Effect of the Addition of Extractives on The Reduction Of Vocs Emissions from Lacquers in the liquid state

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The aim of this study was to determine the effect of the addition of extractive substances on the VOC emission of lacquer products in the liquid state. Three water-soluble acrylic resin products were investigated using the stationary phase microextraction technique in combination with gas chromatography coupled with mass spectrometry (SPME-GC/MS). The extraction of volatile compounds was analysed at three temperatures: 22 °C, 35 °C and 45 °C. 20 μg of an extract obtained from the leaves, branches and bark of black cherry (Prunus serotina Erhr.) were added to commercial products. Flavonoids accounted for almost 75% of the total phenols in the used extract. The spectrum of volatile compounds emitted by the liquid coating products selected for the studies was examined before and after adding the extract to them. It was found that the addition of black cherry extract caused a significant reduction in the emissions of volatile compounds emitted by the researched products. The compounds, whose amounts did not decrease under the influence of the addition of the extract, were esters of propenoic acid. The applied extract was a source of emissions from an additional compound: benzaldehyde. The total VOC emissions of the investigated liquid coating products was reduced by 8-55% and depended on the extraction temperature. The paper also proposes the mechanism of chemical reactions between phenolics and VOC, which may cause the reduction in VOC emissions from lacquer products. The IBM RXN tool was utilised to find possible reactions.

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Introduction

Finishing the surface of wood products with lacquers has been done for many years. This type of surface finishing is aimed at, among others, giving various materials the desired aesthetic features and protecting them against the effects of harmful external factors.
The application of lacquer, depending on the type of product and the application technique, may contribute to unfavourable changes in the natural environment and contamination of the microclimate of production halls. A large part of the environmental hazards arising from the reasons for applying lacquers are directly related to the organic solvents contained in them, the main purpose of which is to provide the products with appropriate properties during the application. The lacquer products used to refine surfaces in the furniture industry are a source of volatile organic compounds (Bongivanni et al. 2002; Salthammer et al. 2002, Salthammer 2006, Uhde and Salthammer 2007, Kagi et al. 2009, Salthammer and Müfit 2009, Broekhuizen 2012). The research by Stachowiak-Wencek and Prądzyński (2015) showed that the application of an appropriate method of product application, mainly automated lacquering lines, reduces VOC emissions to the air in production halls.

Not only does the application of lacquers contribute to VOC contamination of the environment of production halls, but also products enriched with them release these compounds into the air. (Guo and Murray 2001, Wiglus et al. 2002 a, b; Gaca and Dziewanowska-Pudliszak 2005, Stachowiak-Wencek and Prądzyński 2005, Dziewanowska-Pudliszak 2007).

VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. Compounds are lipid-soluble compounds and can cross the blood-brain barrier, causing neurological health problems (Brinke et al. 1998; Domingo and Nadal 2009; Radheshyam and Puneeta 2018, Ulker et al., 2021). They can be absorbed through the skin, mucosa, and human digestive tract, leading to headaches, dizziness, nausea, poisoning, and prolonged exposure can have depressing and narcotic effects. For several years, the aim has been to create products with low VOC emissions.

Attempts are increasingly being made to replace harmful chemicals with alternative substances found in nature, such as vegetable oils, bark, waxes, and resins. Recently, there have been reports on the possibility of using extracts obtained from natural raw materials. The literature reports that extracts can significantly improve the durability of the coating as well as the bond between the surface and the lacquer (Hse and Kuo, 1988). Tomak et al. (2018) report that these substances can also become natural ultraviolet absorbers additionally an alternative to pigments, organic, and inorganic UV absorbents. Extracts obtained from various natural raw materials are rich in phenols.

Phenolics constitute a wide group of compounds that occur naturally in plants. Phenolics are synthesized in the chloroplast with exposure to light (Kefeli V.I. et al., 2003). An interesting source of phenolic compounds is invasive alien plant species (IAPS). According to the national law in Poland, landowners on whose property IAPS grow are responsible for their removal (Journal of Laws 2021 item 1718). The removal of IAPS results in the obtaining a large amount of biomass which must be disposed of. Black cherry (Prunus serotina Erhr.) is an invasive alien plant species and is one of the greatest threats to the forest ecosystem in central Europe, mostly because of its ability to grow on poor soils, early maturation with a high abundance of fruits and the ability to vegetatively propagate. (Grajewski et al., 2010). Previous studies have shown that black cherry is a rich source of phenolic compounds. One of the phenolic groups, the most abundant in Prunus serotina, is flavonoids (Brozdowski et al. 2021). Flavonoids constitute a group of secondary metabolites, which are synthesized in light from precursors such as chalcone and phenol-carbonic acid in the chloroplast and cytoplasm of the plant. According to Muzafarov et al. (1986; 1989), flavonoids play a key role in photosynthesis, as well as are substrates, energy sources, and regulators. Plant polyphenols are compounds with high reactivity, are very unstable, and undergo many reactions, both chemical and biological, after harvesting the plant source, in addition exhibit antioxidant, anti-inflammatory, and antibacterial activity. Because of those properties, phenolics are now in the centre of many studies on how to use them in cosmetics, the food industry, or packaging, e.g. coatings and foils. Polyphenols are easily extracted by water, alcohol, and other solvents. By using different solvents, we can influence which phenolic group will be dominant in our extract.

Although the interest in reducing volatile organic substance emissions from lacquer products is not a new topic, the means and methods of reducing VOC emissions from lacquer products, both in the liquid state and the coatings produced with their use, are still being sought. The importance of this issue has been high for several years. The discovery of new methods to limit the emissions of volatile organic compounds into the air is necessary to improve the hygiene of rooms and the health of their users.

Therefore, the aim of this study was to determine the effect of the addition of extractive substances on the emissions of volatile organic compounds from lacquer products in the liquid state.

Material and methods

Material

Three lacquer products were selected for the study, belonging to one of the most important groups of liquid refining materials used by the wood industry, in particular the furniture industry. All the lacquer products belong to water-based products based on acrylic resin. According to the information provided by the manufacturer, these products are intended for the surface finish of wood materials, made of various types of wood, used indoors. They belonged to multi-layer materials that can be used as basecoats and topcoats.

Detailed information on the physicochemical properties of the lacquer products mentioned above is presented in Table 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Lacquer I</th>
<th>Lacquer II</th>
<th>Lacquer III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding agents</td>
<td>acrylic dispersion</td>
<td>water/water with extract</td>
<td></td>
</tr>
<tr>
<td>Solvents</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Content of solids [%]</td>
<td>30</td>
<td>32</td>
<td>36</td>
</tr>
<tr>
<td>Density [g/cm³]</td>
<td>1.03</td>
<td>1.05</td>
<td>1.06</td>
</tr>
<tr>
<td>Commercial viscosity at temp. 22 ± °C [s] *</td>
<td>30</td>
<td>33</td>
<td>38</td>
</tr>
<tr>
<td>Other</td>
<td>colourless product</td>
<td>product with addition of brown pigment</td>
<td>product with addition of black pigment</td>
</tr>
</tbody>
</table>

Extract

The raw material for the extract was obtained from the leaves (30%), branches (40%), and bark (30%) of black cherry. The harvested material was dried and ground. The extract was prepared from the raw material according to the method optimised in a previous study (Brozdowski et al. 2021) with some modifications. 0.5 g of ground material was placed in a tube and then 8 ml of distilled water was added. The material was then extracted at 40 °C in an ultrasonic bath (Bandelin Sonorex, Germany), at the frequency of 35 kHz for 45 min. The tube was then placed in a centrifuge at 4000 rpm for 15 minutes. After the centrifugation process was complete, it was filtered through a cellulose filter and stored at -32 °C. The extract preparation process was repeated 5 times. The obtained extracts were mixed before application. Water was used in the extraction process as it is a diluent for the investigated lacquer products. The obtained extract was dosed to each of the lacquer products in the amount of 10%.

VOC chromatographic analysis

The volatile organic compounds emitted by the researched lacquers were measured using the SPME-GC/MS method.

The individual lacquer products in the amount of 0.2 g were placed (in the liquid state, prepared for application) in 40 ml vials and thermostated at a temperature of 22 ± 1 °C (similar to indoor temperature) for 20 minutes. After 20 min, SPME fibres coated with active carbon (carboxen TM) and polydimethylsiloxane (CAR/PDMS), with a film thickness of 75 μm (Supelco Inc., Bellefonte, PA), were introduced into the headspace. Volatile compounds were extracted from the researched samples of liquid lacquers for 35 min. The study of the chromatographic profile of volatile organic compounds from the lacquer products without and with the addition of extractive substances was carried out at three temperatures: 22, 35 and 45 °C.

Desorption of the compounds adsorbed on the fibres was carried out in a hot gas chromatograph feeder coupled with a mass spectrometer at the temperature of 200 °C for 5 min. with a closed stream divider (splitless). Chromatographic analysis was performed under the conditions presented in Table 2. The analysis was conducted on three samples and in triplicate for each variant.
Table 2. Parameters of GC/MS analytical system

<table>
<thead>
<tr>
<th>System element</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas chromatograph</td>
<td>TRACE GC, Thermo Quest.</td>
</tr>
<tr>
<td>Column</td>
<td>DB-30MS, 30 m x 0.25 mm ID, Df - 0.25 μm</td>
</tr>
<tr>
<td>Detector</td>
<td>Mass spectrometer (SCAN: 10 – 350)</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Helium: 100 kPa, ~2 cm³/min⁻¹.</td>
</tr>
<tr>
<td>Temperature setting</td>
<td>40 °C for 2 min, 7 °C min⁻¹ to 200 °C, 10 °C min⁻¹ to 230 °C, 230 °C for 5 min</td>
</tr>
</tbody>
</table>

Identification of the volatile compounds was made by comparing the mass spectra of the compounds with the spectra contained in the spectrum library NIST MS Search – programme version 1.7 – and was confirmed by comparing the mass spectra and retention times of these compounds with the spectra and retention times of the appropriate standards. The number of compounds isolated by the SPME technique was expressed as the total area of their peaks.

Content of Phenols and Flavonoids

The total phenolic content and the total flavonoid content was determined based on spectrophotometric assays optimised by Pękal (2014). The total phenolic content assay was conducted with Folin-Ciocalteu reagent in an alkaline environment. Absorption was measured at the 765 nm wavelength. Gallic acid was used as the reference substance. The results are presented in mg/g of gallic acid equivalent (GAE). The colour reaction with aluminium ions was utilised to determine the content of flavonoids. Absorbance readings were taken at the wavelength of 420 nm. The reference substance was quercetin and the results are presented in mg/g of quercetin equivalent (QE).

Predicting reactions contributing to VOC reduction from liquid lacquers

To find possible reaction routes between the phenolic compounds from the P. serotina extract and VOC from wood lacquers, the IBM RXN predict forward reaction tool was used. The reaction models were predicted by means of artificial intelligence (AI), which uses deep machine learning to analyse chemical reactions collected in available databases.

Results and discussion

Table 3. Emissions from Prunus serotina extract

<table>
<thead>
<tr>
<th>VOC compound</th>
<th>Temperature</th>
<th>[%]</th>
<th>[%]</th>
<th>[%]</th>
<th>[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>22 °C</td>
<td>48837323</td>
<td>99</td>
<td>515459656</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>35 °C</td>
<td>515459656</td>
<td>99</td>
<td>553370085</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>45 °C</td>
<td>553370085</td>
<td>99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trifluoroacetic acid n-octadecyl ester</td>
<td>2748460</td>
<td>&lt;1</td>
<td>3006944</td>
<td>&lt;1</td>
<td>3089383</td>
</tr>
<tr>
<td>Hexadecane acid</td>
<td>1884482</td>
<td>&lt;1</td>
<td>2053058</td>
<td>&lt;1</td>
<td>2250326</td>
</tr>
</tbody>
</table>

Amount of volatile compounds expressed as total area of obtained peaks and their percentage

Table 3 presents the types and amounts of volatile compounds emitted by the extract obtained from black cherry (Prunus serotina Erhr.) added to the lacquer products. The main compound found in the extract was benzaldehyde. It accounts for 99% of the total emissions.
Table 4 shows the change in VOC emission by the examined coating products with the extract addition. The results are presented as the percent of reduction (-) or increase (+) and standard deviation of the VOC emissions from the coating product after the addition of the extract. The change in emissions was calculated based on the peak area of the emitted compounds.

### Table 4. Difference in emissions between lacquer without and with extract addition

<table>
<thead>
<tr>
<th>VOC compound</th>
<th>Temperature</th>
<th>Emission [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Propenoic acid, 2-methyl-, butyl ester</td>
<td>22 °C</td>
<td>+266 ± 15</td>
</tr>
<tr>
<td></td>
<td>35 °C</td>
<td>+29 ± 11</td>
</tr>
<tr>
<td></td>
<td>45 °C</td>
<td>+100 ± 9</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td></td>
<td>+NE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+NE</td>
</tr>
<tr>
<td>Dipropylene glycol</td>
<td></td>
<td>-82 ± 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-67 ± 17</td>
</tr>
<tr>
<td>1-(2-methoxypropoxy)-2-propanol</td>
<td></td>
<td>-62 ± 13</td>
</tr>
<tr>
<td>2-ethyl-1-hexanol</td>
<td></td>
<td>-90 ± 11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-71 ± 11</td>
</tr>
<tr>
<td>2-(2-butoxyethoxy)-ethanol</td>
<td></td>
<td>-63 ± 4</td>
</tr>
<tr>
<td>Propanoic acid, 2-methyl-, butyl ester</td>
<td></td>
<td>+9 ± 12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-7 ± 4</td>
</tr>
<tr>
<td>2-ethyl-3-hydroxyhexyl 2-methylpropanoate</td>
<td></td>
<td>+8 ± 9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+7 ± 10</td>
</tr>
<tr>
<td>2-(2-butoxyethoxy)-ethanol</td>
<td></td>
<td>-97 ± 5</td>
</tr>
<tr>
<td>Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl-1 ester</td>
<td></td>
<td>+84 ± 13</td>
</tr>
</tbody>
</table>

**Product II**

<table>
<thead>
<tr>
<th>VOC compound</th>
<th>Temperature</th>
<th>Emission [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-butoxyethanol</td>
<td></td>
<td>-54 ± 14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-50 ± 10</td>
</tr>
<tr>
<td>2-butoxyethanol</td>
<td></td>
<td>-34 ± 12</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td></td>
<td>+NE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+NE</td>
</tr>
<tr>
<td>n-Nonane</td>
<td></td>
<td>-35 ± 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-83 ± 17</td>
</tr>
<tr>
<td>2-ethyl-1-hexanol</td>
<td></td>
<td>-32 ± 1</td>
</tr>
<tr>
<td>2,5-dimethyloctane</td>
<td></td>
<td>-23 ± 15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-67 ± 8</td>
</tr>
<tr>
<td>2-(2-butoxyethoxy)-ethanol</td>
<td></td>
<td>-11 ± 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-64 ± 5</td>
</tr>
<tr>
<td>Butanoic acid, butyl ester</td>
<td></td>
<td>-21 ± 7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-50 ± 14</td>
</tr>
<tr>
<td>2-Propenoic acid, 2-methyl-, butyl ester</td>
<td></td>
<td>-30 ± 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-25 ± 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+93 ± 17</td>
</tr>
</tbody>
</table>

**Product III**

<table>
<thead>
<tr>
<th>VOC compound</th>
<th>Temperature</th>
<th>Emission [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-butoxyethanol</td>
<td></td>
<td>-57 ± 12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-42 ± 3</td>
</tr>
<tr>
<td>2-butoxyethanol</td>
<td></td>
<td>-65 ± 7</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td></td>
<td>+NE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+NE</td>
</tr>
<tr>
<td>Dipropylene glycol</td>
<td></td>
<td>-56 ± 15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-40 ± 11</td>
</tr>
<tr>
<td>1-(2-methoxypropoxy)-2-propanol</td>
<td></td>
<td>-63 ± 13</td>
</tr>
<tr>
<td>2-(2-butoxyethoxy)-ethanol</td>
<td></td>
<td>-65 ± 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-46 ± 12</td>
</tr>
<tr>
<td>2-(2-butoxyethoxy)-ethanol</td>
<td></td>
<td>-61 ± 5</td>
</tr>
</tbody>
</table>

NE – new emission
Based on the obtained results summarised in Table 4, it can be stated that the emissions (VOC) from the water-soluble acrylic binder, and the liquid lacquer products, both in terms of the type and amount of emitted compounds, varied. The dominant compound secreted in the highest amounts by the two studied products (II and III) in the liquid state was 2-butoxyethanol. This compound represented 46 to 96% of the total emissions, depending on the extraction temperature. In the case of Product I, it was 2-methyl-2-ethyl-3-hydroxyhexyl propionate, whose emissions, depending on the extraction temperature, were 32.5-46.4%. The second largest emission compound released by the colourless Product I was 2-ethylhexanol (2.9-3.8%), and in the case of Product III they were dipropylene glycol, 1-(2-methoxypropoxy)-2-propanol, and 2-(2-butoxyethoxy) ethanol. Their total emissions at the temperature of 22°C was 13.8%. Product II also released in relatively large amounts 2-propeno-2-methyl acid butyl ester (26.95-37.97% of the total emissions) and 1-(2-methoxypropoxy)-2-propanol (11.5-20.3%).

It was found that after adding the extract to each of the researched products, the spectrum of VOC compounds emitted by these products changed slightly. In each of the investigated products there was an additional peak of benzaldehyde, whose share in the total emission of the studied products ranged from 0.03% to 19.11%. Its source was the extract, the emission of which also noted the presence of this compound.

The comparison of the results obtained for the lacquer products without the addition of the extract and after its addition shows that the emission of most of the compounds released by the examined products was significantly reduced. The compounds, whose amounts did not decrease under the influence of the addition of the extract, were esters of propenoic acid (2-methyl-2-propenoic acid butyl ester, 2-methylpropenoic acid butyl ester, and propenoic acid 2-methyl-1-(1,1-dimethylethyl)-2-methyl-1,3-propanedioic acid ester).

The emissions from Products I and III in the liquid state decreased significantly. The decrease in the emissions of all the compounds emitted for Product I was 34 to 51% and for the product with the addition of Product III from 42 to 55%, depending on the extraction temperature. For Product II, the reduction in emissions was much lower and ranged from 9 to 12%. The butyl ester of 2-methyl-2-propanoic acid had the greatest impact on the recorded level of reduction in VOC emissions. The amount of this compound was limited depending on the extraction temperature only by 7-8%. On the other hand, the emissions of the dominant component emitted by Lacquers I and III, i.e. 2-butoxyethanol, decreased to a much greater extent, ranging from 46 to 55%.

The reduction in VOC emissions with the help of the phenolic-rich extracts has not been extensively researched to date; however, the results of the existing studies are promising. The study by Kahar et al. (2022) showed that the addition of the Sansevieria extract reduced the emission of benzene by 98.73%. These results are in accordance with the present study, which confirms that the addition of natural extract can lead to a reduction in VOC emissions. The researchers suggested that reduced VOC are converted into organic acids, sugars, and amino acids. The results of studies on extract additions in coatings indicated that it can improve the barrier and mechanical properties of the coating (Ikhmal et al. 2022). Using various extracts, it is possible to produce coatings with antimicrobial properties or smart coatings, which react to changes in pH or are able to protect the surface against changes caused by UV radiation (Ong et al. 2021).

The measured contents of total phenols and flavonoids in the researched extract are presented in Figure 1. The results show that almost 75% of the total phenolics in the extracts are represented by flavonoids. The phenolic content of the P. serotina extract in this study is in the same range as in a study from 2021 (Brozowski et al. 2021).

![Fig. 1. Content of total phenolics and total flavonoids in P. serotina extract](image-url)
As a result of the calculations, the following reactions are proposed, the result of which may be a reduction in VOC emissions from the lacquer product. The prediction was based on the IBM RXN prediction tool (https://rxn.res.ibm.com/rxn/sign-in). The prediction was based on known reactions between the organic compounds.

Simulations were made for the reaction of caffeic acid, gallic acid, and epicatechin with 2-methylbutyl ester of 2-propenoic acid and 2-butoxyethanol. The simulations are shown in Figures 2-5. The dominant products resulted from the transesterification and esterification reactions between the esters and phenolic acids present in the matrix. The presence of organic acids and other proton donators facilitates esterification reactions. Also, the resulting products probably move to the organic phase, and thus the reaction equilibrium is rather shifted towards creating new esters and polar products that are less polar.

Fig. 2. Simulation of reaction between caffeic acid and 2-methylbutyl ester of 2-propenoic acid

Fig. 3. Simulation of reaction between gallic acid and 2-butoxyethanol Variant I

Fig. 4. Simulation of reaction between gallic acid and 2-butoxyethanol Variant II

Fig. 5. Simulation of reaction between epicatechin and 2-methylbutyl ester of 2-propenoic acid
Conclusions

1. The addition of an aqueous extract obtained from the leaves, branches, and bark of black cherry (Prunus serotina Erh.) resulted in a statistically significant reduction in the emission of the most volatile organic compounds emitted by the investigated lacquers. The total VOC emissions from the studied liquid coating products was reduced from 9 to 55%, depending on the coating product.
2. The spectrum of VOC released by the researched coating products changed after the extract was added to them. An additional peak was observed for benzaldehyde, which was also found in the extract itself.
3. The compounds, the amount of which did not decrease under the influence of the addition of the extract, were esters of propenoic acid.
4. The performed simulations of possible chemical reactions show that the interactions between the phenols and VOCs result from esterification and transesterification reactions.

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