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Wooden Musical Instruments

Reconstructing historical recipes of linseed oil/colophony varnishes: Influence of preparation processes on application properties

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ABSTRACT

Mixtures of siccative oil with *Pinaceae* resin are among the most widespread natural formulations used for varnishing before the introduction of synthetic varnishes in the 1900s. In this work, varnishes containing linseed oil and colophony in different proportions were recreated. Heat treatment is necessary to mix the two components; time and temperature of heating have to be carefully chosen, in accordance with proportions, in order to obtain homogeneous and translucent mixtures. The effects of heat treatment on the mixtures' properties were evaluated for five temperatures and three durations fitting these requirements, and various proportions were prepared. The application properties of the various reconstitutions, including a varnish prepared by a violin-maker, were studied through rheological measurements. These data were used to discuss the varnishes' brushing, leveling and sagging properties, by comparing them to industrial criterions. Intensifying the heat treatment by increasing its temperature and length was shown to exponentially increase the mixtures' viscosity. Size exclusion chromatography was used to evidence the polymerization reactions responsible for this behavior. The effect of colophony proportions was also investigated: colophony acts as a thickener increasing the mixtures' viscosity. All the varnishes exhibited thixotropic behavior. The higher the colophony proportion, the lowest is the shear rate at which shear-thinning behavior occurs, and the longer it takes to regain the initial viscosity. The easiest mixtures to apply as a coating were the ones with intermediate colophony proportions (33 to 58 wt%). Also, varnishes containing lower colophony proportions (20 wt%) could conveniently be coated if they were prepared using a strong heat treatment (long time and/or a high temperature). In the same way, higher colophony proportions (66 wt%) could be used if the mixture was heated at a lower temperature. These selected mixtures have a low viscosity at high shear rates, allowing brushing them easily. The time for viscosity recovering is long enough to allow good leveling and they have a quite high zero-shear rate viscosity, acting against sagging.

1. Research aims

Mixtures of siccative oil with *Pinaceae* resin were commonly used for instrument varnishing purposes in the 16th to 18th centuries. However, historical written recipes are scarce and often do not mention the parameters of the heat treatment used to mix the two ingredients, as well as the proportions that may have been used. As proportions and heat treatment have a strong influence on the application properties of the varnishes, we recreated different recipes and systematically studied and quantified the application properties of the obtained varnishes through rheological measurements. Our aim is to enhance the knowledge of what may have been oil/colophony varnishes recipes of the past.

2. Introduction

Varnishes have been used for centuries to protect and/or modify the visual appearance of various objects and works of art. These liquid solutions had first to be prepared from natural substances using

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various processes, before being coated onto pieces of furniture, horse carriages, musical instruments, tools, decorative artifacts, etc. The materials and techniques to prepare such varnishes have been written down as recipes, eventually collected in manuscripts, books and discussed in treatises [1–5]. Also, numerous artifacts varnished in the past are still preserved today, allowing for the study of their stratigraphy and chemical composition using micro-imaging and analytical chemistry methods. A specifically strong interest has grown for varnishes of musical instruments – and of 16th to 18th century Italian violins in particular – at least since the beginning of the 19th century [6]. Numerous books have been published since [7–9], and numerous tentative experimental developments or reconstructions have been realized by violin-makers, which constitute a lively craftsmen's community, grounded in a centuries-long tradition.

Chemical analysis of varnishes coating various European musical instruments dating from 16th to 18th century revealed the extended use of drying oils and *Pinaceae* resin mixtures for varnishing purposes [6]. In particular, they have been identified on 16th century Bolognese lutes [10], a 17th-century Paduan lute [11], on an early 18th century violin made by Jacques Boquay in Paris [12], on five instruments made by Antonio Stradivari in Cremona, Italy (late 17th–18th c.) [13], as well as on an 18th-c. Marchi violin [14]. Such coatings have also been evidenced in furniture varnishing [15], easel paintings [16,17] and in decorative arts [18]. The identification of these organic materials is mainly based on the qualitative detection, using chromatographic analysis, of molecular markers of the botanical origin or of the oxidation state of the material [11,14,16]. However, chemical analysis on aged historical micro-samples is at the time restrained to qualitative or semi-quantitative aspects [19,20], whereas quantitative analyses would be needed to attempt retrieving the proportions of the ingredients in the mixture. Furthermore, we have recently shown that the amount of ageing markers in oil/*Pinaceae* resin varnish films after a few months drying strongly depends on the oil/resin ratio, which indicates competition between different mechanisms [21]. Neither do analytical chemistry methods give any indication on parameters such as nature and quantity of volatile liquids used as solvents or heating temperature and time employed to prepare varnishes.

Other historical sources of interest are the above-mentioned collections of written recipes. The search for recipes mentioning both a drying oil and at least one *Pinaceae* resin in the online VERNIX database [22], gathering approximately 400 varnish recipes dating from 15th to 18th century, led to approximately 70 results. Most of these recipes contain few ingredients but some are very complex (up to 12 ingredients), and may mention the addition of other resins (often amber, sandarac or copal, sometimes mastic) [23]. Twelve recipes seem to be compatible with the above-mentioned analytical results obtained on historical musical instruments. The only ingredients mentioned in these recipes are indeed *Pinaceae* resin along with drying oil (most often linseed oil), and no other resinous or gum material (Table 1). It is quite remarkable that the oil-to-resin ratio, when stipulated, varies greatly, from 2:1 to 1:3. Different heating modes (boil, warm, melt) are indicated as well as different order of addition of the components. Qualitative indications concerning time and temperature of heating are sometimes given, in particular some recipes mention to cook the mixture until is homogeneous ("well mixed") or until the adequate viscosity is reached.

However, it clearly appears that the study of historical writings (recipes) or material (varnish samples from historical artefacts) is not able to provide sufficient information on the numerous parameters (proportions, quantities, order of addition, temperature, time of heating, etc.) involved in the varnish preparation. Also, it is not able to provide information in terms of application properties, which are closely connected to the varnisher's technique and extremely important in the varnishing process: they strongly influence the penetration of the material into the wood [24], the thickness range achievable, the nature of the tool required to apply the coat and even the visual aspect of the varnish film [25]. The handling and application properties of fluids like varnishes and paints are related to their flow properties [26] and can be studied through rheology, which is the study of distortion and flow of matter. Coating materials' texture and handling properties are usually described qualitatively (fluidity, thickness, stickiness, easiness of application. . .), however, in the field of industrial coatings, an extensive effort has been made to rely these qualitative terms to rheological properties [27–30]. Moreover, though rheology has been rarely used in the field of artistic materials, recent studies have demonstrated its usefulness to study complex coating like varnishes [31], and oil paints [32,33].

We present here a complementary approach, based on experimental reconstructions of linseed oil/colophony mixtures, whose aim is to study the influence of parameters involved in the mixing process on the rheological properties of the varnishes. In order to ground as much as possible this study into the reality of varnish preparation in a craftsman workshop, we also studied a varnish prepared by a violin-maker, containing as sole ingredients linseed oil and colophony. As many of his colleagues, this craftsman developed a strong and valuable know-how in optimizing a varnish that he would find satisfying in every aspect (easiness of application, pleasant appearance).

3. Materials and methods

3.1. Corpus of varnishes

Experimental varnishes were realized, using a systematic protocol to insure reproducibility of the different steps. Linseed oil (Huilerie de l'Orme Creux, France), kept under constant stirring, was first heated in a glass beaker, during 30 min, until it reached the desired temperature, and kept for 30 min at this temperature. Colophony (Domaines & Patrimoine, France), previously ground in a mortar, was then added slowly to the hot oil. During this mixing step, heating was constantly adjusted so that the temperature does not vary more than ± 5 °C around the desired temperature. The mixing step duration varied with the amount of colophony added but did not last more than 10 min. The mixture was then kept at the desired temperature during various durations, still under constant stirring. Then, heating was cut and the mixture was allowed to cool down until it reached room temperature. The mixture was poured in a closed 10 mL vials which had been flushed with nitrogen, and kept in the dark at room temperature (20–23 °C).

The various proportions, temperatures and duration of heating that were experienced, are summarized in Fig. 2. These three parameters (proportions, temperatures and duration of heating) were chosen because they seem to heavily influence rheological properties, according to violin-makers practical experience. The values' ranges of these parameters were chosen relying on ancient recipes' indications and/or limited by practical reasons. We tested various oil/colophony proportions since, as we already mentioned, a wide range of ratios is indicated in ancient recipes. However, with colophony proportion over 66 wt%, we did not manage to make a varnish sufficiently fluid to be handled. Heating time is not quantitatively mentioned in ancient recipes, however indications like "until it is well mixed" or "until it is viscous" suggest that the mixture was kept on the fire until a satisfying state is reached and that no specific (over)-cooking of the mixture was performed. In this spirit, we tested time of heating from 10 up to 100 min. Heating temperature was limited by practical conditions: below 170 °C oil