


Article

Original Varnish Recipes in Post-Byzantine Painting Manuals

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Abstract: During the last decades, manuscripts have become increasingly available through digitization and deposition in online repositories. This trend has very much facilitated primary source research, as scholars are no longer subjected to time- and effort-consuming processes such as travel, applications for photography permissions, and so on. In this framework, the authors set forth the results of research that deals with post-Byzantine panel-painting varnish recipes which were found in a hitherto unpublished Greek painting manual dating back to 1824. The recipes in consideration are compared to those existing in the renowned “Hermeneia” by Dionysios of Fourni (early 18th century) painter’s manual. A brief discussion dealing with various pertinent terms, along with a note on data deriving from the analytical investigation of varnish samples stemming from post-Byzantine icons are also included in this work. The study reveals a shift towards lean and intermediate varnish recipes during the early 19th century that might reflect the progression of resins and oleoresins, and the gradual replacement of oil-based varnishes. In addition, a unique recipe describing various methods of varnish application is transcribed and commented upon. Finally, the analytical data revealed an unexpected employment of a protein-based varnish in a mid-19th century icon.

Keywords: linseed oil; mastic; colophony; rosin; turpentine; spirit; ATR-FTIR



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1. Introduction

Varnish is an essential component of paintings because it offers protection against wear and the action of various environmental factors, while it also improves the appearance of a painting through color saturation and imparting gloss [1,2]. Varnishes have been employed by painters since ancient times, and this is well inferred by sporadic references in antiquity texts [3]. Although very little is known regarding the compounds used for varnishing in ancient times, there is a considerable body of information regarding medieval and later varnishes: on this basis, it appears that up to the 16th century (henceforth c.), heat-treated mixtures of drying oils (e.g., linseed or walnut oil) and resins (e.g., sandarac or mastic) were practically the sole means of varnishing paintings [3,4]. Coatings of this type are often called “oil-resin” or “fat” varnishes [1,5], and occasionally contained ingredients beyond resins and drying oils (e.g., solvents, coloring agents). From the late 16th c. onwards, a new type of painting varnishes emerged, namely those produced through dissolution of resins in volatile organic compounds, that is, the so-called “solvent-type” or “lean” varnishes [1,3,5]. In-between these two types of varnishes, one may also recognize an intermediate group, namely those that contained both resins and oleoresins (raw exudates, e.g., Venice turpentine from European larch), that may be designated “semi-fat” or “mixed” varnishes [5]. It is also worth noting that beyond oil or/and resin-containing varnishes, egg glair (often combined with other water-soluble substances, such as gums) was occasionally used for varnishing purposes as well [2,3].

Information pertaining to varnishes and the process of varnishing appears sporadically in some antiquity sources, yet detailed varnish recipes are mostly found in texts

dating from the 8th c. AD onwards [3]. Research in relevant archival material has been very much facilitated during the last decades, as there is a growing tendency towards digitization of manuscripts and pertinent archival material; in addition, pre-existing manuscripts' reproductions (e.g., microfilms and photographs) are also digitized and stored in repositories [6,7]. Quite often, the relevant archives are made publicly available through the web, thus resulting in the creation of several open access online repositories, such as those of the British Library (<http://www.bl.uk/>, accessed: 3 August 2021), the Vatican Library (<https://digi.vatlib.it/>, accessed: 3 August 2021), and the National Library of Greece (<https://www.nlg.gr/>, accessed: 3 August 2021). In addition, publications of primary sources (i.e., manuscripts) that have gone out of copyright are also digitized and made freely available through various internet platforms; examples include the monumental two-volume work of Mary Philadelphia Merrifield on original painting treatises that was digitized by Google [8], and the 1900 edition of the Dionysios of Fourni "Hermeneia of the art of painting" [9], which was digitized in the context of a University of Crete initiative (for a recent reprint of the most complete 1909 edition of the latter text see [10]). Besides, digitization has very much facilitated the research of primary sources, as scholars may avoid the effort- and time-consuming processes (such as travel, applications for study/photography permissions, etc.) that are often prerequisites when it comes to the study of library, archival, and museum objects.

Varnish recipes survive in a great number of technical texts/painting manuals. For instance, the first book of the circa 1100 AD Theophilus' "De diversis artibus" (or "Schedula diversarum artium") contains two extracts on the preparation of heat-treated oil plus resin varnishes [11]. A similar recipe describing the preparation of varnish through heat-treatment of a linseed oil plus resin mixture is found in the "Liber diversarum artium" manuscript ("Montpelier MS"), which is dated to ca. 1300 AD [12]. Interestingly, within the renowned and very detailed "Il libro dell' arte" (ca. 1400 AD), Cennino Cennini makes frequent reference to a certain "liquid varnish" ("vernice liquida"), yet he says nothing of its ingredients; this led the translator and commentator of Cennini's text, Lara Broecke, to assume that Cennino purchased this varnish ready-made [13]. However, the somewhat later (ca. 1425–1450 AD, [14]) "Il libro dei colori" (also known as the Bolognese manuscript) does include several "vernice liquida" recipes, revealing that the latter were in fact mixtures of drying oil(s) plus resin(s) [8]. Several varnish recipes are included in the Strasburg Manuscript, a German recipe compilation dating to 1400–1570 AD [14], while relevant recipes are also found in many later-written sources [15]. It is worth noting that recently, several attempts to reconstruct varnish recipes and characterize (by means of analytical techniques) the pertinent products have emerged [5,16–19]. Such studies lead to a considerable improvement of our understanding as regards the nature and properties of the original varnishes, and can also shed light on the processes involved in varnish degradation.

However, when it comes to the Greek technical literature, one finds that the information is very scarce. Indeed, up to today only a couple of medieval Greek texts that pertain to painting have been spotted [20,21], none of which contains reference to varnish(ing). The same appears to apply for the first part of the post-Byzantine period (i.e., the period following the Seize of Constantinople by Ottomans/1453 AD), yet the picture changes abruptly during the 18th and 19th centuries, when tens of painting manuals were circulating among Greek painters [22]. Undoubtedly, the most famous Greek manual is the so-called "Hermeneia of the art of painting" (henceforth "Hermeneia") that was compiled in circa 1730 AD by the hieromonk and icon painter Dionysios, who gathered and rearranged several pre-existing texts, adding some prototype contributions [10,22]. This manual is comprised of a detailed technical and an extended iconographical part, and was obviously designated to serve as a handy guide for the practitioners of painting [14]. The tens of "Hermeneia" copies that survive today [22] obviously indicate that it had gained wide circulation among painters. The most accurate, critical Greek publication of the text is due to A. Papadopoulos-Kerameus and emerged in 1909 (Figure 1 left). In

addition, the “Hermeneia” text stimulated the interest of several non-Greek scholars, and it ended up being gradually translated into various languages [22]. However, the Dionysios’ “Hermeneia” is by no means the sole representative of the Greek post-Byzantine technical literature on painting. Indeed, recent research has brought to light several sources that deviate substantially in terms of content from the aforementioned text, indicating the existence of at least three groups of different Greek painting manuals [23]. In addition, quite recently, two other Greek “Hermeneia” texts were transcribed and printed in Greek [24,25].

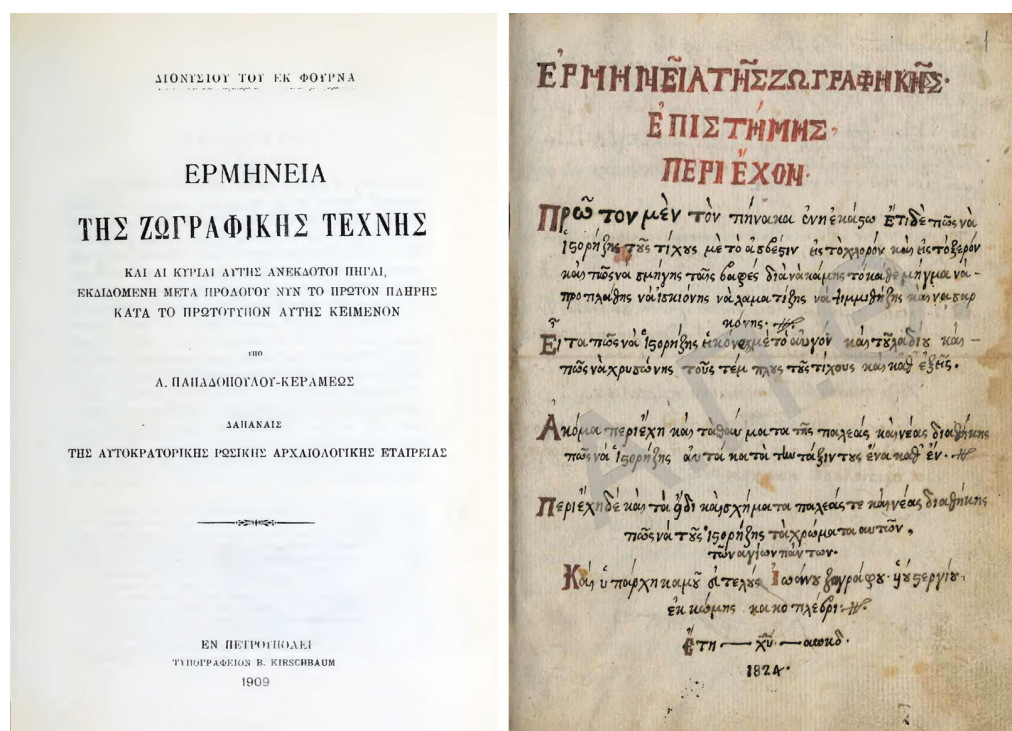


Figure 1. (Left): the title page of the 1909 Papadopoulos–Kerameus’ critical edition of the “Hermeneia”; image non-subject to copyright. (Right): the title leaf of the 1824 AD Ioannis Zografos’ painting manual. Reproduced by permission of the Aristotle University of Thessaloniki library.

The primary scope of the current study is to bring forward and present varnish-related material from a largely unknown and hitherto unpublished painting manual that was compiled by a Greek painter named Ioannis Zografos in 1824 AD (Figure 1 right). The varnish recipes found in the latter text are compared with those of the renowned Dionysios’ “Hermeneia” manual, thus revealing interesting trends as regards the varnish raw materials and application methods employed by late icon painters (18th–19th c., Greece).

Deeper insights on the subject are also attempted through the analytical (FTIR-ATR, see next for details) investigation of varnish samples from selected post-Byzantine icons. Besides, analytical/spectroscopic techniques are of indispensable value when it comes to the study of artifacts’ manufacturing materials and techniques, as they allow for their proper identification [26–29]. Note also that the data deriving from the scientific investigation of artifacts may considerably facilitate decision making and lead to optimized strategies in the field of conservation/restoration [16,30,31].

2. Materials and Methods

2.1. The Painting Manuals in Consideration

Recipes relevant to varnish(ing) appearing in two painting manuals will be herein discussed. The “Hermeneia” painter’s manual that was compiled in circa 1730 AD by the hieromonk and icon painter Dionysios of Fourni (village in Evrytania territory, central

Greece) is in fact a collection of various pre-existing texts that were rearranged and enriched by certain prototype passages of Dionysios [10,22]. This particular text is composed of two distinct parts, namely a technological and an iconographical one. The former contains a relatively detailed reference to the materials and techniques of panel (i.e., icon) and wall painting; among the various technological dictations, Dionysios has included five varnish recipes (see next for details).

The second source in consideration is the digitized (yet hitherto unpublished) manuscript No. 19 (inv. number: 36161) of the Aristotle University of Thessaloniki Library, which was compiled by Ioannis Zografos (*“Ioannis the painter, son of Stergios”*) in 1824 [32,33]; at that time, Ioannis lived in the village of *“Kakoplevri”*, which is located in modern-day Trikala territory (NW Thessaly, Greece) [34]. This particular manuscript shows an overall similar structure with that of Dionysios’ manual, and it embodies distinct technical and iconographical sections too. Part of the technical dictations are practically identical to those of Dionysios; however, the manual in consideration contains several recipes that either deviate substantially, or do not exist in Dionysios’ *Hermeneia*. For instance, Ioannis Zografos has included more than thirty (!) varnish-related recipes, while Dionysios’ manual contains only five.

2.2. FTIR-ATR Analysis of Selected Post-Byzantine Icons’ Varnishes

For the sake of the critical evaluation of the recipes in consideration, varnish micro-samples were collected from certain post-Byzantine Greek icons and analyzed through attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). In detail, a few milligrams of varnish were removed using surgical scalpels from the surfaces of nine post-Byzantine icons that are dated from the 17th to mid-19th c. (Table 1). Through meticulous study of the icons in consideration, it was confirmed that six of them bear their authentic varnishes (i.e., they remained hitherto uncleaned), two have undergone re-varnishing (therefore bear two successive varnish layers), while a single icon bears a *“restoration”* varnish (i.e., a varnish applied after cleaning/removal of the authentic one) (Table 1). The raw (i.e., non-pretreated) varnish samples were analyzed through Fourier transform infrared spectroscopy in attenuated total reflectance geometry (FTIR-ATR). For the latter purpose, a PerkinElmer Spectrum 100 FT-IR spectrometer was used; the employed spectrometer utilizes the Universal ATR accessory, which, through the use of a pressure arm, allows for the optimal contact of samples with the diamond/ZnSe crystal and the acquisition of high-quality spectra. In the case of the samples in consideration, spectra were collected in the range of 4000–380 cm^{-1} (8–24 scans/spectrum, depending on sample quality).

Table 1. The sampled icons.

Icon	Date	Provenance	Notes	Varnish Components (FTIR-ATR)
Transfiguration	17th c.	Unidentified	Two varnish layers preserved: a first/early and a second/latter intervention (samples 1 & 2)	Oil, resin (sample 1) Oil, resin, protein (sample 2)
St Nikanoras	Late 18th c.	Northern Greece (?)	Two successive varnish layers; sample collected from the second (latter) one	Resin, minor oil
Triptych	Early 19th c.	Northern Greece (?)	Old <i>“restoration”</i> varnish	Resin, minor oil, protein
St Anna	Mid-19th c.	Unidentified	Authentic varnish/unrestored item	Resin, protein
Jesus Christ	Mid-19th c.	Evia Island (central Greece)	Authentic varnish/unrestored item	Resin (+minor oil?)
St John the Forerunner	Mid-19th c.	Evia Island	Authentic varnish/unrestored item	Protein (+minor oil?)
Painted offering box	Late 19th c.	Evia Island	Authentic varnish/unrestored item	Resin, oil
Annunciation	1884 AD	Tinos Island (Cyclades)	Authentic varnish/unrestored item	Protein, resin
St Nikolaos	Late 19th c.	Northern Greece	Authentic varnish/unrestored item	Resin (+protein?)

3. Results and Discussion

3.1. Dionysios of Fourni Varnish Recipes

The “Hermeneia” text contains only seven recipes that pertain to varnish(ing). Besides, the Dionysios’ varnishes are manufactured using a rather limited number of raw materials and by employing simple processes/steps. First, the text describes the thickening of linseed oil (πέζιρη—*peziri*) through prolonged exposure to summer sun in an open baking pan, and then the separation of colophony/rosin (πέγυλα—*pegula*) from pine resin through thermal treatment is dictated (recipes §28 & §29 respectively, [9]; readers are directed to [35] for the key English translation of the “Hermeneia” text); these are the two basic raw materials to be used for varnishes. Indeed, the “fat” varnish described in §30 consists of the two aforementioned materials (100:75—linseed oil:rosin); however, there is also the option to substitute part of the rosin for mastic resin. In case that the outcome (: varnish) is rather thick, it can be thinned out using either spirit of turpentine (νέφτι—*nefti*) or crude linseed oil (§30, op. cit.). Here we shall note that Hetherington [35] translates “νέφτι” as “*naphtha*”, i.e., a petroleum derivative, yet to the authors’ view this term shall be better translated as “oil of turpentine”, an organic solvent still being traded under the label “νέφτι” in the Greek paint supplies market.

The next recipe (§31) describes the preparation of another “fat” varnish, which is simply made through the thermal treatment of a santalozi resin (σανταλόζι) (probably the solid residue of the sandalwood exudate, i.e., sandalwood resin) plus thickened linseed oil mixture. On the contrary, recipes §32 and §34 dictate the preparation of two “lean” varnishes: the first one is made of sandarac plus rosin dissolved in spirit of turpentine, while the second consists of the same resins dissolved in spirit of wine (ρακή πολλα δύνατη) (op. cit.) (Table 2). Finally, there is also a recipe describing the preparation of a yellow-tinted varnish, to be used for covering white silver leaves for gold-imitation: sandarac resin (σανδράκα) along with aloe are thin-grinded and shifted, then placed into a pot jar over a fire until melted, and finally, thickened linseed oil is added. Note that “σανδράκα” most probably pertains to “sandarac”, i.e. the yellowish resin collected from the ever-green tree of the *Cypressaceae* (cypress) family *Tetraclinis articulata* [18].

Table 2. Recipes per varnish type in the Dionysios of Fourni and Ioannis Zografos manuals and a list of the corresponding materials mentioned in the texts.

Authorship	Date	Number of Recipes/Varnish Type				
		Fat	Lean	Intermediate	Tinted	
Dionysios of Fournà	ca. 1730 AD	2	2	-	1	
Ioannis Zografos	1824 AD	9	11	11	3	
Employed Materials						
Author	Solvent(s)	Oil(s)	Resin(s)	Oleoresin(s)	Pigment(s)/Dye(s)	Other
Dionysios of Fournà (~1730 AD)	turpentine spirit wine spirit	linseed oil (raw / thickened)	rosin mastic sandarac		aloe	
Ioannis Zografos (1824 AD)	turpentine spirit wine spirit	linseed oil (raw / thickened) linseed oil (+siccatives)	rosin mastic sandarac copal shellac amber incense	Venice turpentine turpentine	aloe ground glass “gotagoma” (gomma gutte) litharge lead oxide (?) umber	onion leaves bread camphoralum

3.2. Ioannis Zografos Varnish Recipes

On the contrary, Ioannis Zografos’ manual contains significantly more varnish-related recipes. Besides, the latter amount to thirty-six, most of which pertain to paintings; a few recipes deal with wood coatings and varnishes to be used on metallic objects, yet

trend might well reflect the progression of new materials (e.g., soft resins, turpentine) in the local markets or/and a shift in craftsmen's taste towards thinner/less viscous varnishes. Besides, from the early 18th c., western European texts on painting were being increasingly available to Greek craftsmen through translations, a characteristic example being Panagiotis Doxaras, who translated several Italian texts [36,37].

It is worth noting that the Ioannis Zografos text contains a detailed description of varnishing, of which there is no parallel in any of the hitherto published Greek post-Byzantine painting manuals. To the authors' opinion, the significance of the particular content calls for its transcription, being thus the first ever published detailed account on the varnishing methods of the Greek post-Byzantine painters, which offers a unique insight on these very processes. The recipe begins with the description of an oil painting varnishing, and this obviously indicates that the drying oil media were already (i.e., by the early 19th c.) widely used by Greek painters. Although this point might at first sight appear to be of no importance, one shall bear in mind that egg tempera is regarded as the "traditional/proper" painting medium in the context of the rather conservative Greek post-Byzantine religious painting [38].

The recipe in consideration starts in the verso of folio 30 and is entitled "*On how you shall varnish an icon*". The original text (transcription & translation) appears below (in italics); inserts of plain text (not italics) within parentheses correspond to explanatory notes that were added by the current authors.

If the icon is painted in oil, first spread on it a layer of walnut oil (the process taking place) under the sun, and (note that) the walnut oil shall be very thin ("απαλόν" in the Greek text). And let it dry, then spread a layer of turpentine spirit, let it also dry, and when it is dry too, spread varnish; yet both the icon and the varnish shall be hot, and when this has dried, (folio 31r) spread (on the icon) again three and four layers ("χέρια") until it (i.e., the varnished icon) looks like crystal; and you shall use a soft brush, not your hand.

If on the other hand, the icon is painted in egg, first heat it up (by exposing it) to the sun, then mix a bit of trimentina with spirit of turpentine and first spread over the areas where the green—that is verdigris—and the lake and the indigo stand, and when this is well dried spread over it varnish three (to) four times until you find that you like it, that is it looks like clear glass; and always (keep in mind that) when you varnish the icon must be warmed, and when you use a lean varnish ("του ισκίου") you must not pass your brush over a given area multiple times because the colors ("αι βαφές") are mixed.

And if you wonder ("θαυμάζης") why verdigris, lake, and indigo are first covered by trimentina, (know that this is done) in order to avoid whitening or change (of the colors) and to keep them always soft and sound colors ("τροφερές και καλές βαφές").

And you should also know that all the sun varnishes (i.e., the fat ones, those that dry upon exposure to sun) are spread using the palm and the fingers of the hand, (while) the lean ("του ισκίου") varnish is spread using the brush; yet always the icon must be (first) warmed and then apply three and four layers (of varnish) until you like very much its glassy-like appearance, and this is enough.

In both egg tempera and oil paintings, the described varnishes consist of at least two different materials, applied in multiple successive layers. Of particular interest is the case of egg paintings, where the areas painted in specific pigments are to receive a special pre-treatment before the application of the final varnish. This definitely aims at preventing interaction between these very pigments and the final varnish and reflects empirical knowledge of the solubility of verdigris-type pigments in coniferous resins plus solvent mixtures [39,40]. Note that a relevant dictation appears in the circa 1400 AD Cennino's painting manual [13], while similar dictations in other Greek manuals were recently brought to light [23].

However, the most notable part of the recipe is the final one, where it is stated that the fat varnishes should be applied by bare hand, whereas the lean ones should be applied by brush. The application of oily varnishes on icons by hand is dictated by Cennini [13], yet it has been considered as a trend from Russia [41], where it is still being (albeit infrequently)

practiced by some icon painters. The fact that a relevant dictation appears in a Greek 19th c. painting manual suggests a wide (and persistent) employment of the method in consideration and offers a unique insight into the varnish application methods used by local (Greek) painters.

3.3. ATR-FTIR Analyses of Post-Byzantine Greek Icons' Varnishes

The results obtained through the FTIR-ATR analysis of varnish samples from the aforementioned nine post-Byzantine Greek icons are rather complex, indicating employment of multiple organic components; in fact, it appears that most of them contain both resinous and oily compounds (Table 1, Figure 3). A close inspection of the high frequency region of the spectra (3800–2700 cm^{-1} , Figure 3 left) reveals the presence of intense methylene (CH_2) absorptions at ca. 2920 cm^{-1} and 2850 cm^{-1} , which are indicative of linseed oil, while the peaks appearing at ca. 2935 cm^{-1} and 2875 cm^{-1} pertain to methyl/methylene stretching vibrations in diterpenic resins' molecules (colophony and sandarac) [16,42]. The mixing of oils with diterpenic resins is also evident upon examination of lower frequency regions (Figure 3 middle), where carbonyl ($\text{C}=\text{O}$) absorptions appear simultaneously at ~ 1695 – 1715 cm^{-1} (due to diterpenic resins) and ~ 1735 cm^{-1} (linseed oil) [16,42,43]. Interestingly, admixture of triterpenic resins (presumably mastic or dammar) in many of the studied varnishes is suggested by the presence of absorption peaks emerging at ~ 2955 cm^{-1} (C–H, appearing as a “shoulder” on the major 2920–2935 cm^{-1} absorption) and ~ 1715 cm^{-1} ($\text{C}=\text{O}$) (Figure 3 left, middle). Besides, the FTIR-ATR analyses reveal that in some cases, mixtures of linseed oil with diterpenic and triterpenic resins have been employed (Figure 3 left, middle). These findings are more or less in accordance with the recipes in consideration that often call for the preparation of complex mixtures, as well as with the results of previous analytical studies of post-Byzantine icons' varnishes that indicated a prevalence of resin plus oil varnishes as well [44,45].

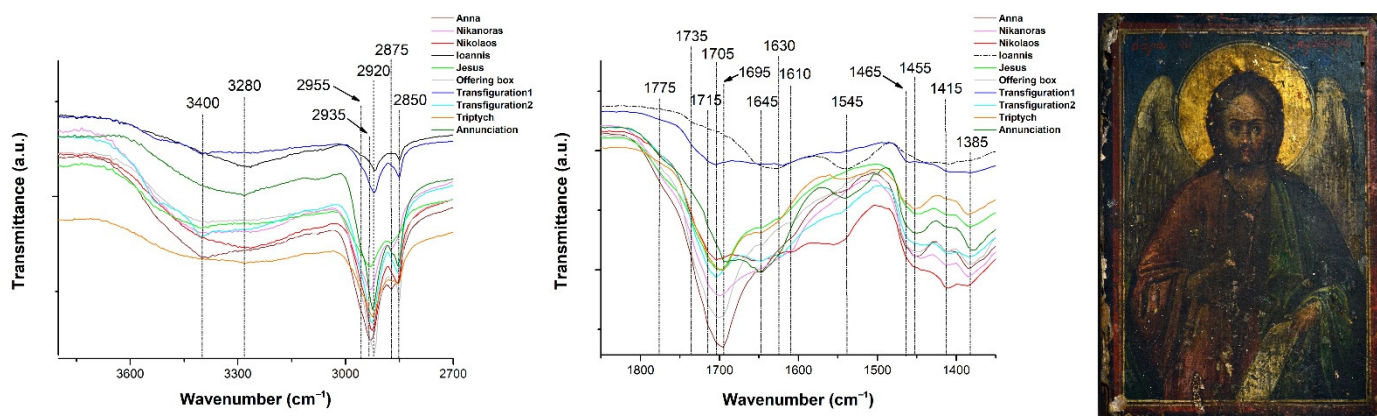


Figure 3. (Left): high frequency region of ATR-FTIR spectra obtained through the analysis of varnish samples from post-Byzantine icons. (Middle): same spectra, mid-frequency region. (Right): mid-19th c. icon of St Ioannis Prodromos.

A notable exception is the varnish of a mid-19th c. icon depicting St Ioannis Prodromos (St John the Forerunner) (Figure 3 right). The pertinent spectrum shows predominant carbonyl absorption bands at ca. 1645 cm^{-1} accompanied by an intense absorption at 1545 cm^{-1} ; these correspond to the so-called amide I and amide II vibrations, respectively, and reveal the employment of a protein-based substance [43,45–47], presumably an egg white varnish. In addition, intense amide absorption bands accompanied by resin-related ones appear in the spectrum from a late 19th c. icon varnish (Annunciation, Figure 3 middle). Although a glair-based varnish is not documented in the Greek painting manuals under consideration, there are several mentions of the use of beaten glair as a varnish in various European technical texts [3], as well as in some painting manuals compiled by Balkan painters [41]. For instance, Cennino suggests the application of beaten glair

as a temporary varnish, to be employed before the final cover of a painting with a fat varnish [13].

However, faint amide I and II absorption bands appear also in a couple of spectra where resin or/and oil absorption peaks predominate, and this seems quite odd, as none of the documented recipes dictates the mixture of pertinent components. Detection of protein in oil/resin varnishes is also mentioned by Lazidou et al. [45], who suggest that proteins might have been diffused from the paint layers. In addition to this possibility, one must bear in mind that icons, being veneration objects, were ordinarily receiving “washing”, “cleaning”, and/or re-varnishing treatments with the purpose of reviving their appearance [3,23,41]. Therefore, a varnish that is nowadays present on an old icon may not correspond (only) to the authentic/initial one, hence the corresponding analytical results must be critically evaluated (see also a relevant remark in [44]). Note that one may overcome some of the pertinent issues through the analysis of sample cross-sections, where the various varnish layers can ideally be analyzed one by one [48].

4. Conclusions

Post-Byzantine painting manuals are a very important source of information on the materials and techniques employed by the corresponding craftsmen, and through their digitization, they are currently becoming increasingly accessible. A study focusing exclusively on the varnish recipes of two manuscripts revealed an interesting shift towards lean and intermediate varnishes during the early 19th c.; this trend possibly reflects the progression of new materials (resins & oleoresins) in the eastern Mediterranean market, and/or the gradual replacement of oily varnishes that presumably took place simultaneously with a dissemination of material from translated western European painting manuals. A unique, rather detailed dictation of varnishing processes was spotted in an early 19th c. manuscript and was herein published for the first time. This particular passage calls for the application of oily varnishes by bare hand, a practice not documented hitherto in any of the known Greek painting manuals. Finally, analytical investigation of several post-Byzantine icons' varnishes revealed the extensive use of resinous and intermediate varnishes, as well as the employment of a protein-based varnish on a mid-19th c. icon. The latter finding is of importance because the known Greek painting manuals do not mention the employment of protein-based materials for varnishing purposes.

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