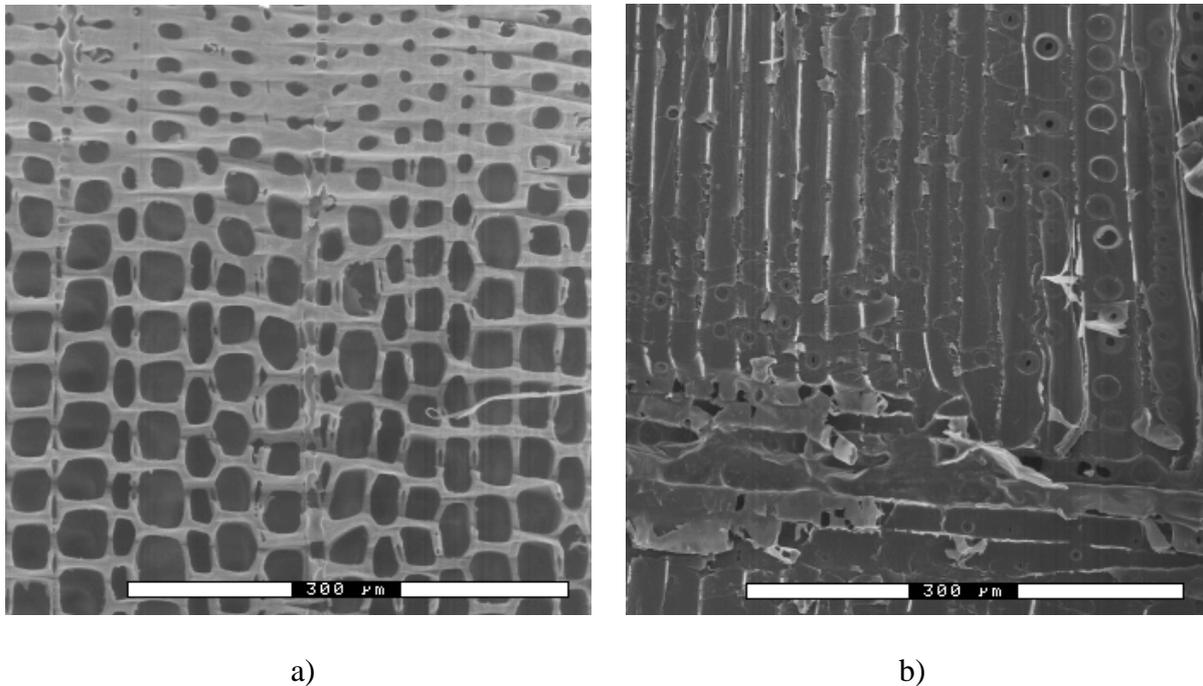


Figure 2. Photomicrographs of the structure of pine wood (*Pinus silvestris* L.) a) cross section (prepared by laser ablation) and b) radial section (cut by wood chisel).

The cells formed first in the growing season, i.e. the earlywood cells, are characterized by large cavities (lumens) and thin walls, in contrast to the cells formed later in the growing season, i.e. the latewood cells, with smaller cavities and thicker walls. Somewhat simplified, the tracheid cell-wall may be considered to be composed of several layers, of which the central, so-called, S2 layer is responsible for many of the physical and mechanical properties of wood. To enable liquid transport between the cells in the living tree, the radial cell-walls of the tracheid are perforated by pits, see the ring-formed structure shown in Figure 2b. In addition, other important features of the coniferous wood structure are the radially oriented ray-cells (see horizontal oriented structure in Figure 2b), which take care of the radial liquid transport in the stem; and resin canals for the distribution of extractives.

On the submicroscopic (molecular) level, wood may be considered to be a natural composite, consisting of cellulose, hemicelluloses, lignin and extractives. These compounds are mainly formed by biological processes in the living tree. Cellulose and hemicelluloses are polysaccharides, while lignin is a phenolic polymer substance consisting of an irregular array of various phenylpropane units (Petersen 1984; Sjöström 1981) with a rather complex and still not fully understood

structure. The wood substance may also be pictured as a reinforced composite where the cellulose chains, gathered into thread-shaped bundles known as microfibrils, represent the reinforcement, which is embedded in a matrix of hemicelluloses and lignin.

The extractives are intrinsic wood compounds which, according to Sjöström (1981), can be divided into two main categories. The first type, sometimes referred to as pathological resin, is located in resin canals and is composed mainly of resin acids and monoterpenes. Their primary function is to preserve the wood against degradation by e.g. microorganisms and insects if the protecting bark of the stem is injured. In general, the inner part of the stem in a mature tree, i.e. the heartwood, does not participate in the transport of the sap, and is therefore often naturally preserved with various extractives. The second type, sometimes referred to as physiological resin, is located in the parenchyma cells and is rich in fats and constitutes a supply of reserve nourishment.

The extractive substances vary greatly in composition and quantity both within and between species, and also within the stem. For instance, pine heartwood typically contains more extractives than the sapwood; and the extractive components in heartwood consist mainly of resin acids, fatty acids, and pinosylvins, whereas in the sapwood they consist mainly of resin acids and triglycerides (Sjöström 1981). Saranpää and Höll (1989) investigated the distribution of soluble carbohydrates (hydrophilic extractives) in pine and showed that the amounts of various sugars and starch were greatest in the outer sapwood and decreased gradually towards the heartwood. In contrast, the concentration of arabinose/galactose increased towards the heartwood. It is important to note that most of the wood extractives in their natural state within the stem are mobile and that some of them are stored under high pressure inside the resin canals, which enables rapid transport to points of injury (Sjöström 1981).

All major extractives in wood can be extracted using either organic solvents or water. Extractives such as resin acids, fats, phenolic compounds, and terpenes can be extracted with e.g. a series of solvents such as ethanol, acetone, petroleum ether, and dichloromethane, whereas carbohydrates, tannins and inorganic salts can be extracted with water (Sjöström 1981). During drying, some extractives will be redistributed and, for example, Boutelje (1990) and Terziev *et al.* (1993) found a migration and an increase in the content of low-molecular sugars and nitrogenous compounds at the surfaces of dried lumber of spruce and pine sapwood.

Sorption of liquids in wood

The wood substance is formed in a water-saturated environment in the living tree, and generally, in wood or wood-based applications, most of the water is removed before use. However, in a normal climate, wood always retains a certain amount of moisture and continuously exchanges moisture with its surroundings. In other words, non-saturated (dry) wood substance is hygroscopic, which means that it has a high affinity for various polar liquids, especially water.

There is some confusion in the literature in the use of the terms adsorption, absorption and sorption. See therefore the following quotation from 1994–1998 Encyclopædia Britannica:

“*Adsorption* refers to the collecting of molecules by the external surface or internal surface (walls of capillaries or crevices) of solids or by the surface of liquids. *Absorption*, with which it is often confused, refers to processes in which a substance penetrates into the actual interior of crystals, of blocks of amorphous solids, or of liquids. Sometimes the word *sorption* is used to indicate the process of the taking up of a gas or liquid by a solid without specifying whether the process is adsorption or absorption.”

Both non-polar and polar liquids can absorb into the porous cell structure of wood, but only polar liquids can penetrate into the non-porous bulk material with resulting swelling. Thus, the term adsorption is more informative than absorption when the focus is on the uptake of polar liquids or vapors in the wood bulk material causing swelling and a significant release of heat, and not on the transport process, i.e. the penetration process. In wood science, the term sorption is often used, without specifying whether the process is adsorption or absorption.

The phenomenon of sorption of water or other polar liquids in wood is rather complex and not yet a fully understood field in wood science. Many different theories have been suggested to explain the sorption processes of polar liquids in wood. Generally, these theories are based on molecular multilayer (like the modified BET theory) or cluster formation models, which all involve the adsorption of molecules on so-called sorption sites in the wood substance (see e.g. Siau 1984; Skaar 1988; Hartley and Avramidis 1993).

1.3 WETTING PHENOMENA. BASIC CONCEPTS AND DEFINITIONS

Adhesion

The term adhesion may be defined as the attraction between one material and another (Marra 1992). Similarly, Kinloch (1987) defines adhesion simply as the attraction between substances. Schultz and Nardin (1999) pointed out, however, that the term adhesion is ambiguous and covers a variety of concepts and ideas. In fact, adhesion could represent both the formation of interfacial bonds and the mechanical load required to break an assembly. Further, the term cohesion is defined as the attraction that exists within a material. It is important to note that ideal adhesives should have a high capacity to achieve both adhesion and cohesion.

The six main mechanisms of adhesion are (Schultz and Nardin 1999): 1) mechanical interlocking; 2) wetting theory (also referred to as adsorption theory); 3) diffusion theory; 4) electronic (electrostatic) theory; 5) theory of boundary layers and interphases; and 6) chemical bonding theory.

It has been generally accepted that each of these theories may be appropriate and valid to some extent in certain circumstances and to a particular class of adhesives (Schultz and Nardin 1999; Kinloch 1987; Pizzi 1992). Therefore, they may all contribute to the intrinsic adhesion forces which act across the interface between adhesive and substrate, and their respective importance depends strongly on the

system chosen. The wetting theory is, however, certainly the most widely used approach in adhesion science at present (Pizzi 1992; Schultz and Nardin 1999), and this work considers only this type of adhesion phenomena, also referred to here as wetting phenomena. The wetting theory involves interatomic and intermolecular forces acting across an interface, provided that intimate contact is achieved. Pizzi (1992) pointed out that these forces can be of any type, including e.g. secondary forces such as Van der Waals and hydrogen-bonds, electrostatic forces, and primary forces such as ionic, covalent, and metallic coordination bonds. In wood adhesion however, it is commonly accepted to consider only the influences of secondary forces in the wetting theory (Pizzi 1992).

It may also be preferable to distinguish between 1) fundamental, 2) thermodynamic and 3) practical approaches to the question of adhesion. The first is traced to the molecular level and involves theories about the origins of intermolecular forces, e.g. understanding about van der Waals forces, hydrogen bonding, and Lewis acid-base interactions. The second is related to the macroscopic level, and to phenomenological observations expressed in terms of thermodynamic wetting parameters, such as the contact angle and work of adhesion. The third is related to bond or joint strength, expressed in terms of peel, pull, shear strength, etc. This work considers mainly the second approach to adhesion, i.e. wetting phenomena.

Surface and interface

A *surface* may be classified according to the state of aggregation of the phases which they separate such as liquid-gas, liquid-liquid, solid-gas, solid-liquid, and solid-solid surfaces. Surfaces between "condensed" phases, i.e., between two liquids, two solids, or a liquid and a solid, are also referred to as *interfaces*. An interface (or a surface) is strictly a mathematical two-dimensional plane, i.e. with no thickness. An *interphase*, on the other hand, has a certain thickness and is situated between two other phases. A, so-called, weak boundary layer, a term which was introduced by Bikerman (1961), is equivalent to a weak interphase.

Surface tension and surface free energy, γ

A way to describe wetting and capillary phenomena is to assume the existence of surface tension and surface free energy. Surface tension is a property of a liquid-gas surface. The surface tension acts along the surface and tends to minimize its area. Its dimension is force per length. When an area, A , of a new surface is created, work, W , must be done. Surface free energy is then defined as the ratio W/A . Its dimension is energy per area. The dimensions of surface tension and surface energy are therefore identical. In this work, the symbol γ represents both surface tension and surface free energy, and the two terms are treated as equivalent.

Analogous to the surface tension and surface free energy of liquid-gas or solid-gas surfaces, the terms interfacial tension or interfacial free energy may be used in the case of interfaces between condensed phases. The interfaces between two liquids show the same tendency to contract as liquid-gas surfaces. In contrast to the obvious contraction effects at liquid-gas surfaces and liquid-liquid interfaces, no such comparable effects have ever been observed for solid-gas surfaces and solid-

liquid interfaces (Adamson and Gast 1997). Hence, there is no empirical evidence for the existence of surface free energy of solids and interfacial free energy of the boundaries between solids and liquids.

Definition of the term ‘wetting’

The term ‘wetting’ may be defined as “macroscopic manifestations of molecular interaction between liquids and solids in direct contact at the interface between them” (Berg 1993a). Such manifestations involve 1) the formation of a contact angle θ at the solid/liquid/fluid interline, 2) the spreading of a liquid over a solid surface, and 3) the wicking of a liquid into a porous solid. However, in this definition, wetting does not include dissolution or swelling of the solid by the liquid or any kind of chemical reaction between the materials that changes the system composition.

Wetting phenomena may be characterized by using thermodynamic wetting parameters, for example contact angles, surface free energy, and work of adhesion. It is important to remember that such parameters are by definition bulk measurements, and they do not directly describe the interaction at a molecular level.

Any understanding of the wetting phenomena must, however, be traced to the origin and nature of intermolecular forces. Overviews of fundamental theories and basic knowledge about intermolecular forces and wetting phenomena can be found in e.g. Jensen (1991), Lee (1991), Mittal and Anderson (1991), Mittal (1993), van Oss (1994), Good (1993), and Berg (1993a). Intermolecular forces may be divided into physical and chemical related forces. Recently, it has been proposed that the former can collectively be referred to as “van der Waals” forces, and, in case of wetting-related phenomena, the latter can mainly be considered as acid-base interactions (Fowkes 1983; van Oss *et al.* 1987; Berg 1993a). In such acid-base interactions, an electron pair is donated by the base (electron-donor) and is shared with the acid (electron-acceptor), together forming an “adduct”.

It is of great importance to find and develop methods for measuring and evaluating the strength and role of these intermolecular forces in wetting phenomena.

Some basic relations for the study of wetting phenomena

Consider a liquid drop placed on a smooth, non-porous rigid solid, both exposed to a gas. If the whole system is in an equilibrium state, the *contact angle* θ is then defined as the angle between the tangent to the liquid surface and the liquid/solid surface at the point of liquid/solid contact (see Figure 3). Thomas Young (Young 1805) formulated (without using equations) the relation between the surface tension of a liquid and a solid, the interfacial tension between the solid and the liquid, and the contact angle θ for a drop of liquid deposited on a flat horizontal surface. This formulation is usually expressed as Young’s equation:

$$\gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL} \quad (1)$$

where γ_{LG} and γ_{SG} are the surface free energies of the liquid and the solid, respectively, exposed to a gas (G), and γ_{SL} is the solid-liquid interfacial free energy.

Bikerman (1958), argued that equation (1) only balances forces in the plane of the surface and that there is no balance to the force normal to solid surface. Good (1993) states however, that there exists a strain field in the solid ‘below’ the three-phase line, which balances the upward force $\gamma_{LG} \sin\theta$ (see Figure 3). If the system is not in equilibrium and the liquid ‘wets out’ the solid then the liquid exhibits a contact angle of zero against the solid. In other words, if $\gamma_{SG} > \gamma_{SL} + \gamma_{LG}$, then $\cos\theta = 1$ (Good 1993).

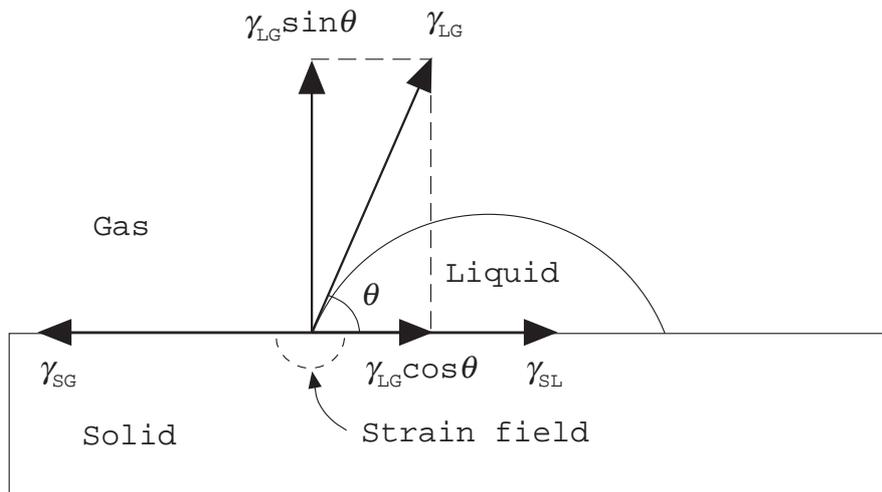


Figure 3. Equilibrium state of a drop of liquid on a smooth, non-porous, and rigid solid, surrounded by a gas.

Zisman (see e.g. Zisman 1964) and co-workers provided the incitement for nearly all later wetting studies, and brought reproducibility into the field mainly by studying well-defined systems using refined techniques for the measurement of contact angles (Johnson and Dettre 1993). Fox and Zisman (1950) introduced the well-known concept of critical surface tension, γ_c , an empirical method where the measurement of θ for a series of homologous liquids on a solid allows an estimate of γ_s , the surface free energy of the solid. In this case, an approximate linear relationship is often found if $\cos\theta$ is plotted vs. γ_L . The ‘critical’ value, γ_c , of γ_L where $\cos\theta = 1$ (determined by extrapolation, if necessary), i.e. the situation when an actual or hypothetical liquid will just spread on the solid, is considered to be an estimate of γ_s . Zisman himself however, emphasized that γ_c was not the surface energy of the solid but only a closely related empirical parameter. Johnson and Dettre (1993) also emphasized that, when e.g. hydrogen bonds are involved in the interfacial interaction between a solid and a liquid the plot of $\cos\theta$ vs. γ_L shows curvature and the points no longer fall on a single curve. The Zisman approach is not applied in the present work.

Perhaps the most convenient way of interpreting the wettability of a low-energy surface, such as that of various polymer or ligno-cellulosic materials, is by the formulation of the work of adhesion, W_a , defined (Dupré 1869) as the work required to separate unit area of the solid-liquid interface, i.e.

$$W_a = \gamma_S + \gamma_L - \gamma_{SL} \quad (2)$$

where γ_S and γ_L are the surface free energies of the solid (S) and liquid (L) surfaces in vacuum, and γ_{SL} is the solid-liquid free energy. W_a is also equivalent to the negative free energy change of adhesion, ΔG_a , i.e., $W_a = -\Delta G_a$.

The surface free energy per unit area (or surface tension) γ_i of the substance i is defined as half the work of cohesion W_c , i.e.:

$$\gamma_i = \frac{1}{2} W_c \quad (3)$$

Assuming that $\gamma_L \approx \gamma_{LG}$ and $\gamma_S \approx \gamma_{SG}$, combination of equations (1) and (2) leads to the Young-Dupré equation:

$$W_a = \gamma_L (1 + \cos \theta) \quad (4)$$

Hence, if the contact angle, θ , of a well-defined probe liquid against a solid is measured, the work of adhesion can be determined.

The assumption that $\gamma_S \approx \gamma_{SG}$, may in some cases be incorrect. If vapor from the liquid adsorbs onto the solid surface, the surface free energy of the solid is reduced. The reduction is referred to as the equilibrium film pressure π_e (see e.g. Good 1993) and it should be added to the right-hand side of equation (4). However, π_e is probably negligible on low-energy surfaces for liquids that form non-zero contact angles (Fowkes 1983). The contact angle data used in the present study is significantly greater than zero, and the influence of π_e is therefore assumed to be negligible.

The following descriptions (equations [5]-[12]) briefly summarize the *Lewis acid-base concept* in wetting-related phenomena (see also Jensen 1991; Good 1993; Berg 1993a; van Oss 1994; Chehimi 1999). According to Fowkes (1983) and van Oss *et al.* (1987), the total work of adhesion in interfacial interaction between solids and liquids can be expressed as the sum of the Lifshitz-van der Waals (LW) and the Lewis acid-base (AB) interactions, viz.

$$W_a = W_a^{LW} + W_a^{AB} \quad (5)$$

The separation of the work of adhesion into LW and AB components is also applicable to the surface free energies according to:

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \quad (6)$$

A breakthrough for the understanding of wetting phenomena was without doubt the Good-Girifalco-Fowkes ‘geometric mean’ combination rule for the LW interactions between two compounds i and j , (Good and Girifalco 1960; Fowkes 1963), which can be expressed as:

$$W_a^{LW} = 2\sqrt{\gamma_i^{LW}\gamma_j^{LW}} \quad (7)$$

Fowkes and Mostafa (1978), related the acid-base contribution to the work of adhesion, W_a^{AB} , to the molar enthalpy of acid-base adduct formation, ΔH^{AB} , as follows:

$$W_a^{AB} = f(-\Delta H^{AB})n^{AB} \quad (8)$$

where f is a factor that converts enthalpy into free energy and n^{AB} is the number of acid-base bonds per unit area. ΔH^{AB} may then be evaluated with the Drago four-parameter equation (Drago and Weyland 1965):

$$-\Delta H^{AB} = C^A C^B + E^A E^B \quad (9)$$

where C^A and C^B characterize the ‘softness’ or covalent contribution and E^A and E^B the ‘hardness’ or electrostatic contribution to the enthalpy of an acid-base adduct formation. Evidence for the usefulness of equation (9) in predicting enthalpies of acid-base adduct formation was provided for polymer adsorption on various substrates by Fowkes (1983). Berg (1993a) pointed out that the most serious present limitation of the Drago parameter approach is that it treats all compounds as monofunctional acids or bases. For example, water is treated as a monofunctional acid, although it is known to be a bifunctional liquid. The Drago approach is not applied in this work.

Furthermore, ΔH^{AB} may be evaluated using inverse gas chromatography (IGC) (see e.g. Lloyd *et al.* 1989) combined with the semi-empirical Gutmann approach (Gutmann 1978) where the acid-base properties of solids and liquids are characterized by their acceptor (AN) and donor (DN) numbers, representing their electron acceptor (acidic) or donor (basic) ability, respectively. In addition, Riddle and Fowkes (1990) redefined a new acceptor number (AN^*) on the same scale and same unit (kcal/mol) as the donor number.

The acceptor and donor number may then be related to ΔH_A^{AB} by the expression (Saint Flour and Papirer 1982; Schultz *et al.* 1987):

$$-\Delta H_A^{AB} = K_A DN + K_B AN^* \quad (10)$$

where K_A and K_B are dimensionless acceptor and donor constants of the investigated material, respectively. The plot of $-\Delta H_A^{AB}/AN^*$ versus DN/AN^* for different probes should thus be linear and K_A and K_B can be determined from the slope and the intercept, respectively, of this linear function.

van Oss *et al.* (1987) suggested that the acid-base interactions comprise two different and independently variable properties expressed in the electron-acceptor (γ^+) and the electron-donor (γ^-) surface free energy parameters, and suggested that W_a^{AB} can be expressed as:

$$W_a^{AB} = 2\sqrt{\gamma_i^+ \gamma_j^-} + 2\sqrt{\gamma_i^- \gamma_j^+} \quad (11)$$

where $\gamma_{i,j}^+$ stands for the electron-acceptor component and $\gamma_{i,j}^-$ for the electron-donor component of the surface free energy of substance i or j .

The complete van Oss-Chaudhury-Good (vOCG) equation can be expressed as (Good 1993):

$$(1 + \cos \theta) \gamma_L = 2(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}) \quad (12)$$

Accordingly, if the contact angle is measured on the same surface with three different liquids (each with completely determined γ_L^{LW} , γ_L^+ and γ_L^- values), equation (12) enables the three unknown solid parameters γ_S^{LW} , γ_S^+ and γ_S^- to be determined. As a reference liquid in this model, water is defined (van Oss *et al.* 1987) as having equal acid and base components of the surface free energy ($\gamma_L^+ = \gamma_L^- = 25.5 \text{ mJ/m}^2$). The surface free energy components according to this model have been presented for a series of probe liquids by e.g. van Oss (1994).

Recently, the determination of surface free energy components by the vOCG model approach has been debated and evaluated in many studies (e.g. Kwok *et al.* 1994 and 1998; Lee 1993 and 1996; Berg 1993b; Wu *et al.* 1995; Janczuk *et al.* 1996; Della Volpe and Siboni 1997; Douillard 1997). For example, Kwok *et al.* (1994) and (1998) advocated the use of the ‘equation of state’ for the determination of the solid surface free energy, and rejected the vOCG model on the basis of experimental findings. On the other hand, Wu *et al.* (1995) advocated the vOCG model and rejected the ‘equation of state’ on the basis of experiments which included polar surfaces, in contrast to the experiments by Kwok and co-workers which included only apolar surfaces.

Recently, Della Volpe and Siboni (1997) proposed a modified calculation procedure in order to enable more reliable Lewis acid-base analyses of liquids and solids by the vOCG model. Based on an example of a more proper set of probe liquids and on literature data for contact angles on various polymer surfaces, they found that the ratio of the acid and base parameters, γ_L^+/γ_L^- , for water may be of the order of 6.5:1, i.e. a predominantly acidic character, in contrast to the assumed ratio of 1:1 mentioned above. However, they also suggested that better data on advancing and receding contact angles at fixed temperatures on well-defined surfaces and with controlled purity are necessary. Lee (1996) also suggested that water may have a greater Lewis acidic than Lewis basic component.

Chang and Chen (1989) proposed a semi-empirical approach similar to the vOCG model (see also Chen and Chang 1991 and Qin and Chang 1995). In this model, three surface energetic parameters, P^D , P^A , P^B are defined. P^D is the dispersion parameter. In the present study γ^D is assumed to be equal to γ^{LW} . P^A and P^B are an acid (A) and a base (B) parameter, respectively. Positive value(s) of the acidic and/or basic parameter describe the acidic character of the surface, and nega-

tive value(s) the basic character. The surface is said to be ‘acidic’ if both parameters are positive, and ‘basic’ if both are negative, and hence if they are of opposite sign the surface is bifunctional.

The acid-base component of the work of adhesion between a liquid and solid is then expressed by a combining rule as:

$$-W_a^{AB} = P_S^A P_L^B + P_S^B P_L^A \quad (13)$$

It is important to note that equation (13) allows the acid-base interaction to be negative in contrast to equation (11) in the vOCG model. Furthermore, the total work of adhesion is expressed as:

$$W_a = 2\sqrt{\gamma_S^{LW} \gamma_L^{LW}} - (P_S^A P_L^B + P_S^B P_L^A) \quad (14)$$

Based on published contact angle data for different probe liquids on solid surfaces, Qin and Chang (1996) determined the different surface free energy parameters of some probe liquids by a best least squares fit to equation (14).

It is obvious that most of the concepts for wetting analysis of materials, as presented above, involve the contact angle. In other words, contact angle measurements of well-defined probe liquids on the surface of interest are in most cases the basis for estimations of wetting properties of the material.

Apart from contact angle measurements, e.g. inverse gas chromatography (IGC) (see Paper IV), Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS, also referred to as ESCA), and microcalorimetry are available techniques for assessing, for instance, a material’s wetting properties, surface energetics, surface composition, and acid-base properties (Chehimi 1999). In addition, interfacial force microscopy (IFM), atomic force or scanning tunneling microscopy (AFM and STM) may enable adhesion forces on the molecular scale to be measured (Chehimi 1999). However, the present thesis focuses only on contact angle determination and IGC.

Contact angle measurement techniques and contact angle hysteresis

Neumann and Good (1979) reviewed the classical techniques for measuring contact angles (see also Adamson and Gast 1997). The most widely used technique, also regarding wood, involves direct measurement of the angle from the profile of a drop deposited on a horizontal or inclined surface (referred to here as the drop method). Similar techniques involve digital image analysis of the dimensions of a drop profile on a surface from which the contact angle can be calculated. Other techniques are e.g. the Wilhelmy method (see e.g. Johnson and Dettre 1969 and 1993; Andrade *et al.* 1985), capillary rise on a vertical plate (see e.g. Neumann and Good 1979), and column or thin layer wicking (see e.g. van Oss 1992).

It must be emphasized that if one measures the contact angle of a liquid as it advances slowly over a non-ideal surface (e.g. not chemically homogeneous and not perfectly smooth, as in the case of most practical surfaces) and then measures the corresponding angle when the liquid is receding over the same surface, it is commonly observed that there is an appreciable difference between these two angles, referred to as contact angle hysteresis. Good (1993) urged all investigators of con-

tact angles to measure advancing as well as receding angles. Andrade *et al.* (1985) also pointed out that contact angle hysteresis is a rich source of information when studying polymer-liquid interactions.

Some important causes of hysteresis have been summarized by Andrade *et al.* (1985) and Good (1993):

- (1) *Surface roughness.* Wenzel (1936) showed that surface roughness causes a pronounced contact angle hysteresis, and suggested that a roughness factor, r , i.e. the ratio of the actual to the geometric surface, must be included in the Young equation if the solid surface is not perfectly smooth (see also Johnson and Dettre 1964).
- (2) *Surface heterogeneity.* It is commonly accepted (see e.g. Johnson and Dettre 1993; Good 1993) that the advancing contact angle on a heterogeneous surface tends to represent low-energy regions, and the receding angle represents the high-energy regions, and that this often produces a pronounced contact angle hysteresis (see also Neumann and Good 1979; Dettre and Johnson 1964).
- (3) *Reorientation of molecules and functional groups.* For certain polar solids, the reorientation of molecules or functional groups in the solid surface after contact with a liquid phase is a major cause of contact angle hysteresis. For instance, in some cases hydrophilic hydroxyl groups in a surface are ‘buried’ when the surface is exposed to the inert air, while they ‘turn over’ to form hydrogen bonds when the surface is in contact with water. (see also Holly and Refojo 1975)
- (4) *Penetration, adsorption and swelling.* Timmons and Zisman (1966) suggested that an apparent penetration of water molecules into a surface could cause a significant contact angle hysteresis. They argued that a receding drop in some cases moves over a surface in which the intermolecular pores are saturated with water. Similarly, in the Wilhelmy method when a beaker with liquid is raised over the plate (advancing mode), the liquid edge runs over a dry surface and must displace vapor and air. In contrast, when the beaker is lowered (receding mode) the liquid edge runs over a surface that may have adsorbed liquid, resulting in a significant lower angle than in the advancing case. In addition, as a polymer swells, its contact angle with the swelling liquid may drop (see e.g. Good and Kotsidas 1979). In addition, Andrade *et al.* (1985) stated that the wetting forces may induce surface deformation, leading to contact angle hysteresis; and he also suggested that hysteresis may be due to surface configurational entropy effects.

1.4 WETTING STUDIES ON WOOD

Surfaces like wood, with a heterogeneous, hygroscopic, porous, and rough nature have challenged scientists to develop and further modify new methods for the 'reliable' measurement of contact angles. Historically, wood wettability has been determined by direct optical measurement of static and equilibrium contact angles or time-dependent contact angles caused by liquid absorption. The drop method has been widely used on wood (Gray 1962; Herczeg 1965; Jordan and Wellons 1977; Nguyen and Johns 1979; Liptáková and Kúdela 1994). However, precise direct optical measurement of contact angles to determine the surface thermodynamic characteristics is inherently difficult with wood because of its chemical heterogeneity, surface roughness, porosity, and hygroscopic nature (see e.g. discussion by Marian and Stumbo 1962).

If a liquid contacts a porous media such as wood, and the contact angle formed on the material is less than 90° (see equation [22] in section 2.2), then spontaneous wicking (penetration) of the liquid into the porous medium will occur. Similarly, a surface structure, e.g. like tracks in a gramophone record, may also result in capillary forces, causing wicking of the liquid along the surface (see e.g. Gerdes 1998). All wood surfaces have a pronounced surface roughness. This surface structure mainly originates from the intrinsic wood cell structure. In addition, the processing of wood by different machining operations generally results in an irregular surface structure of damaged and raised wood cells. Accordingly, when a liquid contacts a 'technical' wood surface, the intrinsic wood surface structure combined with the irregular surface structure resulting from different machining processes may cause liquid transport along the surface by capillary forces.

It is also evident that when polar liquids are brought into contact with the hygroscopic wood substance, diffusion and penetration of the liquid into the bulk substance will occur. Subsequently, the adsorption of the liquid on the fictitious 'inner surface' of the bulk phase causes swelling, often with a significant release of heat (heat of sorption). It is thus obvious that molecules from the contacting liquid will easily move across the apparent wood-liquid interface because of these absorption and adsorption processes. In such cases, it is not possible to achieve a wetting equilibrium or static contact angle until the wood is saturated with the liquid.

Extractives play a central role in wetting analyses of wood (Gardner *et al.* 1995). As mentioned above, extractives are stored in the resin channels under pressure and after e.g. machining operations on sawn and dried timber, some extractives presumably migrate to the exterior surfaces. Extractives probably also diffuse to 'newly' created wood surfaces which may be considered as a natural surface inactivation process to lower their energetic state (see also Back 1991; Nussbaum 1996 and 1999).

Zavarin (1984) pointed out that the chemical composition of a machined wood surface is significantly different from that of the bulk of the wood (see also Jaic' *et al.* 1996; Liptakova *et al.* 1995), and that wood surfaces in general are covered with polar and non-polar extractives. He also stated that the conditions and methods of wood surface formation can strongly influence its chemical composi-

tion. For instance, if the easily movable extractives are excluded, cross sections have a chemical composition similar to that of the bulk wood, whereas tangential and radial sections deviate significantly, presumably due to more exposed middle lamella with their high content of lignin (Zavarin 1984).

A large amount of literature (see e.g. Gray 1962; Chen 1970; Nguyen and Johns 1979; Hse and Kuo 1988; Christiansen 1994; Gardner *et al.* 1995; Nussbaum 1999) has dealt with the influence of e.g. aging, drying and extractives on wood wettability and gluability. From these studies, it is clear that significant changes in the wood surface wettability and gluability occur due to aging, and due to the presence and migration of extractives. Gardner *et al.* (1995) suggested that preferential molecular reorientation of the extractives will occur depending on the surrounding environmental conditions. Chen (1970) showed that solvent-extraction of wood surfaces improved their wettability.

Christiansen (1994) summarized the mechanisms for changes of wood surfaces that may influence the physical and bonding properties of wood: 1) migration of hydrophobic extractives during drying 2); oxidation 3); molecular reorientation of functional groups in the surface; 4) acidity or reactivity of extractives affecting the curing time of adhesives; 5) closure of micro-voids in the wood substance which reduces adhesive penetration. Hse and Kuo (1988) also concluded that oxidation of extractives tends to increase the acidity of wood.

Recently, Nylund *et al.* (1998) investigated the surface free energy and wettability of various wood resins in spruce. They found that wood resins were rather hydrophobic, although extensive acid-base interactions with surrounding media were observed. It was suggested that an orientation of the carboxyl groups of the resin acids and fatty acids occurred towards an aqueous phase which enables hydrogen bonds to be formed at the surface.

In summary, because of the intricate nature (e.g. the porosity, hygroscopicity, anatomic complexity, heterogeneity, and the extractive content) of wood and its surfaces, wetting measurements on wood may be inherently difficult. It is obvious that the direct measurement of the contact angle of a drop deposited on the wood surface is an unsatisfactory approach from both an experimental and a statistical point of view. For example, a drop of water on a wood surface will in most cases quickly change its size and shape over time, which will thus lead to a change in the contact angle. The contact angle measurement may therefore be hazardous, and the decision as to which value of a contact angle shall be chosen will strongly depend on the operator of the experimental equipment. This implies that other or new methods for determining the wetting parameters of wood will be necessary.

One way to address some of the difficulties in wood wetting measurements may be to apply the Wilhelmy method (Wilhelmy 1863). In contrast to direct measurement of contact angles, as in the drop method, the Wilhelmy method involves determining the force acting on a specimen when it is immersed in and withdrawn from a liquid. An apparent contact angle can then be estimated from an analysis of the recorded force (Johnsson and Dettre 1993; Vogler 1993; Kistler 1993). The Wilhelmy technique has been applied for determining the wettability properties of wood pulp fibers (Young 1976; Klungness 1981; Hodgson and Berg 1988; Berg

1993b; Deng and Abazeri 1998), and it has also been applied in wetting analyses of solid wood by e.g. Cassilla *et al.* (1981), Gardner *et al.* (1991), Mantanis and Young (1997), and Shen *et al.* (1998a).

Other promising techniques for estimating the surface energetics of wood may be the Axisymmetric Drop Shape Analysis-contact diameter (ADSA-CD) technique (Kazayawoko *et al.* 1997) and a similar technique suggested by Scheikl and Dunky (1998); contact angle measurements determined as constant wetting rate angle values (cwra) presented by Nussbaum (1999); and also a capillary rise technique (column wicking) applied to wood particles by Gardner *et al.* (1999).

Inverse gas chromatography (IGC) is a useful technique for determining surface energetics of particle surfaces (Lloyd *et al.* 1989). By using appropriate gas probes, IGC can provide information on the surface thermodynamic characteristics of particles including surface free energy, acid-base interactions, enthalpy, and entropy. IGC has been applied to many materials such as polymers (see e.g. Lloyd *et al.* 1989), wood pulp fibers (see e.g. Kamden and Riedle 1992; Jacob and Berg 1994; Shi *et al.* 1997), and wood particles (see e.g. Kamden *et al.* 1993; Tschabalala 1997; Gardner *et al.* 1999).

To be able to estimate some basic wetting parameters on wood and to apply various wetting concepts and theories, such as the Lewis acid-base approach, we need to develop appropriate wetting measurement techniques suitable for the complex wood surface.

Based on contact angle analysis and IGC, the Lewis acid-base approach has been applied on wood fibers and cellulose (e.g. Berg 1993b; Jacob and Berg 1994; Dourado *et al.* 1998; Shen *et al.* 1999), and on solid wood and wood particles (e.g. Kamden *et al.* 1993; Gardner 1996; Mantanis and Young 1997; Tschabalala 1997; Shen *et al.* 1998a; Gardner *et al.* 1999). Generally, the results from the contact angle analysis in these studies of both wood and wood fibers show that the surface character of these materials is predominantly Lewis basic. On the other hand, results from IGC show that the corresponding surfaces are pronouncedly bifunctional or predominantly Lewis acidic. Shen *et al.* (1998b) suggested that the acid-base characterization of wood surfaces by wetting methods corresponds to the outermost surface, whereas the characterization by some spectroscopic methods (XPS and FT-Raman) relates to the sub-surface region. They also showed that the sub-surface region of pinewood may exhibit lower basicity than the outermost surface.

When techniques and methods successfully applied to other materials are applied on wood, it is important to pay attention to its complex nature and how this may influence the wetting measurements. This knowledge may make it possible to detect and control such influences, and to develop new and more suitable measurement techniques for 'reliable' wetting studies of wood.

1.5 STATEMENT OF OBJECTIVES

The overall objective of the present thesis is to study wetting phenomena on wood. Knowledge about such phenomena is essential information in the area of wood adhesion science and technology, and may, for example, guide us to improve the interaction between wood and adhesives or coatings. The actual goal of the thesis is to recognize some basic principles and experimental methodologies suitable for the measurement of wetting parameters on wood. This also includes the recognition and interpretation of important factors influencing the wetting properties of wood, such as the influences of wood extractives and surface aging. An effort is also made to estimate and interpret so-called Lewis acid-base properties of the wood material. These acid-base properties of wood and other polymers are presumably of great importance for their wettability.

In practical aspects, it is of crucial importance to characterize and estimate the wettability of the wood substance in order to be able to predict and control its interaction with other materials in certain wood applications. This information could be used to predict and enhance the adhesion properties of wood, which could benefit the development of new efficient gluing and coating technology. For example, it might be possible to develop and tailor new adhesives and coatings in order to suit new combined solid wood products.

2. METHODS

2.1 THE WILHELMY METHOD

The following description and principles are the basis for the wetting measurements in Papers I and II. The force F required to partially submerge a smooth plate in a liquid is given (Wilhelmy 1863) as:

$$F = P\gamma \cos\theta - \rho Ahg \quad (15)$$

where P is the wetted perimeter of the plate, γ is the surface tension of the liquid, θ is the liquid-solid-air contact angle, ρ is the liquid density, A is the cross-sectional area of the plate, h is the depth of immersion, and g is the gravitational constant (see also e.g. Neumann and Good 1979; Adamson and Gast 1997). Figure 4 shows a schematic illustration of the Wilhelmy method for studying the wettability of a plate.

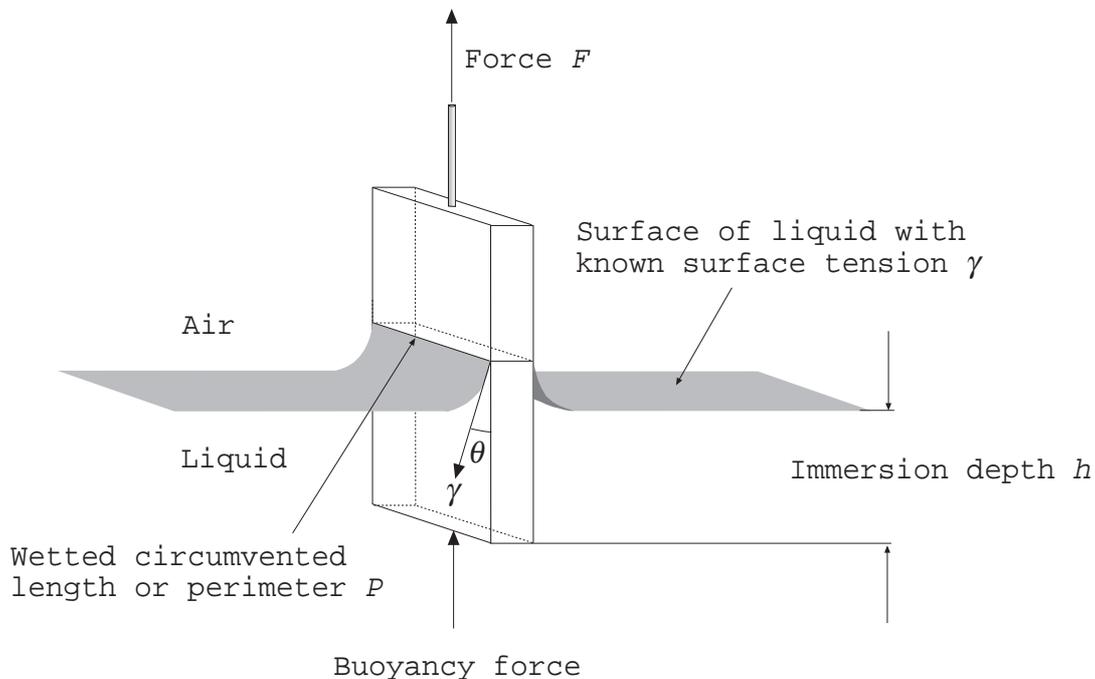


Figure 4. Schematic illustration of the Wilhelmy method. The force F required to partially submerge a plate in a liquid is balanced by the wetting force $P\gamma \cos\theta$ (equal to the weight of the liquid in the formed meniscus) and the buoyancy force (equal to the weight of liquid displaced by the plate).

In the present study, force measurements have been carried out in a dynamic mode by recording the dynamic force during a test cycle when a wood veneer specimen is immersed in and withdrawn from a probe liquid. The velocity of the immersion and withdrawal are comparatively slow, and therefore any dynamic effects on the wetting forces are assumed to be negligible.

This dynamic technique addresses some expected experimental problems caused by the pronounced heterogeneity of the wood surface, by averaging the wetting properties over a large area of the veneer. If the force F is plotted as a function of the depth of immersion h , a straight line should be obtained where the slope is $-\rho Ag$, and the intercept on the F axis is equal to $P\gamma\cos\theta$. Equation (15) is linear with constant slope only if $P\gamma\cos\theta = \text{constant}$. A variation in linearity can therefore be an indication that γ , θ , or P may be changing during the measurements.

If the weight of the plate changes during the experiment, due to wicking (capillary transport) and sorption of the liquid then

$$F(h, t) = P\gamma\cos\theta + F_w(t) - \rho Ahg \quad (16)$$

where $F_w(t)$ is the force due to wicking and sorption of the liquid at time t .

Immersion of wood veneers – Wilhelmy test cycles

In the present study, wood veneers were immersed in the liquids along the grain, i.e. in the fiber direction, to a depth of 10 mm and then withdrawn to about 4 mm above the surface, and thereafter, with no pause, immersed a second time. Recording of data for the second cycle was ended at a depth of about 4 mm. Figure 5 illustrates a plot of the recorded force F vs. immersion depth h during a test cycle when a wood veneer is immersed in and withdrawn from a liquid. No force is recorded until the veneer touches the liquid. The lower (stage a–b) and the upper (stage c–d) curve represent the advancing and receding situation respectively.

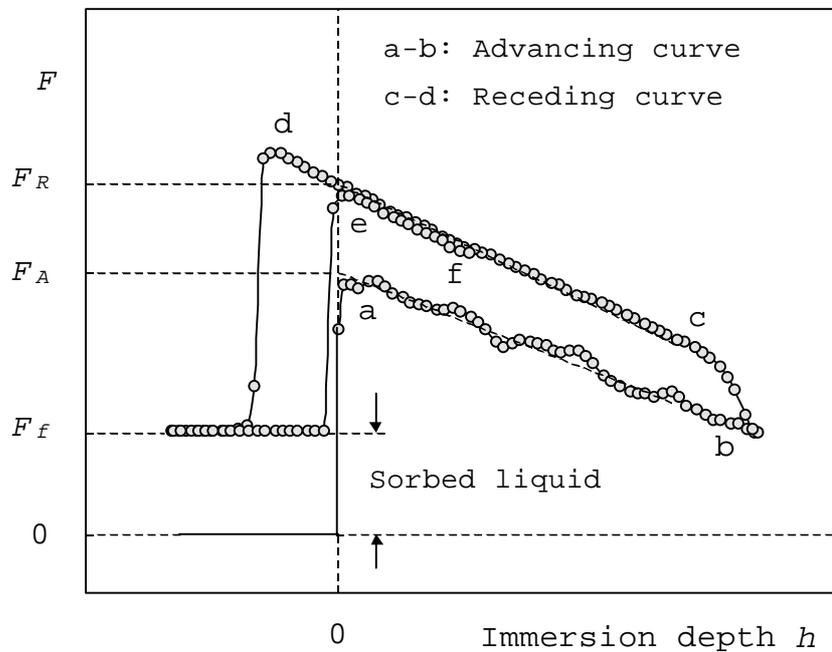


Figure 5. The Wilhelmy plate method illustrated by a schematic plot of the recorded force F versus immersion depth h during a test cycle when a wood veneer is immersed in and withdrawn from a liquid. The abbreviations are explained in the text.

The slope of the advancing curve is uneven, which may be attributed mainly to the heterogeneous composition of the wood surface. The receding curve is less irregular, presumably because the liquid ‘wets’ the surface (resulting in zero contact angle). The intercepts, F_A and F_R , on the ordinate shown in Figure 5 are obtained by linear regression of the advancing and the receding curve respectively. F_f is the final force, i.e. the amount of sorbed liquid during a test cycle equal to the term $F_w(t)$ in equation (16) at the time after the rupture of the meniscus (at $h \approx 0$). $F_w(t)$ is assumed to be zero when the veneer touches the liquid in the first test cycle (at $h \approx 0$). The intercepts for the advancing and receding curves are then given by

$$F_A = P\gamma \cos\theta_A \quad (17)$$

and

$$F_R = P\gamma \cos\theta_R + F_f \quad (18)$$

where θ_A and θ_R are the advancing and receding contact angles respectively.

When the veneer is immersed a second time (see Figure 5, stage e–f) the advancing and receding curves are approximately coincident, i.e. there is no hysteresis, which means that $\theta_A = \theta_R = 0^\circ$ (see also Hodgson and Berg 1988; Mantanis and Young 1997). If the surface tension of the liquid is known, then the perimeter of the test piece can be estimated by equation (18). Vice versa, if the perimeter is known, the liquid surface tension can be estimated.

Determination of surface tension and contamination of probe liquids

The surface tensions γ of the probe liquids used were measured according to a standard procedure using a platinum plate and the Wilhelmy plate method. Table 1 presents the probe liquids used in papers I and II, along with the measured surface tension.

Table 1. Measured surface tension¹ γ at about 22° C of probe liquids.

Liquid	Surface tension γ
	[mN/m]
Water	72.2 (0.25)
Ethylene glycol	47.1 (0.14)
Formamide	58.0 (0.21)
Diiodomethane	51.1 (0.34)
Octane	21.7 (0.07)

¹ Each value is based on 50 replicates. Standard deviations are given in parentheses.

To detect any contamination of the probe liquids, their final surface tension γ_f was recorded after each test cycle. A contamination parameter C_{meas} of the probe liquids could then be expressed as

$$C_{meas} = \gamma - \gamma_f \quad (19)$$

To study any contamination of the probe liquids by wood extractives during the experiments, the apparent surface tension γ_{app} was calculated as

$$\gamma_{app} = \frac{F_R - F_f}{P} \quad (20)$$

where P is the perimeter of the veneer determined by a test cycle in octane. An apparent contamination parameter C_{app} of a probe liquid could then be expressed as

$$C_{app} = \gamma - \gamma_{app} \quad (21)$$

2.2 WICKING (CAPILLARY RISE) METHOD

The following description and principles are the bases for the wetting measurements in Paper III. A liquid may penetrate spontaneously into a porous medium by capillary forces. This process, referred to as wicking, also occurs when the liquid contacts a powdered material or a fiber network. Wicking, i.e. the distance traveled by the liquid front (or the capillary rise of the liquid) in such materials is described by the Washburn equation (Washburn 1921):

$$h^2 = \frac{R_e \gamma \cos \theta}{2\eta} t = Kt \quad (22)$$

where h is the distance traveled by the liquid in time t , R_e is the effective interstitial pore radius between the packed particles or fibers, θ is the liquid-solid-vapor contact angle, and γ and η are the surface tension and viscosity of the liquid, respectively. K is a constant, i.e. a grouping of all constants in equation (22), and is here referred to as the Washburn slope. It is important to note that θ in this situation represents an advancing contact angle, and also, that no spontaneous penetration will occur for θ values $\geq 90^\circ$.

The wicking experiments were performed by immersing columns packed with ground wood particles vertically to a depth of about 5 mm in the probe liquid. Thereafter, the vertical movement of the probe liquid was determined by measuring (using a stopwatch) the time t for the visible liquid front to reach various heights h at intervals of about 3–5 mm, each starting from 5–10 mm above the initial front.

There are two unknowns in equation (22), the effective interstitial pore radius R_e and $\cos \theta$. If a liquid with low surface tension such as methanol or hexane is used, the liquid is expected to spread over the solid surface of the sample particles during the wicking measurements, so that $\cos \theta = 1$, and thus equation (22) can be solved for R_e . This R_e value was thereafter used for the same sample particles to determine $\cos \theta$ for the non-spreading probe liquids: water, ethylene glycol, formamide and diiodomethane.

In addition, the temperature was measured at a low (h_1) and a high (h_2) point within the column during a series of wicking experiments.

2.3 INVERSE GAS CHROMATOGRAPHY (IGC)

The following description and principles are the basis for the inverse gas chromatography (IGC) measurements in Paper IV. The operation of IGC is like regular gas chromatography where gases are injected into an inert gas stream passing through a packed column held in an environmentally controlled oven. As the gases reach the end of the column, they are detected using a flame ionization detector. The gases are separated according to their particular affinity to the column packing material. In normal gas chromatography, the columns are chosen for their ability to separate gases adequately, whereas in IGC, known gas probes are chosen for their ability to interact with an unknown packing material. In normal IGC, the measurements are performed at infinite dilution, which means that only an extremely small concentration of the probe is injected into the columns. For energetically heterogeneous surfaces, this means that such an analysis assesses adsorption only on the high-energy sites. In contrast, e.g. advancing contact angle measurements using the Wilhelmy or drop method assesses mainly the lower energy regions of the surface (Good 1993).

Data analyses

The net retention volume V_N , the fundamental parameter in IGC measurements, is defined as the volume of carrier gas required to elute a given amount of the adsorbate (probe) from the adsorbent (in this case the wood powder) in the column. For IGC measurements carried out at infinite dilution (zero surface coverage), Henry's law region is reached which means that the adsorption isotherm is linear and that the retention mechanism is due only to surface adsorption. From the retention time measured by IGC for a given probe, V_N is given by the following equations (Conder and Young 1979; Chtourou *et al.* 1995):

$$V_N = K_S A = Q(t_r - t_p) \quad (23)$$

where K_S is the surface partition coefficient for the solute (Henry's law constant), A is the total surface area of the adsorbent in the column, Q is the flow rate of the carrier gas corrected for pressure drop caused by gas-phase compressibility, and t_r and t_p are the retention times of the probe and propane, respectively. V_N is then related to the molar free energy change of adsorption, ΔG_A by

$$\Delta G_A = -RT \ln V_N + C \quad (24)$$

where R is the gas constant, T is the absolute temperature, and C is a constant depending on the weight and specific surface area of the packed material in the column and the chosen reference states of the probes in the gaseous and the adsorbed states.

Dorris and Gray (1980) suggested a link between ΔG_A and the work of adhesion across a solid-liquid interface, W_a , given by

$$-\Delta G_A = aNW_a \quad (25)$$

where a is the area covered by one adsorbed probe molecule and N is the Avogadro number.

Based on the geometric mean combining rule (equation [7]), γ_S^{LW} of the investigated material may then be determined by the expression:

$$RT \ln V_N^{alkane} = 2N(\gamma_S^{LW})^{1/2} a(\gamma_L^{LW})^{1/2} + C \quad (26)$$

Thus, a plot of $RT \ln V_N$ versus $a(\gamma_L^{LW})^{1/2}$ for a series of non-polar probes, such as n -alkanes, should be linear, and γ_S^{LW} can thus be determined from the slope of this function.

Because of the additivity of the intermolecular interactions, the molar free energy change due to Lewis acid-base (AB) interactions, ΔG_A^{AB} , can be quantified by comparing the retention behavior between adsorption of non-polar and polar probes. This may be expressed as (Schultz *et al.* 1987):

$$\Delta G_A^{AB} = -RT \ln \left(\frac{V_N}{V_N^{ref}} \right) \quad (27)$$

where V_N and V_N^{ref} are the net retention volumes of an acid-base and alkane probe, respectively, at the same value of $a(\gamma_L^{LW})^{1/2}$. ΔG_A^{AB} is also referred to as the specific interaction.

In addition, the molar enthalpy of adsorption due to AB-interactions, ΔH_A^{AB} , can be determined using the thermodynamic relation:

$$\Delta G_A^{AB} = \Delta H_A^{AB} - T\Delta S_A^{AB} \quad (28)$$

where ΔS_A^{AB} is the molar entropy of adsorption due to AB-interactions. Thus, the intercept of a plot of ΔG_A^{AB} versus temperature is equal to ΔH_A^{AB} . In other words, IGC measurements at a series of different temperatures enables ΔH_A^{AB} to be determined. Furthermore, the Lewis acid-base interactions between the probes and the solid can be characterized using Gutmann's approach as described in section 1.3 (equation 10).

2.4 MATERIALS

For the wetting measurements using the Wilhelmy method, extracted and non-extracted radial sectioned veneers with dimensions of approximately $20 \times 6 \times 1 \text{ mm}^3$ (in the longitudinal, radial and tangential direction respectively) of clear heart- and sapwood of pine (*Pinus silvestris* L.) were prepared (see Paper I for details). To study possible aging effects, the veneers were prepared as fresh and aged surfaces. In all, 12 different samples (test groups), each with 25 independent veneer replicates (test pieces), were investigated: a) heartwood, b) extracted heartwood, c) sapwood, d) extracted sapwood; prepared as i) fresh surfaces, tested within one minute from preparation; ii) one-day-old surfaces; and iii) one-week-old sur-

faces. Test cycles were also performed on thin glass plates (microscope glass cover slips) in octane for comparative reasons.

For the wicking and IGC experiments, extracted and non-extracted samples of clear heart- and sapwood of spruce (*Picea abies* Karst.) were prepared (see Papers III and IV for details). These solid wood samples were cut into thin veneers and thereafter ground in a Wiley mill and passed through screens with different meshes to prepare fractions of a certain particle size. For the wicking and the IGC experiments, the wood particles were packed using an electric vibrator into glass and Teflon columns, respectively. This resulted in a total of four different spruce samples for analysis: 1) sapwood, 2) extracted sapwood, 3) heartwood, and 4) extracted heartwood.

3. FACTORS INFLUENCING MEASUREMENTS OF WOOD WETTABILITY

3.1 CONTAMINATION OF PROBE LIQUIDS BY WOOD EXTRACTIVES

Maybe the most crucial issue in wood wetting measurements is the risk of severe contamination of the probe liquids used. The contamination may occur because of dissolution or because of the presence of mobile extractives at the wood/extractives-liquid interface. The dissolution of extractives into the probe liquid may dramatically change its surface tension and, consequently, in this case the measured contact angle may not represent the pure probe liquid but a mixture or solution between the liquid and various extractives.

Paper I is focused on the influence of extractives during wetting measurements on wood. The wetting behavior of fresh and aged veneers of extracted and non-extracted heart- and sapwood of pine were studied by the Wilhelmy method, involving immersion and withdrawal of the samples in different probe liquids.

Two different contamination parameters, C_{meas} and C_{app} , (see equations [19–21]) were determined. C_{meas} represents the difference between the recorded liquid surface tension before (γ) and after (γ_f) a test cycle, whereas C_{app} represents the difference between γ and the apparent surface tension γ_{app} in the receding part of a cycle. Table 2 presents the contamination parameter, C_{meas} , for the different wood samples immersed in the probe liquids. As can be seen, severe contamination was recorded after immersion of both fresh and aged heart- and sapwood samples in formamide, indicated by a distinct decrease in the surface tension of about 6–17 mN/m. Severe contamination, corresponding to a decrease in the surface tension of about 8–16 mN/m, was also observed in the case of fresh and one-day-old sapwood samples immersed in water. Note that no such contamination was recorded when the extracted wood samples were immersed. Hence, this indicates that in these cases wood extractives are dissolved in the probe liquids during the wetting measurements, which results in a distinct decrease in the liquid surface tension. This may also confirm that the pine heartwood contains mainly hydrophobic extractives, whereas the sapwood contains mainly hydrophilic extractives (see also e.g. Sjöström 1981; Saranpää and Höll 1989). On the other hand, both heartwood and sapwood extractives seems to be easily dissolved in formamide.

It is important to remark that the C_{meas} parameter represents the actual contamination of a probe liquid that may occur, in this case corresponding to a decrease in the surface tension of the ‘bulk’ liquid. However, if there are local effects of contaminants at the solid-liquid-air interline or at the solid-liquid interface, they may not be present in the C_{meas} parameter.

Figure 6 shows examples of test cycles in water for fresh samples of both extracted and non-extracted heartwood. As can be seen, there is a pronounced ‘drop’ (or non-linearity) of the advancing curve in the case of measurements on the non-extracted sample. No such drop is observed in the case of the aged sample or the extracted samples. In addition, the fact that the over-all location of the loops for

the non-extracted is lower than those for the extracted samples shows that the measured wetting forces are distinctly lower in the former case.

Table 2. Measured contamination parameter C_{meas} expressed as the difference between the initial and the final surface tension, $C_{meas} = \gamma - \gamma_f$.¹

Sample	$C_{meas} = \gamma - \gamma_f$ (mN/m)							
	Water		Formamide		Ethylene glycol		Diiodo-methane	
HEARTWOOD								
Fresh surfaces	1.0	(1.5)	13.0	(0.7)	0.7	(0.6)	0.7	(0.3)
One-day-old surfaces	0.1	(0.1)	8.9	(1.9)	0.2	(0.5)	-0.1	(0.2)
One-week-old surfaces	0.1	(0.1)	6.5	(1.7)	-0.2	(0.2)	0.1	(0.1)
EXTRACTED HEARTWOOD								
Fresh surfaces	0.0	(0.1)	0.2	(0.1)	0.1	(0.1)	0.2	-
One-day-old surfaces	-0.1	(0.0)	0.5	(0.7)	-0.2	(0.1)	0.3	-
One-week-old surfaces	0.0	(0.1)	0.1	(0.1)	-0.1	(0.0)	-0.1	-
SAPWOOD								
Fresh surfaces	15.9	(1.0)	17.0	(0.3)	1.7	(0.8)	0.4	(0.4)
One-day-old surfaces	7.7	(2.2)	10.4	(2.1)	0.0	(0.1)	0.0	-
One-week-old surfaces	0.5	(0.4)	6.4	(2.4)	-0.1	(0.1)	0.4	-
EXTRACTED SAPWOOD								
Fresh surfaces	0.1	(0.1)	0.1	(0.1)	0.1	(0.1)	0.2	-
One-day-old surfaces	-0.1	(0.1)	0.1	(0.0)	-0.1	(0.0)	-0.2	-
One-week-old surfaces	-0.1	(0.1)	0.3	(0.3)	-0.1	(0.0)	0.3	-

¹ Each value (except some of the values for diiodomethane) is based on five replicates. Standard deviations are given in parentheses. Test temperature was about 22 °C.

If the receding and the second advancing curves are coincident (i.e. no hysteresis), as described in section 2.1, this represents a situation where $\theta_A = \theta_R = 0^\circ$. It is important to note that no or negligible hysteresis is observed between the receding and the second advancing curves for all the wood samples. This indicates that the liquid edge in these cases runs over a wood surface that has sorbed a significant amount of liquid, which means that the liquid will spread over a layer of its own material, resulting in zero contact angle (see also van Oss *et al.* 1992; Timmons and Zisman 1966). These observations suggest that the receding contact angle is in general zero for, at least, polar liquids on rough and hygroscopic materials like wood (see also Hodgson and Berg 1988 and Mantanis and Young 1997). Good (1993) also states that the receding angle on materials with high surface roughness is often

zero. In the present study, no finite receding angles are observed even for the non-polar liquid diiodomethane.

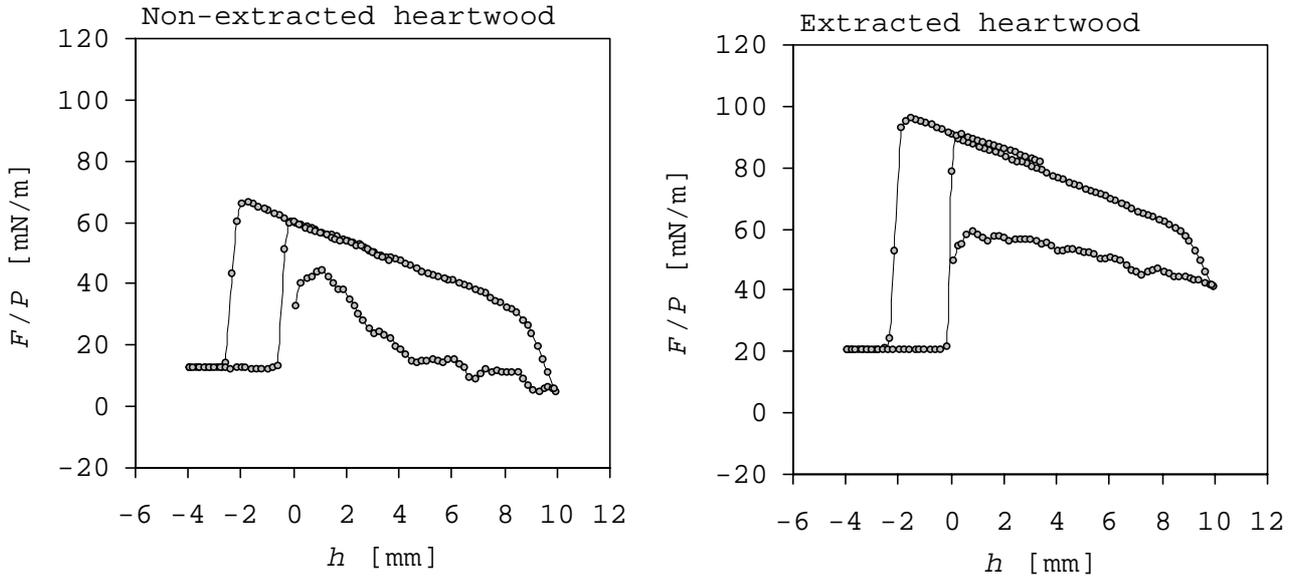


Figure 6. Examples of Wilhelmy test cycles in water for fresh surfaces of non-extracted and extracted heartwood. Contamination of the probe liquid is in this case indicated by a distinct drop of the advancing curve (see diagram to the left).

A zero receding contact angle implies that equation (18) can be applied, either to estimate the perimeter of the sample if the surface tension of the liquid is known, or vice versa to estimate the surface tension of the liquid if the perimeter of the specimen is known. In the present study, the perimeters of the wood veneers were estimated from measurements in the ‘wetting-out-liquid’ octane, and thus the apparent surface tension, γ_{app} , can be determined according to equation (20). Moreover, from Figure 6 it is obvious that γ_{app} is distinctly lower in the case of the non-extracted than for the extracted sample.

Related to this, Figure 7 shows a plot of P against $P\gamma_{app}/\gamma$ for the extracted and non-extracted veneer samples for immersion in water. The greater the shift to the left of the points, the greater is the apparent contamination of the probe liquid, represented by the decrease in its apparent surface tension. As can be seen, no contamination is generally detected in the case of the extracted veneers, whereas the immersion of non-extracted veneers leads to severe contamination. A comparatively small contamination is in general observed when measurements are made in ethylene glycol or in diiodomethane.

In the diagrams presented in Figure 8, the measured and apparent contamination parameters, C_{meas} and C_{app} , are compared. It is evident that, even if there is little change in the surface tension before and after a test cycle (C_{meas}), a high apparent change (C_{app}) in the surface tension may be detected, i.e. there is a significant drop in the apparent surface tension γ_{app} during the measurements.

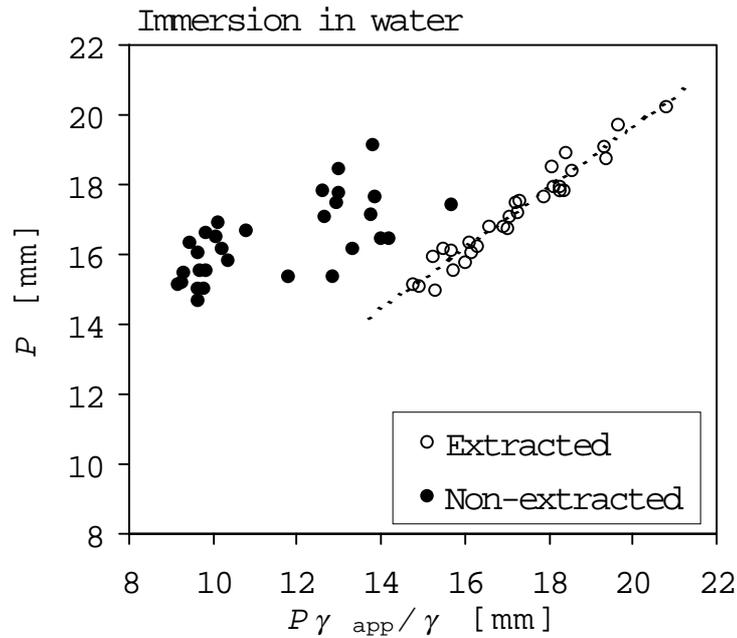
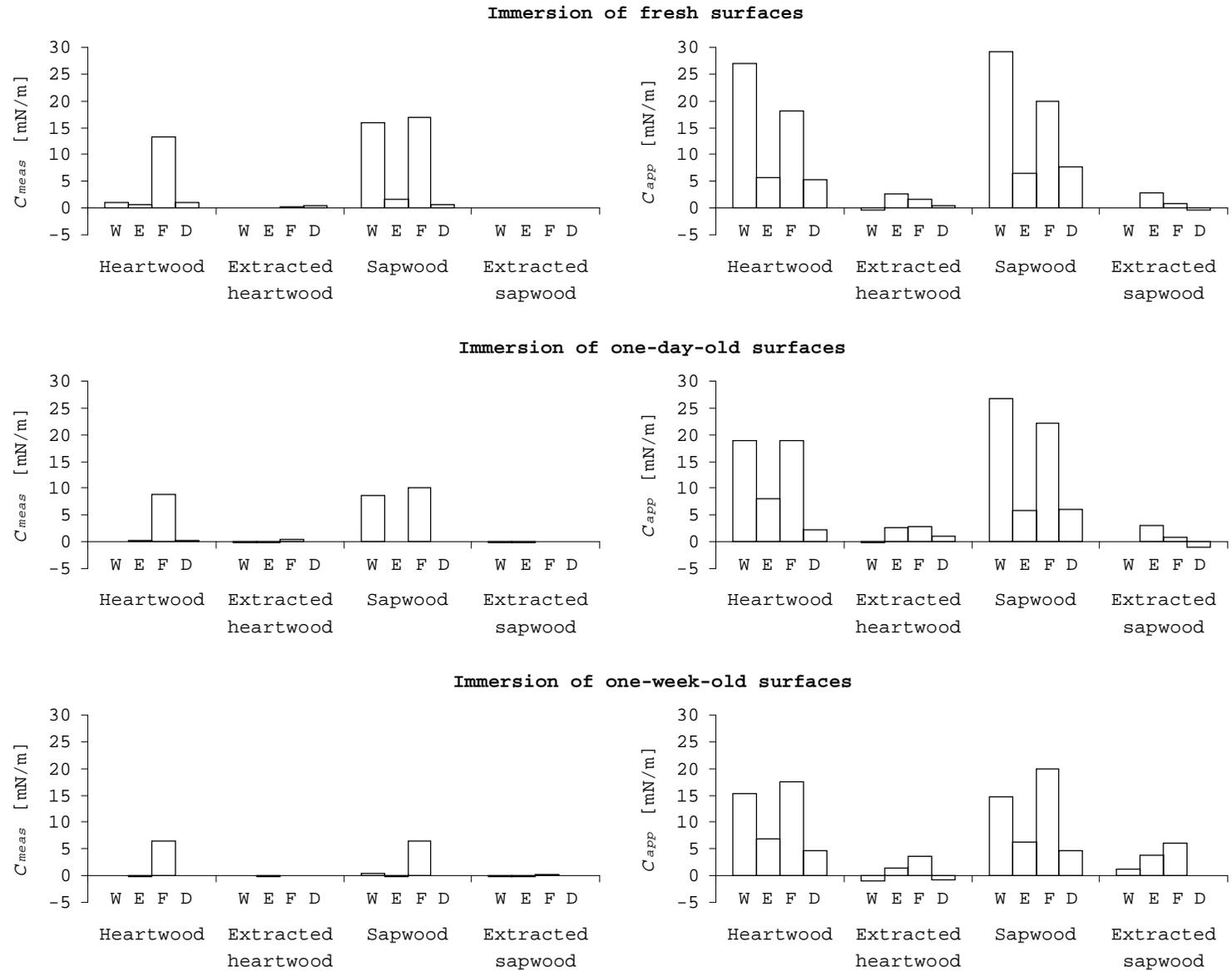


Figure 7. Plot of P against $P\gamma_{app}/\gamma$ for the extracted and non-extracted veneer samples on immersion in water. The greater the shift to the left of the points, the greater is the apparent contamination of the probe liquid, i.e. represented by a decrease in its apparent surface tension.

For example, a drastic drop of about 25 mN/m in γ_{app} when fresh heartwood is immersed in water is not indicated as a drop in the measured γ_f after a test cycle. This may be due to the fact that the contamination occurs only at the wood-liquid interface or at the wood-liquid-air interline, as mentioned earlier. Such contamination may however be detected as a drop in the value of γ_{app} .

Both water and formamide are strong hydrogen-bonding liquids and reorientation of functional groups (see e.g. Gardner *et al.* 1995) at the extractives-liquid interface may therefore occur during the measurements. It is probable that such reorientation may change the apparent surface tension of the liquid, and perhaps also the interfacial tension between the wood/extractives and the liquid. For example, some extractives that are present at the wood/extractives-water interface will probably orient their hydrophilic groups towards the water phase to form hydrogen bonds, thus changing the properties of the wood/extractives-liquid interface. In general, it may also be relevant to distinguish between strong and weak interaction between the extractives and the probe liquid. In this case, the interaction seem to be strong between formamide and both heart- and sapwood extractives. Moreover, as can be seen in Figure 8, there seems to be a comparatively small contamination in the case of measurements in ethylene glycol and diiodomethane.

Figure 8. Contamination of the probe liquids presented as the difference between the measured surface tension before and after immersion for different wood samples ($C_{meas} = \gamma - \gamma_f$, see diagrams to the left); and the difference between the measured initial surface tension and the apparent surface tension in the receding part of a test cycle ($C_{app} = \gamma - \gamma_{app}$, see diagrams to the right).



W = water, E = ethylene glycol, F = formamide, D = diiodomethane

3.2 WICKING EFFECTS

The objective of Paper II was primarily to apply the Wilhelmy method to estimate apparent contact angles on fresh and aged veneers of extracted and non-extracted pine wood veneers. Special attention was paid to the development of means of controlling, first, any wicking effects during the measurements, and second, any contamination of the probe liquids by extractives.

Figure 9 shows Wilhelmy test cycles in octane for a wood veneer and a glass plate. As can be seen, the wood veneer sorbs a considerable amount of liquid during a loop.

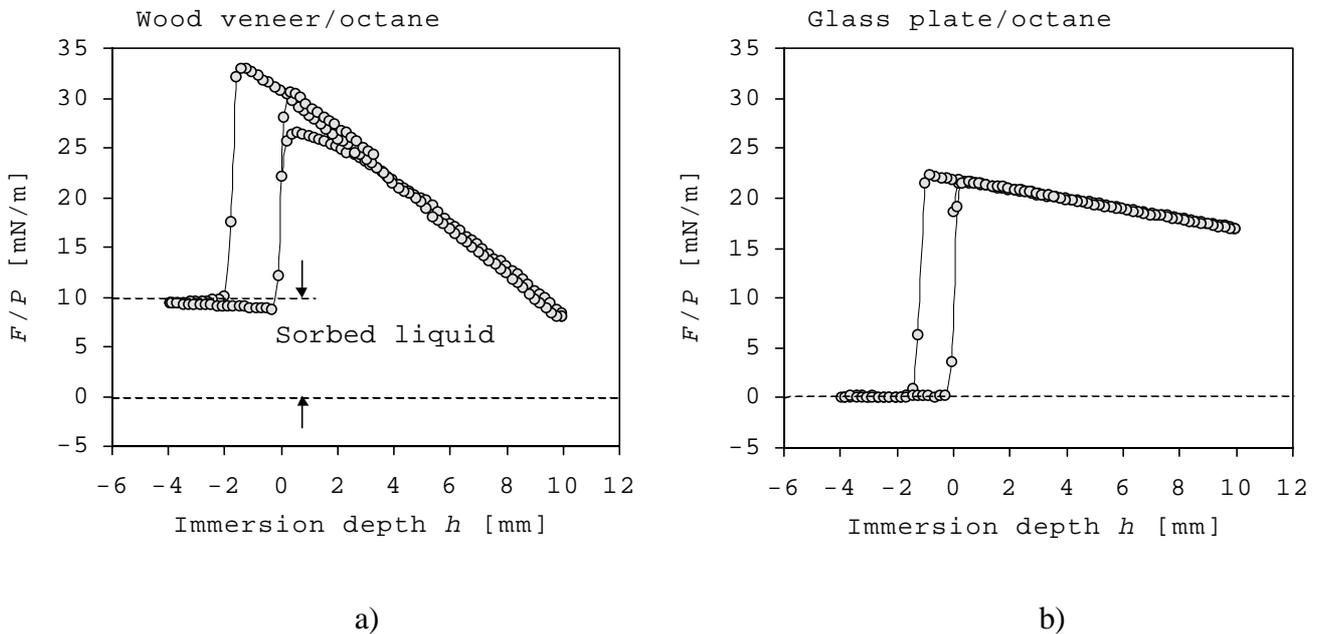


Figure 9. Test cycles of immersion and withdrawal in the ‘wetting-out-liquid’ octane for a) a wood veneer and b) a glass plate.

As indicated in Figure 9a, a non-linearity is observed in the first part of the advancing curve. This observation implies that wicking of the liquid occurs during the measurements. On the immersion of a wood veneer in a liquid with low surface tension, such as octane, the wicking is rapid. The wicking liquid therefore quickly reaches the end of the veneer, in this case at an immersion depth of about 3 mm. No such effects are observed on immersion of the glass plate (see Figure 9b).

Figure 10 shows examples of the initial part of Wilhelmy test cycles in octane for five veneer and five glass specimens. As shown in Figure 10b, the intercept on the ordinate of a linear regression of the plot (excluding the very first part of the immersion) agrees well with the surface tension of octane. In contrast, on immersion of the wood veneer, the corresponding intercept is significantly higher than that of the glass plates. This observation suggests that a very fast ‘initial wicking’ may

occur just when the wood veneers touches the liquid, which results in a notable increase of the measured force.

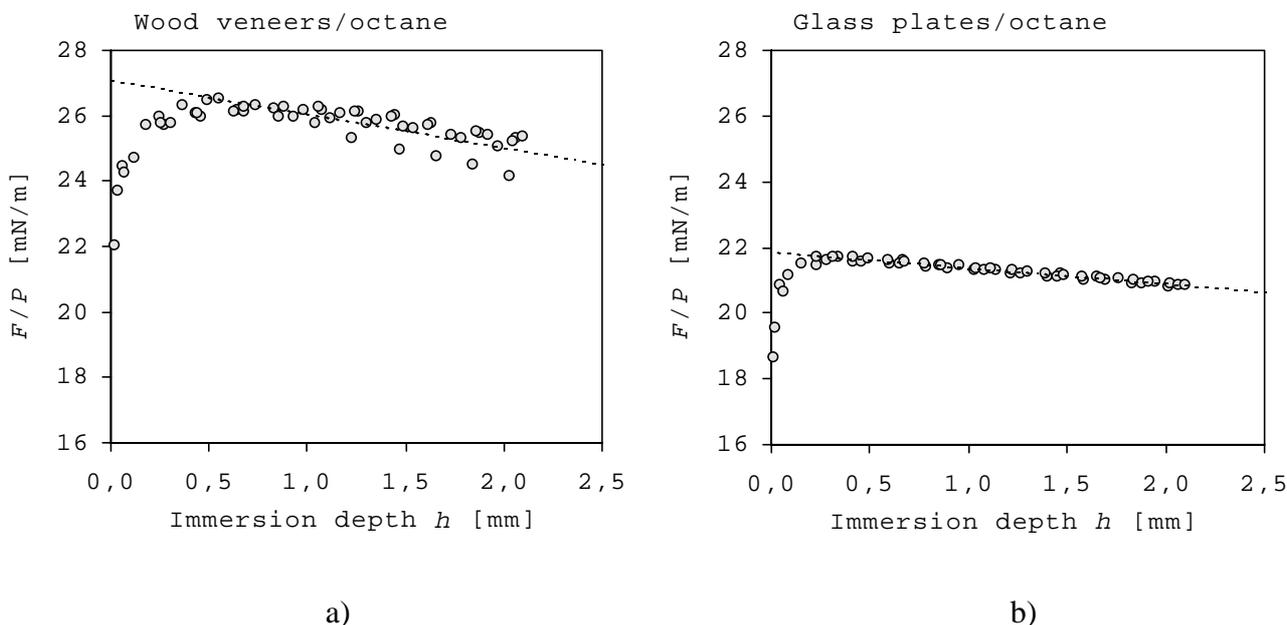


Figure 10. Initial part of test cycles in octane for a) 5 replicates of a wood veneer sample, b) 5 replicates of the glass plate sample

Table 3 presents estimations of such ‘initial wicking’ in the different wood samples on immersion in octane. These values are determined as the difference between the intercepts (see Figure 10a) and the surface tension of octane, and are presented as the term $\rho V_0 g/P (= F/P)$. As indicated in Table 3, there seems to be a notably greater initial wicking in the case of extracted than in non-extracted samples, and in sapwood rather than in heartwood samples. No notable difference is, however, observed between fresh and aged samples. The assumed wicking effect seems to increase the initial force by about 20 % for the non-extracted and by about 30 % for the extracted wood samples. Pine sapwood has in general a higher permeability for liquids than heartwood (see e.g. Siau 1984). It is also probable that extracted wood has a higher permeability than non-extracted wood. Moreover, the surface energetics of aged wood samples tend to be notably different from those of fresh wood (see Paper V). This suggests that the initial wicking may be influenced by the structural properties of the wood samples, and not by their surface energetics.

The very small cavities in wood, e.g. 0.1 μm as measured by mercury porosimetry (Siau 1984), may lead to very high initial wicking velocities (see equation [22]). In fact, equation (22) leads to an infinite wicking velocity close to the moment when a capillary touches a liquid. In other words, when a wood specimen contacts a liquid, an almost instantaneous wicking effect may be immediately expected, and an inertial effect may therefore be present (see Quéré 1997).

Table 3. Measured initial wicking¹, $\rho V_0 g/P$, on immersion in octane of the different wood veneer samples.

	Initial wicking $\rho V_0 g/P$ [mN/m]			
	Heartwood	Extracted Heartwood	Sapwood	Extracted Sapwood
Fresh surfaces	3.2 (0.3)	5.1 (1.0)	4.2 (0.7)	5.9 (0.5)
One-day-old surfaces	3.0 (0.4)	6.1 (0.4)	5.3 (1.4)	6.3 (0.8)
One-week-old surfaces	3.6 (0.3)	5.9 (0.8)	4.5 (0.8)	6.2 (0.9)

¹ Each value is based on 5 replicates. Standard deviations are given in parentheses.

Apart from an initial wicking effect, it is obvious that a continuing ‘secondary wicking’ occurs during the test cycles in all the probe liquids. This capillary liquid transport may occur e.g. along ‘tracheid channels’ in the surface; and into the end-grain cavities, pit openings, and wood rays (see the examples in Figure 2 of the microscopic structure of pinewood). During test cycles in polar liquids such as water and formamide, sorption of liquid into the wood substance also occurs. Figure 11 shows examples of test cycles for extracted sapwood in water and formamide. In this figure, the secondary wicking and sorption are presumably represented by the non-linearity (i.e. a slightly decreasing slope) of the first advancing curves (see also Figure 9a). The wicking of the liquid along the wood surfaces is sometimes visible as a lustre on the surface in advance of the liquid front line of the meniscus, especially for octane, formamide and diiodomethane.

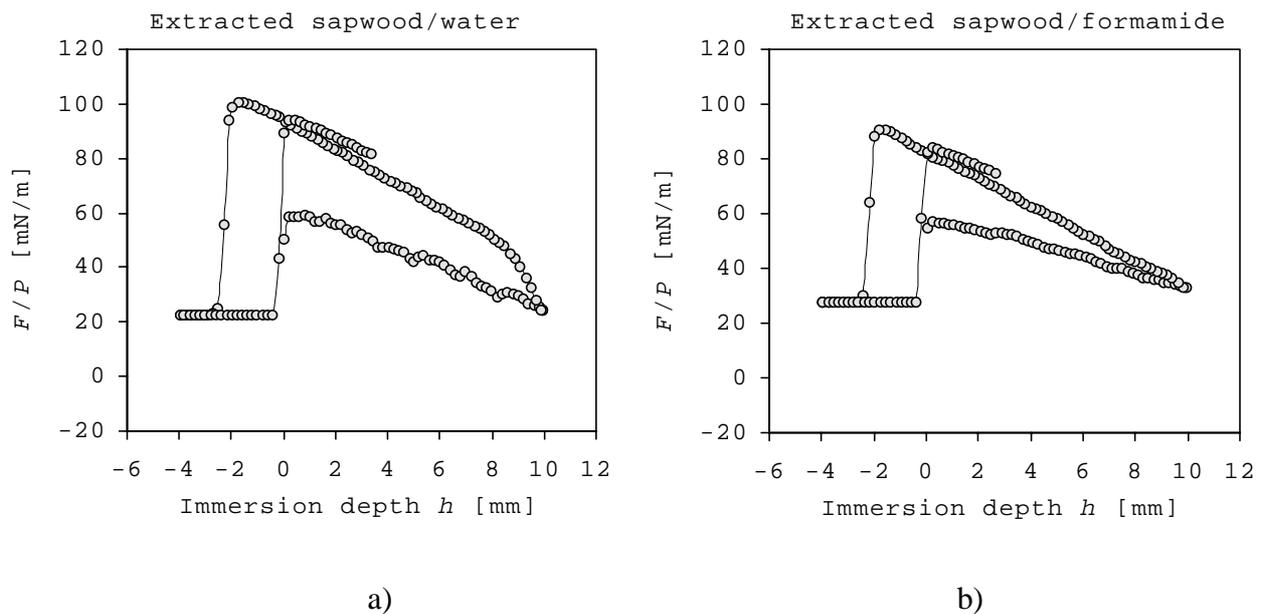


Figure 11. Test cycles in a) water and b) formamide. Sample: fresh surfaces of extracted sapwood.

Based on these observations of wicking effects, it is suggested that the force due to wicking and sorption $F_w(t)$ in equation (16) may be expressed as an initial wicking constant $\rho V_0 g$ and a secondary time-dependent wicking and sorption function $F_{sw}(t)$. Equation (16) then becomes:

$$F(h,t) = P\gamma \cos\theta + \rho V_0 g + F_{sw}(t) - \rho A h g \quad (27)$$

where V_0 is the volume of the liquid resulting from the fast initial wicking during a very short time. This volume is assumed to be independent of the viscosity and surface tension of the liquid, and also of the surface energetics of the specimen. Hence, the initial wicking volume, V_0 , is assumed to be the same for different probe liquids but to depend on structural properties of the wood veneers.

3.3 ESTIMATION OF APPARENT CONTACT ANGLES ON WOOD BY THE WILHELMY METHOD

In paper II, apart from the investigation of wicking effects during the wetting measurements, an attempt was also made to estimate apparent contact angles on fresh and aged, and on extracted and non-extracted wood veneer samples.

Hysteresis and time-dependent contact angles

As shown in Figure 11, there is a large hysteresis between the advancing and receding parts of the first cycle. One part of this hysteresis is obviously caused by the sorption of the probe liquid along and into the wood specimens. The great hysteresis effect for water, as shown in Figure 11a, suggests that there is a great difference between the advancing and receding contact angles. This indicates that the tested surface is heterogeneous and has a high surface roughness (Good 1993). The advancing contact angle also represents the low-energy sites; and the receding angle the high-energy sites of a surface (Johnsson and Dettre 1993; Good 1993).

As discussed in section 3.1, it is observed, in all cases, that the advancing part of the second cycle and the receding part of the first cycle are approximately coincident. This indicates that the receding angle is zero, presumably because of sorbed liquid in the surface of the wood during the advancing part of a test cycle. A greater hysteresis effect would be expected in such cases when the surface is 'wetted' resulting in a zero receding angle than with a surface that exhibits a finite receding angle. Good (1993) also stated that, when roughness is the cause of hysteresis, it is often observed that the receding contact angle is zero. He also stated that, for certain polar solids, the reorientation of molecules or functional groups in the solid surface after contact with a liquid phase is a major cause of contact angle hysteresis. It is therefore probable that, for instance, hydroxyl groups in the wood surface are 'buried' when the surface is exposed to the inert air, but that they 'turn over' to form hydrogen bonds when the surface is in contact with water. An analogous discussion may also be valid for extractives such as fatty acids on the wood surface. In this case, the hydrophobic chain ('tail') of the fatty acid may be buried and the hydrophilic group turned over on contact with water.

The wicking of the liquid along the surface of the veneer presumably also changes the surface energetics. On immersion in formamide, see Figure 11b, there

is little or no hysteresis between the advancing and receding curves when the specimen has reached the lowest immersion depth of a test cycle. This indicates that the contact angle decreases during the measurements and has become zero when the specimen reaches the lower immersion depths. In other words, the contact angle is time-dependent. A gradual change in the contact angle may also be a contributory cause of the non-linearity of the advancing curves, as shown in Figure 11. Swelling of the wood material may also occur during the measurements, especially with strong hydrogen bonding liquids (see Paper III). However, the influence of swelling of the veneers seems to be small compared to the wicking effect, since a similar non-linear plot is clearly observed even for immersion in the non-polar (and non-swelling) liquid diiodomethane.

Estimation of initial apparent contact angles

Figure 12 shows the initial part of test cycles in water and diiodomethane for five replicates of fresh surfaces of extracted sapwood. From such plots, the initial F/P values were obtained by linear regression of the advancing curves between 0.5 and 2 mm immersion depth, for all the wood samples. By extrapolating to zero immersion depth, the secondary wicking effect can be neglected, i.e. the term $F_{sw}(t)$ in equation (27) is assumed to be zero. It may also be assumed that the effect of any contamination of the probe liquids is low during the initial part of the test cycles.

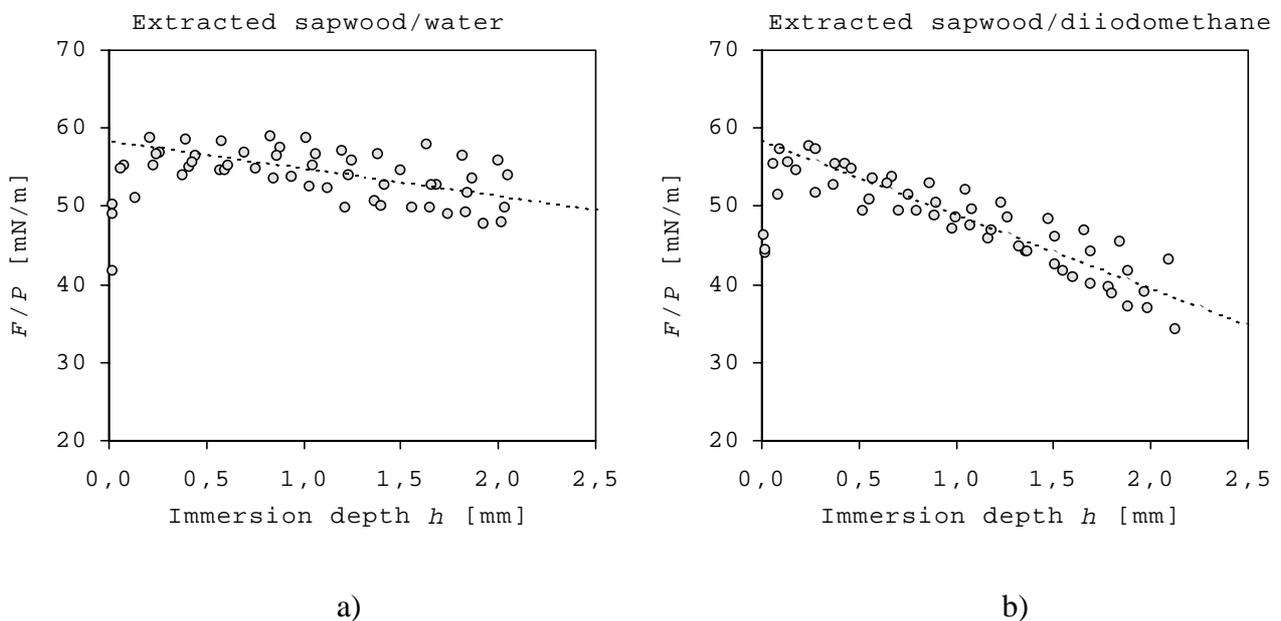


Figure 12. Initial parts of test cycles in a) water and b) diiodomethane, for five replicates of fresh surfaces of extracted sapwood.

The initial value of F/P especially for formamide and diiodomethane is close to or above the surface tension values of these liquids, see e.g. the intercept for diiodomethane in Figure 12b. This indicates that the initial F/P values may be increased by an initial wicking effect, as discussed earlier. The exclusive effect of

density on the initial wicking may also be confirmed by the comparatively high F/P values for diiodomethane (in some cases more than 10 mN/m above its surface tension value) which has about the same viscosity and lower surface tension as formamide, but significantly higher density.

To compensate for the assumed initial wicking effects, an initial wicking constant $\rho V_0 g/P$ for different wood samples immersed in various probe liquids may be estimated by normalizing with respect to the measured wicking constant of octane, as presented in Table 3, by the factor ρ_{oct}/ρ , where ρ_{oct} and ρ are the density of octane and the probe liquid, respectively. Based on the initial F/P value and the estimated initial wicking, an apparent contact angle (advancing) may then be estimated by equation (27).

Table 4 presents the contact angles obtained by this procedure for the different wood veneer samples. As can be seen, the contact angles seem to increase with increasing aging time, as has also been reported in other wetting studies on wood (Gray 1962; Herczeg 1965; Nguyen and Johns 1979; Gardner *et al.* 1995).

Table 4. Apparent contact angles¹ θ (advancing) obtained by the Wilhelmy method for water, ethylene glycol, formamide and diiodomethane on different wood samples.

Sample	θ (degrees)							
	Water		Formamide		Ethylene glycol		Diiodomethane	
HEARTWOOD								
Fresh surfaces	57	(2.9)	36	(1.6)	29	(2.4)	44	(2.1)
One-day-old surfaces	61	(2.0)	36	(3.2)	36	(3.7)	39	(8.0)
One-week-old surfaces	80	(2.6)	37	(2.6)	35	(2.1)	50	(7.3)
EXTRACTED HEARTWOOD								
Fresh surfaces	43	(2.3)	31	(2.1)	27	(2.6)	33	(7.5)
One-day-old surfaces	45	(5.0)	31	(2.7)	30	(1.3)	40	(2.7)
One-week-old surfaces	55	(7.5)	35	(3.8)	30	(2.1)	41	(2.3)
SAPWOOD								
Fresh surfaces	48	(5.0)	41	(2.5)	37	(1.3)	54	(5.3)
One-day-old surfaces	56	(3.4)	41	(2.7)	44	(3.2)	52	(5.1)
One-week-old surfaces	75	(4.3)	48	(4.2)	49	(5.7)	63	(4.1)
EXTRACTED SAPWOOD								
Fresh surfaces	47	(1.9)	42	(3.8)	33	(1.4)	43	(3.3)
One-day-old surfaces	58	(2.3)	41	(2.8)	37	(2.4)	46	(2.9)
One-week-old surfaces	55	(6.7)	44	(2.7)	39	(4.3)	48	(6.0)

¹ Each value is based on five replicates. Standard deviations are given in parentheses. Test temperature was about 22 °C.

It is also evident that the aging effect is more pronounced in the non-extracted samples. This is probably due to a migration of hydrophobic wood extractives to the exterior surfaces after their preparation, as described by e.g. Back (1991) and Nussbaum (1999). The increase in the contact angle, i.e. the reduction in the total surface free energy, with increasing exposure time even for extracted samples may be due to a reorientation of polar groups in the wood surfaces exposed to air (see e.g. Andrade *et al.* 1985; Gardner *et al.* 1995). No distinct increase in the contact angle on the aged samples was observed, however, when non-extracted samples were immersed in formamide. The fact that some of the contact angles in this case are approximately the same for extracted and non-extracted samples may indicate that a severe contamination occurs when the non-extracted wood samples are immersed in formamide, and that this reduces its surface tension and results in lower θ -values.

3.4 ESTIMATION OF APPARENT CONTACT ANGLES ON WOOD PARTICLES BY THE WICKING METHOD

The objective of Paper III was primarily to examine the column wicking method for estimating contact angles on extracted and non-extracted spruce wood particles. This method involves an indirect determination of contact angles by the Washburn equation (see equation [22]) combined with measurement of the velocity of liquid capillary rise in a glass column packed with the wood particles.

Figure 13 shows an example plot (i.e. a Washburn plot) of wicking in the extracted wood particles. Here the wicking of methanol is faster than that of water, which, in turn, is considerably faster than that of formamide.

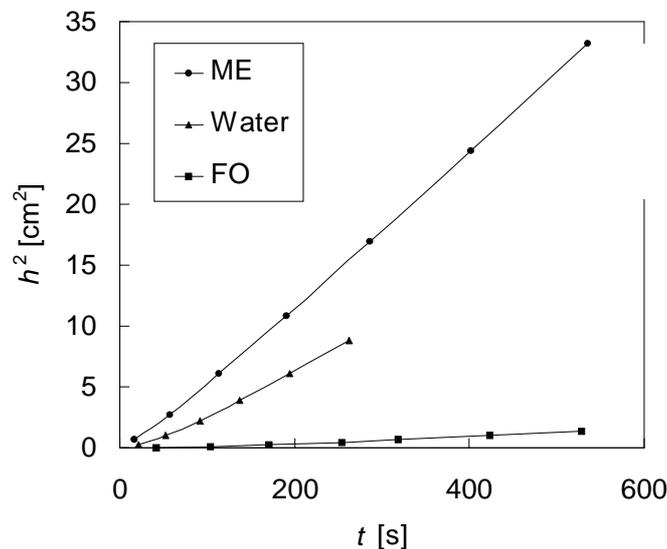


Figure 13. Example of Washburn plot from column wicking measurements. Sample: extracted spruce sapwood, –60 mesh particles. Probe liquids: methanol (ME), water, and formamide (FA).

A closer look at the slope (i.e. the Washburn slope) for the wicking of formamide indicates that the slope increases with time. This may be due to pre-

wetting effects caused by liquid vapor moving in advance of the liquid front line. This tendency is also observed in the case of water and methanol.

For swelling particles in the form of powder rather than fibers (or splinters), significant pore blocking has been observed by Wiryana and Berg (1991). This may also occur in the case of wicking in very fine wood powder. The use of larger particles with a more uniform particle size seems to reduce these effects, presumably due to an increase in the overall rate of capillary rise.

Figure 14 shows temperature measurements at two points within a column during the wicking of water, formamide, methanol and ethylene glycol in the extracted wood particles.

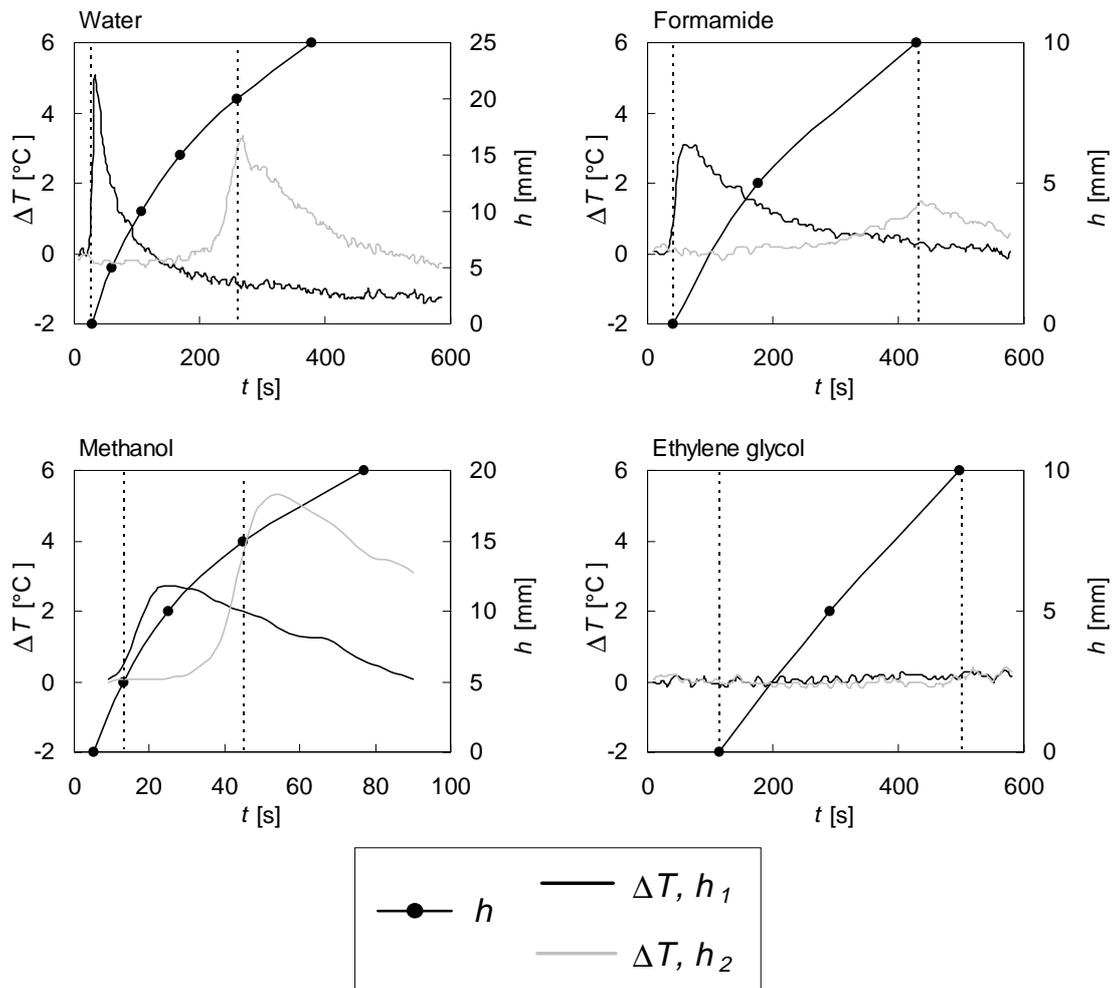


Figure 14. Graphs showing the temperature difference ΔT during wicking measured at two heights within the column versus time t , combined with height h of liquid front versus time t . The vertical dashed lines represent the location of the two temperature measurement points. The h_1 and h_2 temperature measurement points in the case of formamide and ethylene glycol are located at $h_1 = 0$ mm and $h_2 = 10$ mm respectively. Corresponding values for water are $h_1 = 0$ mm and $h_2 = 20$ mm and for methanol $h_1 = 5$ mm and $h_2 = 15$ mm. Sample: extracted spruce sapwood, -60 mesh particles.

The two "peak curves" in the graphs for water, formamide and methanol correspond to the temperature measurements at a low (h_1) and a high (h_2) point within the column, and the continuously increasing curve represents the movement of the visible liquid front line. As can be seen, water, formamide and methanol show distinct temperature increases following the movement of liquid front, whereas ethylene glycol showed no such temperature increase. The latter behavior is also observed, as expected, with diiodomethane and hexane. These temperature measurements suggest that a bulk sorption process occurs during the wicking measurement for methanol, water and formamide, but not for ethylene glycol, diiodomethane or hexane. Since methanol is used as the 'wetting-out-liquid' for the determination of R_e in equation (22), it is clear that this value may not be relevant for any of the other probe liquids.

For wicking of water and formamide, the temperature increase seems to be instantaneously linked to the movement of the visible liquid front at the lower measurement point, whereas at the higher point it is in advance of the moving front (see Fig. 14). This may indicate that vapor from the probe liquid is moving in advance of the liquid front line, and that this results in bulk sorption of vapor with a corresponding release of heat. This may suggest that vapor moves in advance of the liquid front causing "pre-wetting" of the particles, as mentioned above.

Table 5 presents R_e values and apparent contact angles based on wicking measurements in wood samples of $-60/+80$ mesh particle size. Because of the observed bulk sorption in the case of methanol, the contact angles were calculated using R_e values determined from measurements in hexane. Note that the R_e values based on the methanol measurements tend to be lower than those based on the hexane measurements. In general, the contact angles presented in Table 5 tend to be considerably larger than contact angles measured by other methods (see e.g. Gardner 1996; Mantanis and Young 1997; Liptáková *et al.* 1995), but in agreement with data reported by Gardner *et al.* (1999).

Table 5. Estimated contact angles θ , effective interstitial pore radius R_e , (measured with hexane and methanol) for different spruce samples of $-60/+80$ mesh particle size. Values are the average of 2 replicates

Sample	R_e (μm)		θ (degrees)			
	Methanol	Hexane	Water	Formamide	Ethylene glycol	Diiodo-methane
Sapwood	0.8	2.2	85	77	50	69
Extracted sapwood	2.1	2.8	83	72	24	58
Heartwood	0.9	2.8	89	79	48	69
Extracted heartwood	1.6	3.0	85	65	24	59

Parson *et al.* (1993) and Yang *et al.* (1988) also concluded that the capillary rise technique resulted in contact angle values significantly higher than those obtained by other methods. The apparent contact angle values presented in Table 5 for water and formamide are certainly affected by the bulk sorption observed during the measurements. Contamination of the probe liquids in the case of non-extracted samples probably also occurs (see section 3.1). On the other hand, the values for ethylene glycol on the extracted spruce wood particles are close to the values on the extracted pinewood veneers obtained by the Wilhelmy method, see Table 4. Since no bulk sorption is detected for the wicking of ethylene glycol in the wood particles, see Figure 14, combined with no or negligible contamination effects for extracted samples, this indicates that the wicking method using ethylene glycol may provide relevant apparent contact angles on extracted wood.

3.5 SURFACE ENERGETICS OF WOOD PARTICLES STUDIED BY INVERSE GAS CHROMATOGRAPHY (IGC)

In Paper IV, an attempt is made to characterize the surface energetics, i.e. Lifshitz-van der Waals (LW) and Lewis acid-base (AB) properties, of extracted and non-extracted spruce wood particles by means of inverse gas chromatography (IGC). The measurements were performed at infinite dilution, using a series of dispersive *n*-alkanes and Lewis acid-base probes. Figure 15 shows a typical plot of $RT \ln V_N$ versus $a(\gamma_L^{LW})^{1/2}$ for adsorption of the alkane probes, represented by the reference line, and for adsorption of the acid-base probes, represented as single points. This type of plot enables the Lifshitz-van der Waals component of the solid surface free energy, γ_s^{LW} , and the acid-base (or specific) interaction, ΔG_A^{AB} , to be determined.

The results show that the removal of extractives from the wood particles tends to lead to an increase in γ_s^{LW} . The absolute values of γ_s^{LW} were in the range of about 42–45 mJ/m², which is in good agreement with results from other investigations on wood particles (see e.g. Kamden *et al.* 1993; Gardner *et al.* 1999). Lundqvist (1996) and Gardner *et al.* (1999) concluded that γ_s^{LW} values for some lignocellulosic materials obtained by IGC were greater than those obtained by contact angle analysis. The γ_s^{LW} values for both extracted and non-extracted spruce wood particles obtained in Paper IV seem generally to be greater than those obtained by contact angle analysis, as presented in Paper V. In contrast, Shen *et al.* (1999) and Jacob and Berg (1995) found a reasonable agreement between the two approaches regarding the γ_s^{LW} and work of adhesion, respectively.

An example of the specific interaction, $-\Delta G_A^{AB}$, between a sample of spruce particles and chloroform is shown in Figure 15. If $-\Delta G_A^{AB}$ is determined at different temperatures (in the present investigation at 60, 45 and 30 °C) equation (28) may be applied to calculate $-\Delta H_A^{AB}$. In contrast to the γ_s^{LW} , the $-\Delta G_A^{AB}$ values obtained generally decrease with decreasing temperature. In most cases, this results in a negative $-\Delta H_A^{AB}$ value.

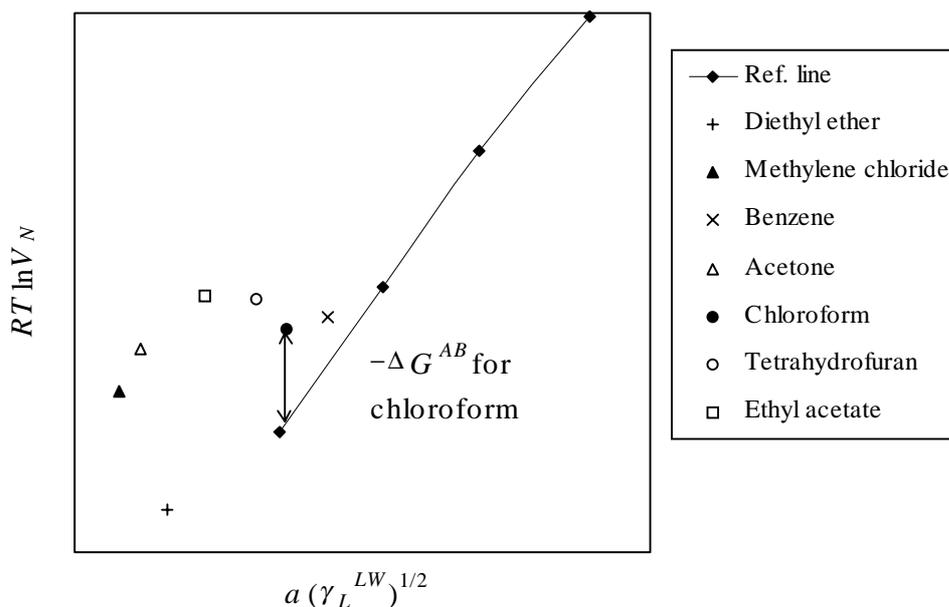


Figure 15. Example plot of $RT \ln V_N$ versus $a(\gamma_L^{LW})^{1/2}$ at a given temperature for the adsorption of a series of non-polar n -alkane probes (ref. line), and also of various acid-base probes (single points) on the spruce wood particles.

Negative enthalpies of adsorption due to acid-base interactions have also been observed for wood or wood fibers by Kamden *et al.* (1993), Shi *et al.* (1997), Gardner *et al.* (1999), Tshabalala (1997), and Czeremuszkina *et al.* (1997). It should be mentioned that wood is a hygroscopic material which changes its adsorption properties and moisture content with temperature and relative humidity. In other words, the temperature change during a normal IGC run may affect the adsorption properties of the wood substance and its strongly hydrogen-bonded water molecules, and this may affect the determination of $-\Delta H_A^{AB}$. Gardner *et al.* (1999) also pointed out that some of the probes, e.g. benzene and acetone, may also act as extractive solvents which remove extractives during the IGC measurements, and that the adsorption measurements may thus be affected. In addition, Czeremuszkina *et al.* (1997) observed that some acid-base probes were preferentially adsorbed on the cellulose, and were removed by injecting water into the column. In other words, this indicates that the elution of these probes was incomplete and therefore, delayed. Hence, a possible explanation for the negative enthalpies obtained in the present study may therefore lie in a preferential adsorption of the acid-base probes on the wood particles. Other ‘critical’ factors may be the conditioning of the wood material before the measurements, and the uniformity of the particle size. Further studies should indeed be performed to evaluate the effect of conditioning time and particle size distribution on the IGC parameters.

Because of the negative enthalpies obtained, the analysis of the acid-base interactions using the relation in equation (10) and the K_A (acidic) and K_B (basic) constants is not meaningful. The specific interaction, $-\Delta G_A^{AB}$, was therefore analyzed at a single temperature for adsorption of the acid-base defined probes on the ex-

tracted and non-extracted wood particles (see also Lundqvist and Ödberg (1997) and Shen *et al.* (1998c)).

Figure 16 shows the $-\Delta G_A^{AB}$ values obtained for the different wood samples at 45°C. As can be seen in this figure, extraction of the wood material seems to result in a distinct change in the interaction with most of the probes. According to the Gutmann approach, and the definition of donor and acceptor numbers, the lower degree of interaction of the acidic probes (chloroform and benzene) with the extracted wood particles than with the non-extracted particles indicates that extraction decreases the basic character of wood. In contrast, extraction of the wood particles results in a greater degree of interaction with the amphoteric or basic probes (acetone, ethyl acetate and diethyl ether), indicating that extraction increases the acidic character of wood. Similar results were obtained by Liu *et al.* (1998) and Tshabalala (1997). In addition, acid-base analyses of cellulose and wood fibers by IGC (see e.g. Lee and Luner 1989; Felix and Gatenholm 1993; Garnier and Glasser 1996, Jacob and Berg 1994; Lundqvist and Ödberg 1997; Shen 1998c; Matuana *et al.* 1999) indicates that cellulose has strong electron-accepting ability or acidity.

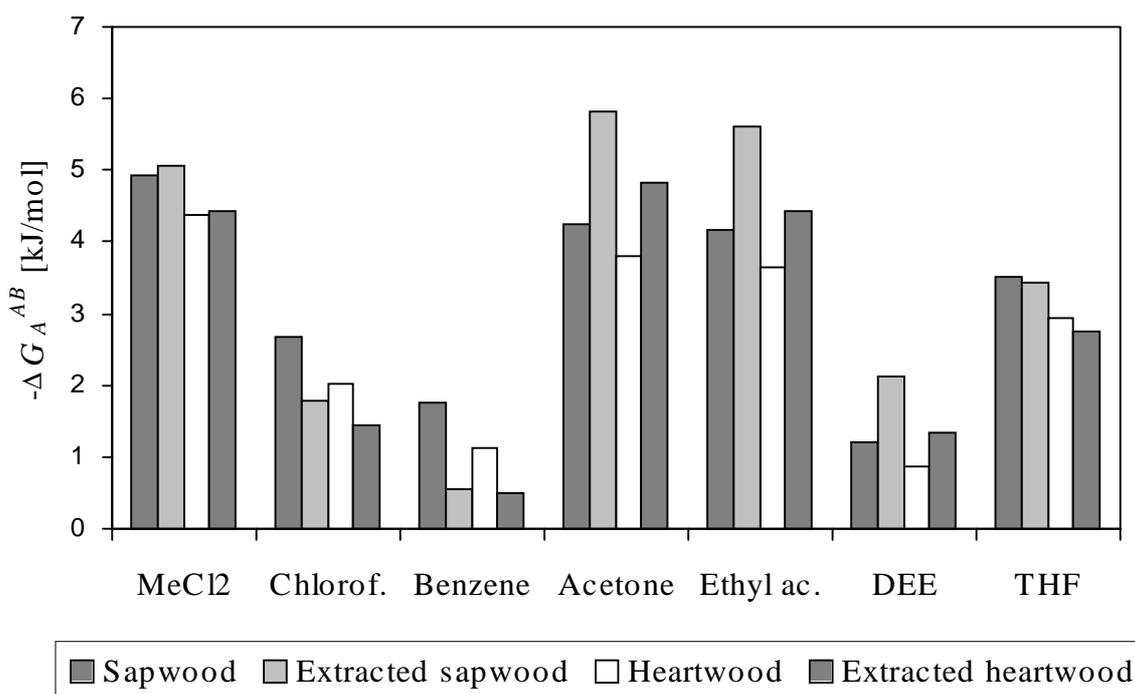


Figure 16. Diagram showing the molar free energy change due to acid-base interactions, $-\Delta G_A^{AB}$, at 45°C for extracted and non-extracted spruce wood particles. MeCl2 = Methylene chloride, DEE = Diethyl ether, and THF = Tetrahydrofuran.

Jacob and Berg (1994) pointed out that one drawback of the Gutmann approach, with defined acceptor and donor numbers, is that it does not distinguish between differences in the "hardness" and "softness" nature of Lewis acids and

bases. For example, methylene chloride ($DN/AN^* = 0$) is a much harder acid than chloroform ($DN/AN^* = 0$) which may lead to a stronger interaction with a soft base. This may explain the deviating acid-base interactions for these probes, as can be seen in Figure 16.

3.6 LEWIS ACID-BASE PROPERTIES OF WOOD DETERMINED BY CONTACT ANGLE ANALYSIS

The objective of Paper V was to study the Lewis acid-base properties of wood by applying basic wetting theory, the van Oss-Chaudhury-Good (vOCG) and the Chang model (see equations (12) and (14), respectively, in section 1.3) to the contact angle data obtained in Paper II. The study is focused mainly on the effects of aging and extractives on these acid-base properties.

Acid-base contribution to the work of adhesion, W_a^{AB}

Figure 17 shows the calculated Lewis acid-base contribution to the work of adhesion, W_a^{AB} , for the interaction between water and the different wood samples. As emphasized in Paper I, the absolute values of W_a^{AB} in the case of non-extracted wood samples must however be considered with caution because of the risk of probe liquid contamination. The contamination generally results in a distinct decrease in the surface tension of the liquids.

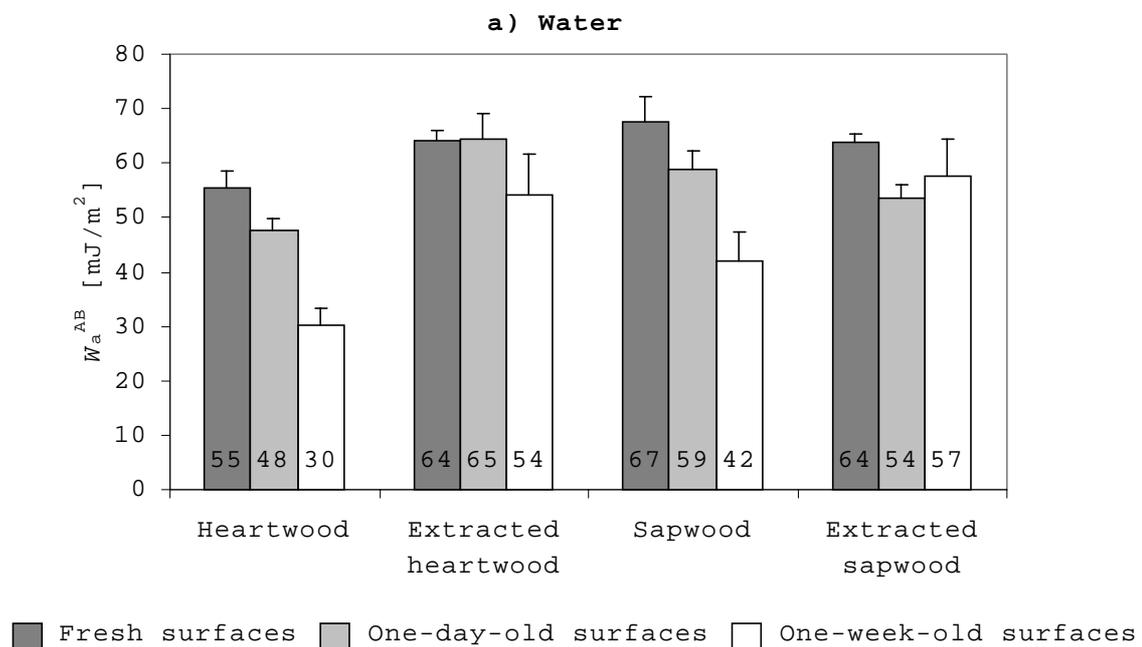


Figure 17. Lewis acid-base contribution to the work of adhesion W_a^{AB} for the interaction between different wood samples and the probe liquid water. Error bars represent the standard deviation based on five replicates of the contact angle measurements.

Despite the expected contamination effects, it may be possible to find trends in the obtained data which indicate changes in the ability of the wood samples to enter into acid-base interactions with the probe liquids. Consequently, the distinct decrease in W_a^{AB} on aging of heartwood and sapwood, as shown in Figure 17, may indicate that extractives migrate from the interior of wood to its exterior surface during the aging, and that this presumably creates a rather hydrophobic and apolar wood surface. Some wood extractives are stored under pressure within the resin canals (Sjöström 1981) and may therefore migrate to the wood surface after its preparation. Nussbaum (1999) also pointed out that a wood surface may be subjected to ‘self-contamination’, resulting from a natural surface-inactivation process where various low-molecular extractives migrate to the surface (see also Back 1991).

If water is assumed to be predominantly acidic (according to probe liquid data obtained by Della Volpe and Siboni 1997), then the decrease in W_a^{AB} between water and aged heart- and sapwood, as shown in Figure 17, can also indicate that the basic character of the wood surface decreases when wood extractives migrate to the surface.

On the other hand, the corresponding W_a^{AB} for ethylene glycol and formamide, first decreases after one-day aging of the surfaces, and then, increases after one-week’s aging. The first decrease is consistent with that observed with water, presumably due to a rapid migration of extractives which may decrease the polar character of the wood surface. The latter increase could be due to reorientation of functional groups, and to the generation of acidic groups by oxidation at the wood/extractives-air interface. Both ethylene glycol and formamide can be considered to be predominantly Lewis basic, and the increase in W_a^{AB} could therefore be due to an increase in the acidic character of the surface.

Surface energy components of wood obtained by the vOCG and Chang models

Table 6 partly shows the surface free energy components obtained by the vOCG model using two different sets of liquid data from van Oss (1994) and Della Volpe and Siboni (1997), respectively. No notable difference is observed between the total surface free energy, γ_s , obtained by the two sets of data. As can be seen, the total surface free energy, γ_s , tend to decrease on one-week-old surfaces of both heartwood and the sapwood, whereas no decrease is observed on the one-day-old surfaces. The decrease is due mainly to a decrease in the apolar component γ_s^{LW} . Also note that γ_s^{LW} tend to increase on one-day-old surfaces of heartwood which indicates that apolar extractives migrate after the preparation of the surface. In addition, only a slight decrease in γ_s or γ_s^{LW} seems to occur on aging of the extracted samples. It is therefore concluded that changes in the surface energetics on the aged wood samples are due mainly to the presence of extractives, in accordance with many other studies (see e.g. Herczeg 1965; Chen 1970; Gardner *et al.* 1995).

With regard to the acid-base characterization (see γ_s^-/γ_s^+ ratios in Table 6), it is obvious that the contact angle analysis using the vOCG model generally indicates that the wood samples exhibit a predominantly Lewis basic character, in accordance with several other acid-base studies on lignocellulosic surfaces using the vOCG

model (see e.g. van Oss 1994; Berg 1993b; Gardner 1996; Shen *et al.* 1999; Gardner *et al.* 1999). However, the basic character is less dominant when the liquid data set of Della Volpe and Siboni (1997) is used.

The change in the acid-base components with aging of the samples is an interesting part of the results, see for example the γ_s^-/γ_s^+ ratios for heartwood and extracted heartwood in Table 6. In fact, for one-week aging of heartwood, the ratio decreases considerably, indicating a change of the surface character from predominantly Lewis basic to a more bifunctional character. For sapwood and extracted sapwood, the same tendency is observed. This agrees well with the discussion above regarding the changes in W_a^{AB} between the polar liquids and the heart- and sapwood samples. The pronounced changes in γ_s^-/γ_s^+ ratios are presumably due to the presence of extractives; and to a reorientation of functional groups, and to the generation of acidic groups by oxidation in the wood/extractives-air interface. It is important to note that, in contrast to W_a^{AB} , the acid-base ratio changes with aging time even for extracted samples, see e.g. the γ_s^-/γ_s^+ ratios on extracted heartwood. This may indicate that a reorientation of functional groups also occurs at the wood-air interface when it is exposed to air.

Table 6 also shows the results of the contact angle analysis using the Chang model. The total surface free energies of the wood samples here seem to be higher than those obtained by the vOCG model, except in the cases of the aged heartwood and one-week-old sapwood surfaces. An interesting result obtained by the Chang model is the negative acid-base contribution to the surface free energy of one-week-old heartwood surfaces. In general, the acid-base character of the samples is bifunctional, i.e. P^A and P^B have opposite signs, except in the case of the one-week-old heartwood surfaces which show only an acidic character. Moreover, the wood surfaces tend to have greater acidic character than that indicated by the vOCG model, which is in agreement with results obtained by Gardner *et al.* (1999). The P^A and P^B parameters of the samples generally increase with aging time, which indicates that the acidic character of their surfaces increases and that the basic character decreases, in accordance with the results obtained by the vOCG model.

The P^B/P^A ratios are somewhat difficult to interpret since they do not directly represent the acid/base ratios. Further studies are needed to compare the vOCG and Chang models and to determine, e.g., the physical meaning of the P^A and P^B parameters.

The results obtained using both the vOCG and the Chang models somewhat contradict the results obtained by inverse gas chromatography (IGC) in Paper IV. In this study, it was indicated that the extraction of spruce wood particles led to an increase in the acidic and to a decrease in the basic character of the particle surface. It must be remembered, however, that IGC mainly assesses the high-energy sites (Jacob and Berg 1994), in contrast to an advancing contact angle which represents mainly low-energy regions of a surface (Good 1993).

The inconsistencies between the acid-base properties of various surfaces obtained by contact angle analysis and those obtained by IGC may suggest that more robust data for the probe liquids and contact angle data at fixed temperatures on well-defined surfaces are necessary.

Table 6. Surface characteristics of different wood samples obtained by the vOCG (using two different sets of liquid parameters) and Chang models. γ_s in (mJ/m²) and P_s in (mJ/m²)^{1/2}.

Sample	vOCG model/van Oss ¹						vOCG model/Della Volpe ²					Chang model ³				
	γ_s	γ_s^{LW}	γ_s^{AB}	γ_s^+	γ_s^-	γ_s^-/γ_s^+	γ_s	γ_s^{AB}	γ_s^+	γ_s^-	γ_s^-/γ_s^+	γ_s	γ_s^{AB}	P_s^A	P_s^B	P_s^B/P_s^A
HEARTWOOD																
Fresh surfaces	46.5	37.5	8.9	1.0	20.2	20.5	45.2	7.6	1.7	8.5	4.9	48.0	10.4	-2.1	5.1	-2.4
1 day old surfaces	46.4	40.1	6.3	0.6	16.8	28.4	45.9	5.8	1.2	6.7	5.5	43.6	3.5	-0.6	5.7	-9.5
1 week old surfaces	38.9	34.3	4.6	3.3	1.6	0.5	38.5	4.2	3.0	1.5	0.5	27.5	-6.8	1.0	6.6	6.6
EXTRACTED HEARTWOOD																
Fresh surfaces	47.9	42.9	5.0	0.2	36.3	211.7	50.0	7.1	0.9	13.2	13.9	55.7	12.8	-2.6	5.0	-1.9
1 day old surfaces	46.9	39.6	7.3	0.4	34.6	89.2	47.9	8.3	1.3	13.0	9.9	52.5	12.9	-2.4	5.4	-2.3
1 week old surfaces	47.0	39.1	7.9	0.7	22.5	32.8	46.3	7.2	1.4	9.0	6.3	48.9	9.8	-1.9	5.2	-2.7
SAPWOOD																
Fresh surfaces	41.8	32.0	9.8	0.7	36.0	54.5	41.7	9.7	1.7	14.0	8.3	48.3	16.3	-3.4	4.8	-1.4
1 day old surfaces	40.9	33.2	7.8	0.6	27.0	48.1	40.9	7.7	1.4	10.4	7.2	42.1	8.9	-1.6	5.7	-3.6
1 week old surfaces	35.2	26.8	8.4	2.2	8.1	3.7	33.4	6.5	2.5	4.2	1.7	28.6	1.7	-0.3	6.1	-20.3
EXTRACTED SAPWOOD																
Fresh surfaces	43.1	38.1	5.0	0.2	36.1	206.9	45.0	6.9	0.9	13.3	14.8	52.0	13.9	-3.6	3.9	-1.1
1 day old surfaces	43.7	36.5	7.2	0.6	22.0	37.6	43.2	6.8	1.3	8.7	6.7	45.9	9.5	-1.9	5.0	-2.6
1 week old surfaces	41.8	35.4	6.4	0.4	27.5	73.7	42.2	6.8	1.1	10.5	9.5	47.0	11.6	-2.6	4.5	-1.7

Liquid parameters from: ¹ van Oss (1994), ² Della Volpe and Siboni (1997), ³ Qin and Chang (1996).

4. CONCLUSIONS AND FUTURE WORK

Measurement of the wetting properties and surface energetics of wood is complicated, but nevertheless an important task. Information about such properties is particularly meaningful for a better understanding of the adhesion and interaction between wood and e.g. adhesives and coatings.

Paper I

The results in Paper I show that a significant contamination of some probe liquids easily occurs during wetting measurements on wood using the Wilhelmy method. The contamination is detected as a decrease in the liquid surface tension, probably caused by dissolution or by the presence of wood extractives at the wood-liquid interface. It should also be remarked that such contamination probably also occurs during wetting studies on wood using other techniques for measuring contact angles. The most obvious contamination occurs on immersion of both heart- and sapwood in water and formamide. In contrast, no notable contamination occurs on immersion of extracted wood samples. A less pronounced contamination is also observed in the case of ethylene glycol and diiodomethane.

Based on these results showing the risk of severe probe liquid contamination, it is recommended that the perimeters of non-extracted wood samples should be determined from independent wetting measurements using a non-polar 'wetting-out-liquid', for example octane, and not from the receding part of the test cycles in the 'non-wetting' probe liquids. The Wilhelmy method seems to be a valuable tool to detect and control contamination of the probe liquids during wetting measurements on wood. In this procedure, to minimize effects of contamination, it is also recommended that only the first part of the advancing curve should be used in the determination of a contact angle, and that wicking effects must be considered. It is suggested that further studies should involve analysis of the solved extractives in the probe liquids, and also analysis of reorientation effects at the wood/extractives-liquid interface.

Paper II

The results indicate that wicking of the probe liquid, presumably along cavities in the fiber direction and into the porous structure of the wood veneer, occurs during the wetting measurements by the Wilhelmy method. The wicking is divided into two stage. First, immediately after that the specimen has contacted the liquid, an instantaneous wicking is observed. It is suggested that this initial wicking is influenced primarily by the liquid density and structural properties of the specimen. Second, a continuing secondary time-dependent wicking is observed.

A procedure to estimate apparent advancing contact angles on wood by the Wilhelmy method is suggested. In this procedure, to eliminate a secondary wicking effect and reduce any contamination effect of the probe liquids, the advancing contact angle is estimated from the initial part of the force versus depth plots. In addition, to compensate for an initial wicking effect, an initial wicking constant is estimated for different wood samples from measurements in octane.

The developed technique seems to be a valuable tool for estimating the wetting properties of wood giving reproducible measurements of apparent advancing contact angles with an efficient control of wicking and contamination effects. It should also be remarked that, because of sorbed liquid in the wood surface during the measurements, no finite receding contact angles seem to exist. Further investigations should be performed to examine the suggested initial wicking effect.

Paper III

The results show that the wicking of water, formamide, and methanol in wood particles gives rise to a considerable temperature increase, caused by bulk sorption. No temperature increase is observed with ethylene glycol, diiodomethane and hexane. An apparent non-linearity in the Washburn slopes is observed, particularly for water, formamide and methanol. The apparent non-linearity in capillary rise seems to depend on the probe liquids used and on the variation in particle size. The use of a more uniform wood particle size is desirable for the wicking analyses. The increase in temperature, measured at a high and a low point within the column, is instantaneous with the rise of the visible liquid front at the lower level, but at the higher level it is in advance of the main front. This may suggest that vapor is moving in advance of the visible liquid front, causing 'pre-wetting' of the wood particles.

The bulk sorption process and resulting swelling effects strongly influence the determination of the effective interstitial pore radius R_e , and thus the determination of apparent contact angles using the Washburn equation.

Paper IV

Inverse gas chromatography (IGC) is a useful technique for determining surface energetics of wood particles. Results from the IGC analysis using an *n*-alkane series indicate that extraction of spruce wood particles increases their Lifshitz-van der Waals (dispersive) surface free energy component. The Lewis acid-base characterization of the wood particles using the K_A and K_B constants is not meaningful since negative values of the enthalpies of adsorption ($-\Delta H_A^{AB}$) were obtained. Further studies should be performed to study this behavior. However, the Lewis acid-base characteristics of extracted and non-extracted wood substance may be compared and interpreted by analysis of the acid-base interaction at a single temperature between the acid-base probes and the different wood particle samples. This analysis indicates that wood substance without extractives has a more acidic (electron-accepting) and a less basic (electron-donating) character than wood substance containing extractives.

Paper V

The Lewis acid-base properties of extracted, non-extracted, fresh and aged pine-wood veneer samples, were determined by contact angle analysis using basic wetting theory and the so-called van Oss-Chaudhury-Good (vOCG) and Chang models. Results indicate that the Lewis acid-base contribution to the work of adhesion, W_a^{AB} , changes with longer aging times, and these changes suggest that the acidity and the basicity of the non-extracted wood increases and decreases, respectively,

with aging time. This is presumably due to the presence of extractives and to the reorientation of functional groups and oxidation at the wood/extractives-air interface.

The results obtained by the vOCG model also indicate that the acidity and the basicity of the non-extracted wood surfaces increases and decreases respectively with aging time. A similar trend seems to appear even for extracted samples, which may be attributed to the reorientation of functional groups in the wood-air interface. The basic character is less dominant when using the liquid data set according to Della Volpe and Siboni than when the van Oss data are used.

The results of the acid-base characterization of the different wood samples by the Chang model are similar to those obtained by the vOCG model. The Chang approach resulted, however, in a repulsive acid-base contribution to the surface free energy of one-week-aged heartwood. Further studies to compare the vOCG and Chang models should be performed.

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APPENDED PAPERS (I–V)

Division of the work in the appended papers:

- I. Wålinder, M.E.P. and I. Johansson
“Measurement of wood wettability by the Wilhelmy method. Part 1. Contamination of probe liquids by extractives”

Johansson initiated the work. Wålinder performed the experiments, and mutually the authors interpreted the results. Wålinder wrote the paper.

- II. Wålinder, M.E.P. and G. Ström
“Measurement of wood wettability by the Wilhelmy method. Part 2. Determination of apparent contact angles”

Wålinder initiated the work. Wålinder performed the experiments, and mutually the authors interpreted the results. Wålinder wrote the paper.

- III. Wålinder, M.E.P. and D.J. Gardner
“Factors influencing contact angle measurements on wood particles by column wicking”

Gardner initiated the work. Wålinder performed the experiments, and mutually the authors interpreted the results and wrote the paper.

- IV. Wålinder, M.E.P. and D.J. Gardner
“Surface energetics of extracted and non-extracted spruce wood particles studied by inverse gas chromatography (IGC)”

Gardner initiated the work. Wålinder performed the experiments, and mutually the authors interpreted the results and wrote the paper.

- V. Wålinder, M.E.P.
“Study of Lewis acid-base properties of wood by contact angle analysis”

Johansson and Wålinder initiated the work.

