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POSSIBILITIES OF USE OF PROPOLIS FOR WOOD FINISHING

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ABSTRACT

Possibilities of use of propolis for finishing of beech, maple and spruce wood were investigated. In the first part of the paper, an overview of propolis composition, properties and applications is given. 33.6 % mixture of propolis with 96 % ethanol was prepared and the ethanol solution of soluble propolis components (29.0 %) was applied to wooden substrates. Thin propolis films were formed on wooden substrates after drying at room temperature or in the laboratory oven at 40 °C. FT-IR spectra indicated that the film formation process was a physical and not a chemical one, only with the ethanol evaporation. The following properties of the propolis films were investigated: surface resistance to cold liquids, resistance to dry and wet heat, gloss, flexibility and contact angles of water. In general, resistance properties of the propolis films were quite inferior. Nevertheless, we think that propolis could be used as an additional component in natural wood finishes based on natural resins, waxes and oils.

KEY WORDS: wood, surface finishing, propolis, FT-IR

INTRODUCTION

The human being is always looking for materials to be in contact with which are friendly for him and also for nature. One of such interesting materials is propolis. Propolis or bee glue is a complex resinous mixture, a dark-coloured material that worker bees (*Apis mellifera* L.) collect from various plant sources from tree exudates, mainly resins of leaf buds. Mixed with beeswax, it is used and modified in a bee-hive: bees apply it to seal walls, to strengthen borders of combs and to embalm dead invaders (Nakajima et al. 2007). Propolis is collected by carefully scraping it off from the frame of the bee-hive. The term "propolis" comes from two Greek words: "pro" which means: before, in front of, in defence, and "polis" which means city, therefore in this case town of the bees – bee-hive. Many sources attribute the word to Aristotle (Ghisalberti EL. 1979).

The chemical composition of propolis is highly dependent on the flora of the region from which it is collected (Melliou et al. 2007). In general, raw propolis is composed of 50 % resin and balsam, 30 % wax, 10 % essential and aromatic oils, 5 % pollen, and 5 % other substances, including wood fragments. More than 180 different compounds were identified as constituents of Brazilian propolis, such as aliphatic acids, esters, aromatic acids, fatty acids, carbohydrates, aldehydes, amino acids, ketones, chalcones, dihydrochalcones, terpenoids, vitamins, and inorganic compounds (Castaldo and Capasso 2002). Mohammadzadeh et al. (2006) assessed by GC/MS analysis of 70 % ethanol extract of propolis, gathered in northern Iran, one hundred and nine compounds in this substance.

Investigations of Ahn et al. (2007) and Mohammadzadeh at al. (2006) showed that propolis has a lot of advantages; it offers anti-septic, anti-biotic, anti-bacterial, anti-fungal and even anti-viral properties. Imhoft et al. (2005) attributed antibacterial properties to p-coumaric acid, ferulic acid, caffeic acid, pinocembrin, galangin, diterpenic acid, syringa aldehyde and lignans. For antimycotic properties, there are responsible benzoic acid, ferulic acid, p-coumaric acid, benzyl ester, caffeic acid, caffeic acid ester, pinocembrin, pinobanksin, sakuranetin and pterostilbene. Furthermore, responsible for antiviral properties are caffeic acid, caffeic acid derivatives, utseolin and quercetin. Nevertheless, there were also some propolis disadvantages reported. So, Lieberman et al. (2002) reported on allergic contact dermatitis to propolis at musicians and instrument makers. Oedema and erithema in the face and hands of violin polishers in Cremona in Italy are related to contact dermatitis with propolis (Monti et al. 1983). Hausen et al. (1987) reported that propolis allergy today is mainly seen in individuals who use propolis in bio-cosmetics and self treatment of various diseases and at beekeepers.

Propolis has been used for thousands of years (Banskota et al. 2001) in traditional medicine all over the world, but for wood finishing applications, propolis is hardly ever mentioned, with few exceptions at musicians and instrument makers. We must not forget the renowned Stradivarius who had hand-mixed his own propolis based varnish to polish his handcrafted instruments for improving the acoustical properties of his musical instruments, and there is no doubt that propolis is partially responsible for their superior tonal qualities. Hammerl and Hammerl (1988) say that for impregnation of the inside of the instruments propolis solution can be used as a primer. This may be prepared and used in two ways. The first one is a 10 % solution of propolis in ethanol and the second one is 5 % mixture of potash in water and then 100 g of propolis is added. Propolis alone, dissolved in a concentrated ethanol can be used also as a colouring varnish and finishing coat. However propolis based varnish is usually used as a mixture with other constituents. Other resins like shellac and soft resin manila copal are added to it to improve its applicability and to make it dry more quickly.

Moreover, Drapak et al. (2006) studied the crystalline structure and optical properties of propolis films grown from the melt and alcohol solutions on various substrates like InSe, glass, sapphire, and Si/SiO_2. He found out that due to low density of dangling bonds on glass, sapphire and InSe surfaces, these substrates support growth of crystalline propolis films from the solutions. Grown from the melt, the propolis films have an amorphous structure irrespective to the substrate type. He concluded that thin propolis films in combination with a naturally layered semiconductor can be used for optoelectronic device applications.

The aim of our investigation was to estimate possibilities of use of propolis solution in ethanol for wood finishing. In order to assess its applicability and its drying/curing mechanisms, we used various standard methods, established for wood coatings, as well as FT-IR spectroscopy.

MATERIAL AND METHODS

The propolis was freshly collected in eastern Slovenia. 33.6 % mixture of propolis with 96 % ethanol was prepared: We put 400 g of propolis into 1000 ml of 96 % ethanol and left the mixture covered at normal room conditions for about three weeks. In the first week, the mixture was stirred with a magnetic stirrer and then left to stand for about two weeks. After then, the solution of propolis components, soluble in ethanol, was separated from the insoluble part (decantation). The propolis solution was evenly applied on surfaces of wood blocks with a brush of a 60 mm width. For our investigations, we used ten blocks of beech (*Fagus sylvatica* L.), maple (*Acer pseudoplatanus* L.) and spruce (*Picea abies* (L.) Karst.) wood. The wooden blocks were characterized by the following dimensions: length 200 mm, width 200 mm, and thickness 20 mm, previously dried to 14 % of equilibrium moisture content. The coatings were dried at room temperature in air and in a laboratory oven at 40 °C.

Measurements of the drying stages

The drying stages of the propolis – ethanol films that were drying at room temperature in air and in a laboratory oven at 40 °C were determined according to the DIN 53 150 standard. On each wood sample, we applied the propolis solution four times (in four layers). After each application, the drying stage was measured. The duration of load was 60 s and we used 20 g, 200 g, 2 kg and 20 kg weights. The drying stages, loadings and film damages are presented in Tab. 1.

Tab. 1: Drying stages (2, 3, 5 and 7), load and film damages, according to DIN 53 150

Drying stage	*Load*	*Film damage*
2	Load with 20 g (specific load 5 g/cm^2)	Paper is not adhering to the surface
3	Load with 200 g (specific load 50 g/cm^2)	Paper is not adhering to the surface
5	Load with 2 kg (specific load 500 g/cm^2)	Paper is not adhering to the surface. On the loaded surface there are no visible changes.
7	Load with 20 kg (specific load 5000 g/cm^2)	Paper is not adhering to the surface. On loaded surface there are no visible changes.

Assessment of surface resistance to cold liquids and assessment of surface resistance to wet and dry heat

According to the SIST EN 12720, SIST EN 12721 and SIST EN 12722 standards we exposed the coated surfaces of maple, spruce and beech specimens to various liquids (Tab. 2) and against wet and dry heat. For the assessment of surface resistance against wet heat we placed a standard aluminium alloy block with a specified temperature 70 °C as a heat source on a damp cloth in contact with the surface coated with propolis. After 20 minutes, the aluminium block and the damp cloth were removed. For the assessment of surface resistance against dry heat, we used the same materials and method, but without a damp cloth. For testing of our propolis surfaces against honey, we used Slovenian robinia (*Robinia pseudoacacia* L.) honey (commonly named as "acacia honey") with 16 % water content. The damage caused by cold liquids, wet and dry heat was assessed by reference to a descriptive numerical rating code (Tab. 3).

Tab. 2: Liquids and time of exposure

Liquid	Time
Coffee	1 hour
Ethanol (48 %)	1 hour
Acetone	2 min
Oil	24 hours
Distilled water	24 hours
Honey*	3, 7, 28 days.

**Honey is not included in the standard.*

Tab. 3: Descriptive numerical rating code

Rating	Description
5	No visible changes (no damage)
4	Slight change in gloss and colour visible only when the light source is mirrored in the test surface on or quite near the mark and is reflected towards the observers eye, or a few isolated marks just visible
3	Slight mark visible in several viewing directions
2	Strong mark, the structure of the surface being however largely unchanged
	**Strong mark, distinctly visible or region of slight discoloration or region of slight disturbance of the test surface
1	Strong mark, the structure of the surface being changed or the surface material being totally or partially removed or the filter paper adhering to the surface
	**Strong mark, or region of distinct discoloration or region of distinct disturbance of the test surface

***Description is related to assessment of surface resistance to wet and dry heat according to SIST EN 12721 and SIST EN 12722.*

Measurements of contact angles of water on surfaces, coated with a propolis film

In this study, contact angle analysis was used to determine the hydrophobic / hydrophilic properties of propolis surfaces. A digital camera was used to photograph drops of water placed on the propolis coating surface. Contact angles of water were determined from the water droplets photographs by drawing lines at the water – propolis surface intersections. The angles were calculated from the line coordinates by the computer program for picture analysis (CorelDraw 10.0). The contact angle measurements were performed on the final fourth layer of each wood specimen. We compared water contact angles on propolis coated surfaces with those on untreated samples.

Gloss measurements

Gloss of the coatings made of propolis – ethanol solutions was measured with the ERICHSEN Glossmaster according to SIST EN ISO 2813. The angle of rays was set at 60°. The measurements were performed parallel to the grain direction, five times per each specimen.

FT–IR investigations

With a Fourier transform infrared (FT-IR) spectroscopic study we wanted to find out if the propolis film formation was only a physical process of evaporation of ethanol during drying or there were some chemical reactions of curing involved. We used the spectrometer Spectrum one, Perkin Elmer instruments. We recorded FT-IR spectra of solutions of propolis and compared them with the spectra of solutions of the same concentration of dry propolis films, re-diluted in a 96 % ethanol. The FT-IR spectra were recorded in the ATR technique, in a 4000 cm^{-1} to 650 cm^{-1} wave number range.

Assessments of some other properties

Some other properties, determined throughout our research are briefly presented in Tab. 4.

Tab. 4: Some additional properties of the propolis–ethanol coatings that were also investigated

• Determination of non-volatile matter of paints, varnishes and binders for paints and varnishes according to SIST EN ISO 3251
• Determination of film thickness according to SIST EN ISO 2808
• Determination of flexibility according to DIN 53 155:1971

RESULTS AND DISCUSSION

As determined gravimetrically, by drying the ethanol solution of soluble propolis constituents, used for film formation on wood specimens, the content of non-volatile matter in the solution was 29.0 %: we were drying 1 g of the propolis solution (supernatant) for 24 hours in the laboratory oven at 105 °C and during the drying period, 0,71g of ethanol evaporated, leaving 0.29 g of dry matter. The difference between 29.0 % dry matter in the supernatant and 33.6 % concentration of the original ethanol-propolis mixture is in correspondence with the insoluble propolis constituents, precipitated on the bottom of the beaker.

Thicknesses of propolis films on wood specimens were varying from 10 µm - 15 µm on beech, 20 µm - 35 µm on maple and 15 µm – 25 µm on spruce wood.

The results of drying stage determinations (DIN 53 150) are shown in Tab. 5. The propolis films, prepared by drying at room temperature or in the laboratory oven at 40 °C, remained soft, even after prolonged times of drying. It was also stated that the increase of the drying temperature significantly shortens the drying time of propolis films. However, we could not reach the final drying stage (with the load of 20 kg) of the fourth layer.

Contact angels of water on propolis films are shown in Tab. 6. The films exhibited hydrophobic properties. It is also obvious that there were not any significant differences in contact angles of water, depending on the number of film layers, substrate types and the drying temperatures.

Tab. 5: Loads, drying stages and drying times of propolis films (according to DIN 53 150)

MAPLE								
Load (g) / drying stage	Drying time (min)							
	1 application		2 application		3 application		4 application	
	20 C°	40 C°	20 C°	40 C°	20 C°	40 C°	20 C°	40 C°
20000g/7	**102**	**15**	**249**	**162**	**7140**	**437**	**NO**	**NO**
2000g/5	75	10	155	100	4320	190	4320	600
200g/3	50	5	83	20	2880	80	2880	360
20g/2	21	3	35	15	1380	35	1380	180
SPRUCE								
Load (g) / drying stage	Drying time (min)							
	1 application		2 application		3 application		4 application	
	20 C°	40 C°	20 C°	40 C°	20 C°	40 C°	20 C°	40 C°
20000g/7	**1440**	**25**	**4260**	**132**	**16140**	**397**	**NO**	**NO**
2000g/5	87	20	1440	102	6060	100	NO	450
200g/3	21	10	292	42	5760	60	8400	360
20g/2	18	5	70	10	4320	25	7200	60
BEECH								
Load (g) / drying stage	Drying time (min)							
	1 application		2 application		3 application		4 application	
	20 C°	40 C°	20 C°	40 C°	20 C°	40 C°	20 C°	40 C°
20000g/7	**114**	**25**	**340**	**117**	**7140**	**485**	**NO**	**NO**
2000g/5	39	20	305	52	4320	183	10080	600
200g/3	27	10	81	20	2880	85	2880	360
20g/2	25	5	36	10	1380	50	1683	120

Tab. 6: Average contact angles of water on propolis films on maple, spruce and beach wood specimens, dependent on the drying conditions

SUBSTRATE TYPE	CONTACT ANGLES OF WATER (º)								
	Untreated samples	1 application		2 application		3 application		4 application	
		20 C°	40 C°	20 C°	40 C°	20 C°	40 C°	20 C°	40 C°
MAPLE	40,5	101,2	94,7	78,4	74,7	87,4	71,7	87,5	85,0
SPRUCE	45,2	107,2	113,1	85,1	87,1	79,7	85,4	81,3	82,0
BEECH	56,2	95,5	93,8	100,7	81,1	76,1	83,1	84,4	82,5

Resistance of the propolis films against cold liquids (SIST EN 12720) and also resistance against wet and dry heat (SIST EN 12721) and (SIST EN 12722) were poor (Tab. 7), the only positive exceptions were resistance against honey (4, Tab. 7) and oil (5, Tab. 7). The test with honey was interesting because of a possible application of propolis as a protective coating inside (and maybe also on the outer surfaces) of decorative wooden pots containing honey, to be sold as a souvenir.

Tab. 7: Average assessments of propolis film (on maple, spruce or beech wood) resistance (SIST EN 12720) against various agents. The films were dried at room temperature and in the laboratory oven at 40 °C

REAGENT	TIME OF EXPOSURE	MARK	
		40 °C	20 °C
Distilled water	24 hours	1	1
Coffee	1 hour	2	2
Ethanol (48 %)	1 hour	1	1
Acetone	2 min	1	1
Oil	24 hours	4	4
Honey*	3 DAYS	5	5
	7 DAYS	5	5
	28 DAYS	5	5
DRY HEAT 70 °C	20 MIN	1	1
WET HEAT 70 °C	20 MIN	1	1
FLEXIBILITY	/	3	3

The propolis films were brittle and non-flexible (Table 7). The addition of some soft resins should be considered in future to improve this property.

The highest average value of gloss of the four-layer propolis surface system was detected on the maple wood substrate, and the lowest one on beech wood, reflecting differences in wood structures (Tab. 8).

Tab. 8: Average gloss of the four-layer propolis coating system. The film was dried in the laboratory oven at 40 °C

SUBSTRATE	AVERAGE GLOSS (%)
MAPLE	84,1
SPRUCE	64,9
BEECH	61,6

FT-IR investigations

Comparison of FT-IR spectra of 96 % ethanol and of the 29.0 % solution of propolis in 96 % ethanol clearly showed some bands that can be assigned to vibrations in propolis containing compounds (the most prominent distinctions are designated with arrows in Fig. 1)

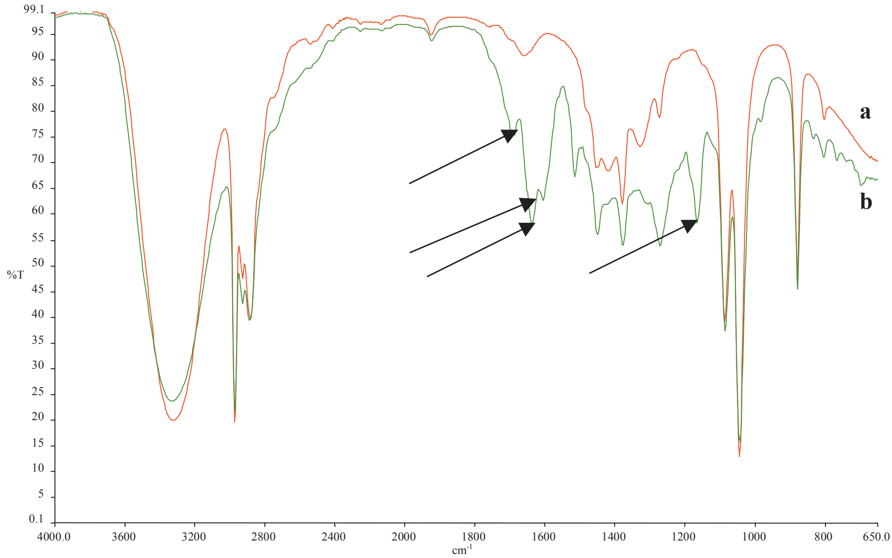

Fig. 1: FT-IR spectra of 96 % ethanol (spectrum a) and of the 29.0 % solution of propolis in 96 % ethanol (spectrum b)

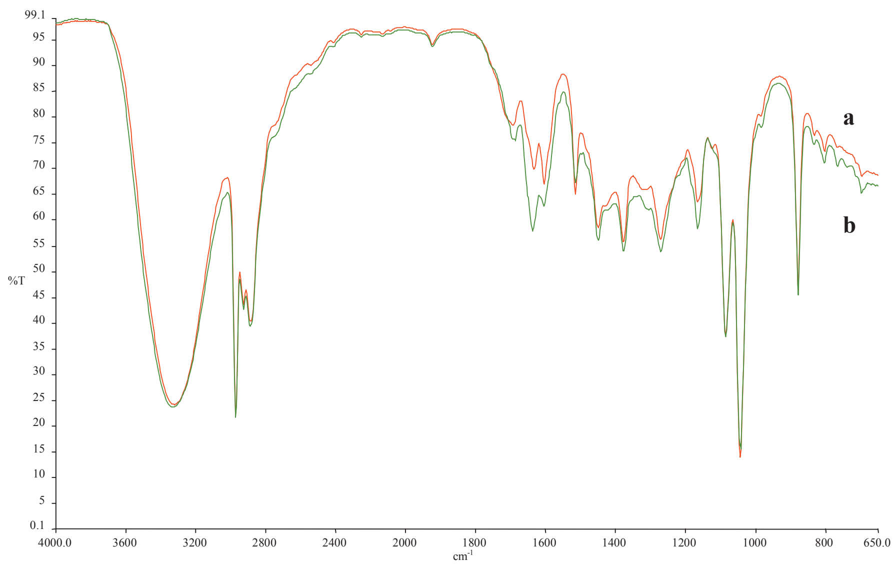

Fig. 2: FT-IR spectra of the 29.0 % solution of propolis in 96 % ethanol before drying (a) and of the dried residue (105 °C in laboratory oven for 2 days) of the same solution, dissolved again in 96 % ethanol (b)

From Fig. 2, it is obvious that there are not any significant differences between spectra of 29.0 % solution of propolis and of the dried residue of this solution, dissolved again in ethanol. Due to this fact we believe, that formation of a propolis film was just a physical process of evaporation of ethanol, leaving propolis film residue on a substrate surface. If there had been any chemical changes (like for instance cross-linking) during the drying process, we would probably not be able to dissolve the whole dried film in ethanol again, or at least we would notice some differences in FT-IR spectra, exhibiting formation of new bonds, etc. However, this topic should be studied in more details, possibly also with some other instrumental techniques (like for example: thin-layer chromatography, gas chromatography, high-performance liquid chromatography (HPLC), HPLC–mass spectrometry or similar.

CONCLUSIONS

Our investigation showed that drying of the supernatant (29.0 % solution of propolis in 96 % ethanol), obtained by decantation from 33.6 % mixture of propolis with 96 % ethanol, resulted in formation of a thin propolis film, which could be applied to various wooden substrates. The drying time of an ethanol solution of propolis was very long and the dried propolis films remained soft. FT–IR spectroscopy investigations showed that formation of a propolis film was most likely only the physical process of evaporation of ethanol during drying of the propolis solution. It was found out that the propolis films had hydrophobic properties. Resistance characteristics were generally low, with the exceptions of resistance against oil and also honey. An interesting option, coming out from the latter fact, could be production of decorative souvenir wooden pots for honey, with interior surfaces protected with propolis. Otherwise, propolis seems to have very limited possibilities for application as a wood finish. Nevertheless, on the basis of outcomes of our research, we think that propolis might be used as an additional component of natural ("bio") wood finishes, in combination with various natural materials such as resins, waxes and drying oils. Further research is needed to check this possibility.

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