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Study of stability of brown-gray inks on paper support

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Abstract

Research into paper artworks and the identification of drawing techniques dating from the 15th to the 19th century from the collection of Slovak National Gallery revealed that the most frequently used means of writing was a set of brown-gray inks. This set includes bistre, sepia, and iron-gall inks (IGI). The light fastness of these organic compounds is not considered very high. Moreover, iron gall inks attack paper support by the processes commonly known as iron gall ink corrosion. In the experimental part of the research, the stability of three different brown-gray inks was studied. Model inks, i.e. bistre, sepia and IGI with two molar ratios Fe : gallic acid were prepared according to historical recipes. Whatman paper was used as a support material. Samples were submitted to accelerated aging in closed vessels at 100°C with and without the presence of NO₂ in concentration of 100 ppm as well as to the light aging in a light chamber. Changes of mechanical, optical and chemical properties of the samples as well as spectra in the IR region were studied. The observed changes allowed an evaluation of the effect of particular inks on paper support and effect of various external factors of aging (temperature, light, pollutants) on the model systems. Simultaneous thermal analysis (DTA/TG) was carried out in order to study the thermo-oxidative stability of the materials. Sepia and bistre inks have been assessed as generally more stable than iron-gall inks.

Keywords: Historical brown-gray inks, Stability of drawings, FT- IR spectroscopy

Background

Bistre is a brown dye obtained by extraction of soot in boiling water followed by evaporation and drying [1]. Its aqueous suspensions may have a golden-brown, grayish or brown color, depending upon the thickness of the coating. Color is affected by the type of the wood used. The main part of a wood tar composition, which is similar to that of asphalt, is dehydroabietic acid with a lower portion of pyrolytic products [2]. According to other sources [3], the main color components in the bistre ink are formed by substituted, water-soluble phenols. Historical sources refer to the bistre changes of its hue when exposed to light. After being exposed to a strong light source, the tar part oxidizes and the dye gains cooler hue and possibly bleaches [4].

Bistre as a writing material was already known in the Middle Ages [5]. In the 15th century, it was widely used in Italy and subsequently in Northern Europe. In the 17th and 18th centuries, the use of bistre was popular among artists such as Rembrandt van Rijn, Claude Lorrain, Conez Alexander and Thomas Gainsborough. Bistre was often used in miniature drawings. Although the inks used by Rembrandt are described traditionally as bistre, analytical studies carried out on 22 Rembrandt drawings from the collection of the Metropolitan Museum of Art have confirmed that the majority of the 22 drawings were made using iron-gall ink [6].

Sepia ink is obtained by adding gum Arabic into the extracts derived from *Sepia officinalis* cuttlefish. Sepia's main constituents are melanin giving a typical hue of ink and mucous compounds [7]. Grayish brown eumelanin is a macromolecule consisting of 5,6-dihydroxyindol a 5,6-dihydroxyindol-2-karboxylic acid. Melanin significantly absorbs UV and the visible wavelength range and almost all absorbed light energy is converted into the heat [8-11]. Melanin may act as a light stabilizer and this

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fact could explain relatively high light fastness of this organic dye.

Long-term irradiation in the presence of oxygen and UV light, however, results in lightening – the fading of melanin [12,13] that is a result of oxidative degradation, in the process of which the benzene core ring opens [8].

J. Seydelmann was the first person to prepare sepia ink mixed with gum Arabic (as discussed in ref. [14]) as a method of watercolor painting technique in Dresden in 1780. During the 19th century, bistre was gradually substituted by sepia ink.

Main components of iron gall inks (IGI) are hydrolysable extracts from plant materials containing mainly gallo-tannins and ferrous sulfate [15]. A freshly prepared water solution of ink is a colorless complex of Fe (II) with gallic acid. Writing means gain their typical color by oxidation of Fe (II) into Fe (III) supplying the deep black-blue complex with gallates. With the passage of time, a degradation process of paper support was taking place [16]. This “iron gall inks corrosion” is considered to be directly caused by two particular mechanisms: acid hydrolysis of cellulose (in excess of acidic compound presented in IGI) and the oxidative degradation of paper support catalyzed by the transitional metals (Fe, Cu) [17]. After the absorption of light, an excited state of deep-blue complex is created and its reaction with the other ingredients leads to a decomposition into the brown colored compounds [18]. Visual signs of corrosion are brown rims in the ink areas and brown strike through patches of ink appearing on verso.

From the late antique period to the early years of the 20th century, iron gall inks were the most used means of manuscript writing. In 15th century, inks were widely spread and during the following centuries commonly used by the old masters in drawings. At present time, all renowned galleries and museums of the world house the greatest collections of drawings by Leonardo da Vinci, Rembrandt van Rijn, Giovanni Francesco Barbieri known as Guercino, Claude Lorrain, Vincent van Gogh, etc.

The objective of this research was to study the stability of three types of historical brownish gray inks, i.e. bistre, sepia, and iron gall ink on the paper substrate during accelerated thermal aging in dark as well as light aging. This work gives a summary of properties of brown-gray inks based on own survey results. The obtained information can help conservators with an understanding and a broadened knowledge useful in preventive preservation, specifically in determining appropriate storage conditions in depositories and chiefly in expositions. Research into paper artworks of drawing techniques dating from the 15th to the 19th century from the collection of Slovak National Gallery revealed that the using of more kinds of brown-gray inks on one drawing was very frequent [19]. In these cases, the storage conditions must adapt to the most vulnerable ones.

Materials and methods

Materials

Three types of inks were studied: bistre ink 12100 (Kremer Pigmente GmbH & Co KG) – **B**, sepia ink 12401 (Kremer Pigmente GmbH & Co KG) – **S**, iron gall inks prepared from monohydrate of gallic acid (Sigma Aldrich) and ferrous sulfate heptahydrate (Lachema, Czech Republic). The molar ratios of Fe (II) ion: gallic acid were 1:1 and 1:2 – **IGI 11**, **IGI 12**. Solutions of inks were prepared according to Neevel [3]. For their preparation an aqueous (deionized water) solution of gum Arabic (Fluka BioChemika, Sigma-Aldrich) with the mass concentration 7.852 g/100 ml was used. Whatman filter paper (Whatman Lab. Division, Maidstone, England), Cat. No 1001917, 87 g.m⁻², pH 6.7 - purified cotton linter cellulose was used as a substrate – **W**. Paper samples were immersed into the ink solutions for 15 seconds. Excess liquid was removed using two filter papers and then left to dry at room temperature. Water solutions of iron gall inks were applied to the paper substrate after being kept in dark room for seven days and subsequent filtration.

Methods

Accelerated aging methods

Two methods of accelerated aging were employed. Light aging according to ISO 105-B02 [20]: a laboratory device for simulating daylight consisting of a MeX-lamp OSRAM POWERSTAR HQI TS 400/D UV-reduced and two fluorescent lamps with the maximum of emission spectrum in UVA, power 2 × 15 W, temperature 45 ± 5°C, relative humidity 25 ± 5%, exposure dose 105 klx in VIS, 95 mW/cm² in UVA were used. Exposure times were 20, 40, 80, 120 and 160 hours.

Accelerated thermal aging in air with/without pollutant according to ISO 5630-5 [21]: samples were placed in Pyrex® bottles, conditioned for 24 hours at 23°C and 50% RH and closed with polyphenylsiloxane airtight seal with Viton® gasket. NO₂ in a 100 ppm concentration was introduced into selected bottles. Ageing times were 0, 4, 16, 24, 48, 120 hours for pure paper, bistre and sepia and 1, 2, 4, 8 and 24 hours for iron-gall inks.

Degree of polymerization and the rate constant of depolymerization

Viscometric measurements were carried out according to ISO 5351-1 [22] using cupriethylene-diamine (CED) as a solvent. Measurements were performed with a standard capillary viscometer at (25.0 ± 0.1)°C. From the ratio t/t_0 , where t is the efflux time of a sample solution and t_0 is the efflux time of the solvent, the ratio of viscosities of the sample solution and solvent η/η_0 , and intrinsic viscosity $[\eta]$ was obtained. Degree of polymerization, DP , was

calculated from viscometric data using the Mark-Houwink-Sakurada Eq. 1 [7,23,24]:

$$DP^a = K[\eta] \quad (1)$$

The values of constants $a = 0.85$ and $K = 1.1$ for cellulose were used [25]. Rate constants k of degradation were obtained by Least Squares Fit of the experimental data using the Ekenstam equation for the degradation of linear polymers [24,26]:

$$\frac{1}{DP} - \frac{1}{DP_0} = kt \quad (2)$$

where DP_0 and DP are degrees of polymerization at the beginning of aging and after time of aging t .

Folding endurance

15 × 100 mm samples were air-conditioned (24 hours, 23°C, 50% RH) and folding endurance was measured by the MIT method according to [27]. The device used was Tinius Olsen, tension of samples 3 N, average of 10 measurements, standard deviation 35 ± 5%.

Thermoanalytical measurements

Shimadzu DTG-60 simultaneous thermoanalyzer was employed to study the thermal oxidation of the samples. The apparatus involves two thermoanalytical methods, i.e. thermogravimetry (TG) and differential thermal analysis (DTA). The purge gas that was creating the reaction atmosphere was air with a flow rate of 50 ml/min. 2–3 mg samples with circular shape were cut out using a paper hole punch and were placed in standard aluminium pans; the lids of pans were perforated by 7 pinholes to facilitate the contact of the sample with air. The oxidation was studied under non-isothermal conditions applying linear heating with heating rates of 1, 3, 5, 7, 10 and 15 K/min. A new predictive method [28] has been suggested based on the fact that the dependence of oxidation onset temperature on heating rate can be plausibly described by the function

$$T_i = T_\infty(1 - \exp[-\beta^a]) \quad (3)$$

where T_i is the oxidation onset temperature, β is the heating rate, T_∞ means the isoconversional temperature at an infinite heating rate and a stands for an exponent. Knowing the values of the kinetic parameters T_∞ and a , the oxidation induction time (t_i) for a chosen temperature T can be calculated as

$$t_i(T) = (T_\infty - T)a \left(\ln \frac{T_\infty}{T_\infty - T} \right)^{\frac{a-1}{a}} \quad (4)$$

Thermooxidation of both, non-aged and at most aged samples was studied. With regards to thermal ageing, the aging time for the samples **W**, **B** and **S** was 120 hours

and for the sample **IGI 11**, **IGI 12** 24 hours. In the case of light-thermal aging, the aging time was 160 hours for all samples.

Spectroscopic measurements

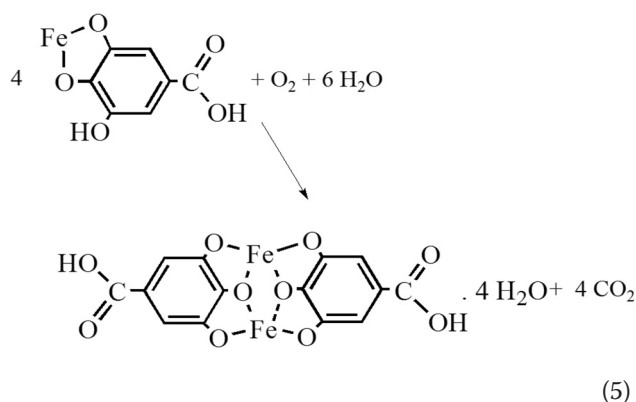
FT-IR spectra of samples on paper support were measured with FT-IR spectrophotometer EXCALIBUR series, FTS 3000 MX (Digilab) and FT-IR microscope Varian 610-3R Series by ATR method with diamond crystal. FT-IR spectra of powder dyes were measured in KBr pellets. Color measurements were done with the SpectroDens A 504009 Premium (Techkon GmbH) spectrophotometer, standard illumination D50, standard observer 2°.

Results and discussion

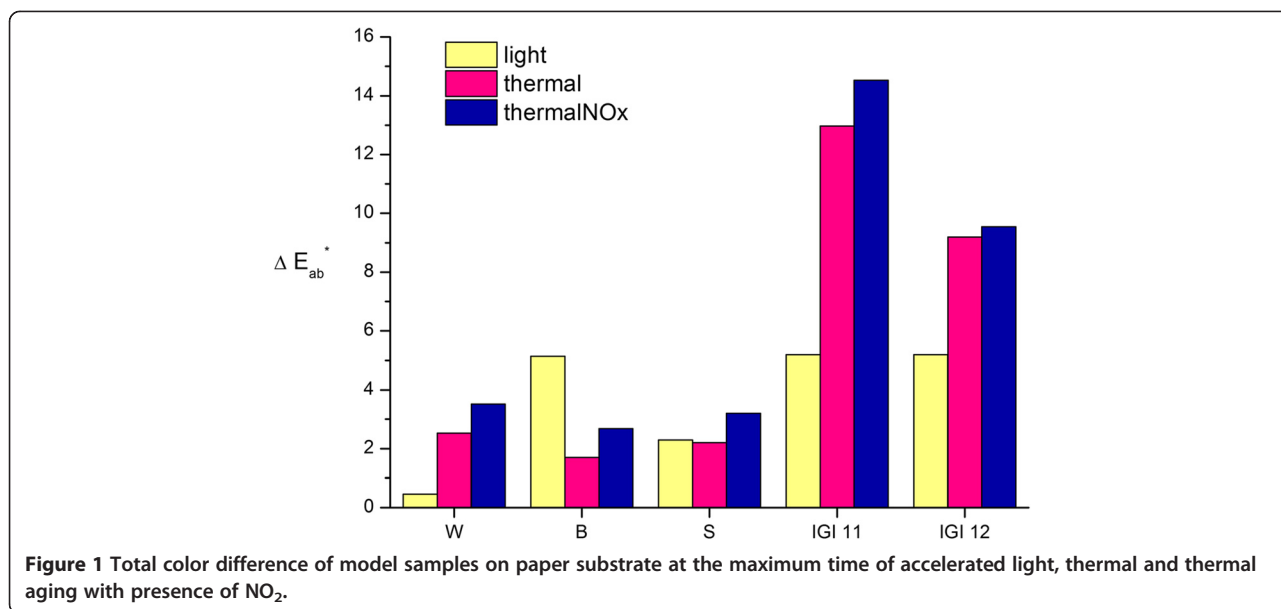
The evaluation of the optical properties

During accelerated light and thermal aging (Figure 1), sepia ink was the most stable one, followed by bistre. Both iron gall inks, where the total color difference ΔE_{ab}^* reached up to 10–15 (by thermal aging), had the lowest color stability.

Interesting view on the aging provides the graph in the in three-dimensional color space Lab (Figure 2): in the first stage of aging (up to 75 h) the value of the lightness L^* decreased, indicating the initial darkening of the ink on the substrate caused by the change of the Fe (II) gallate complex to Fe (III) gallate complex (Eq. 1) [29].



During the further aging, the value of lightness L^* increased (ink faded) and the value of chromatic coordinate b^* was shifted in yellow direction (changing hue). Color stability assessment of the observed materials can be performed with respect to a set of blue wool standards [20] (BWS). BWS samples underwent accelerated aging under the same conditions as ink model samples. The degree of stability of the studied samples was assessed using the method described by Vizarova et al. [30] Results are summarized in the Table 1. All inks, except bistre, were more stable in light than in thermal



aging (at the studied aging times). The presence of the NO₂ pollutant reduced color stability of all the inks by likely acceleration of oxidation-reduction reactions leading to fading and/or hue changing the present dyes/pigments.

The evaluation of the mechanical properties

Folding endurance of the papers with sepia and bistre ink was very high during the light aging (Figure 3) (and thermal one, too). These samples showed up to 10 times higher folding endurance compared to the paper pad and decreased only slightly during aging. The presence of a binder (gum Arabic) which provides initial strengthening

of paper pad, was the reason of heightened values of folding endurance. The loss of original mechanical properties of IGI's systems was very fast at thermal aging with/without pollutant. Number of double folds of iron gall inks papers decreased to zero already after 24 hours of accelerated aging. It was the evidence of strong attack of iron gall inks oxidation products on paper. These results correspond with results of determination of rate constant of support degradation (below).

Determination of depolymerisation rate constants

Depolymerisation reactions of cellulose pads during the *thermal aging* were influenced by the kind of inks and pollutants present. Whatman with sepia degraded relatively slowly, followed by Whatman substrate and Whatman with bistre. Depolymerisation rate constants for the samples with iron gall inks were higher almost by two orders of magnitude (Table 2, bold data). Thermal aging at elevated temperature, relative humidity and the presence of pollutant seems to be very dangerous for the papers containing IGIs via accelerating reactions leading to the reduction of DP.

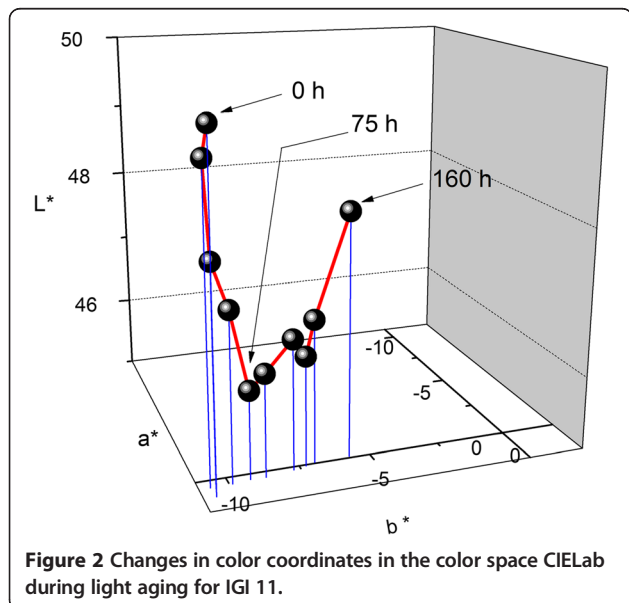


Table 1 Evaluation of ink's stability considering stability of blue wool standards (minimum 1, maximum 8)

Sample	Degree of stability at the maximal aging time of		
	Light aging	Thermal aging	Thermal aging with NO ₂
W	8	7	6
B	6	7	7
S	7	7	6
IGI 11	6	4	4
IGI 12	6	5	5

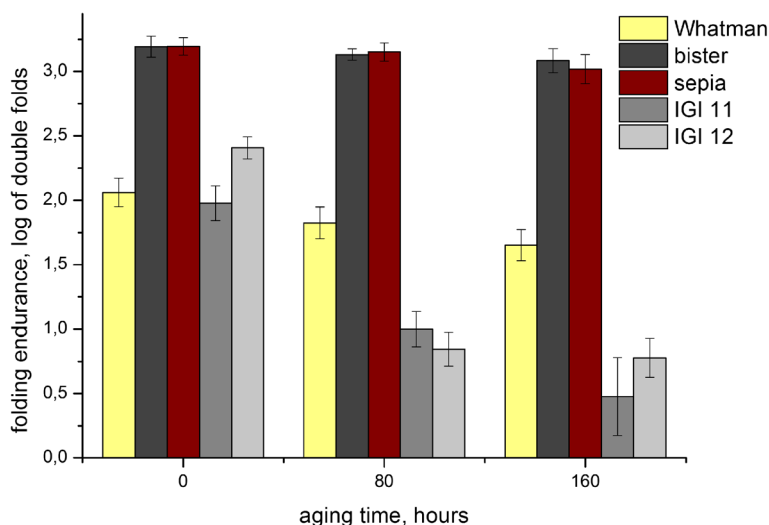


Figure 3 Changes of the folding endurance of model samples on paper at the time of accelerated light aging.

Similar trends were observed for *the light aging* but the depolymerisation rate constant was of the same order (Table 2).

Degradation of paper pad depended on the ratio of Fe : gallate in the iron gall ink, the most noticeable was at Fe : GAL = 1 : 1. This piece of knowledge corresponds with results of optical stability as well (Figure 1, Table 1).

Evaluation of thermooxidation

The aim of the thermoanalytical methods – thermogravimetry (TG) and differential thermal analysis (DTA) – was to assess the role and proportional representation of depolymerisation and thermooxidation reaction pathways during the aging process. A detailed experimental description and evaluation procedure were published elsewhere [31]. The progress of thermooxidation during accelerated ageing can be characterized by applying the criterion of residual stability [32]. The residual stability of a sample is defined as

$$R = \frac{t_i}{t_{i0}} \tag{6}$$

where t_i and t_{i0} are the oxidation induction times for the aged and unaged sample, respectively. The oxidation induction times should decrease during accelerated ageing so that the residual stabilities should possess values from the range <0;1>; the value 1 corresponds to the unaged sample and the value 0 for the sample exhibiting no stability after the ageing. The residual stabilities of the aged samples are summarized in Table 3. The 95% reasonability ranges shown also in Table 3 have been obtained as a conjunction of the range <0;1 > and the 95% confidence limits.

The values of R for the Whatman paper after aging can attain any value from the range <0;1 > so that no conclusion on the decrease of thermooxidation stability of the sample W during aging can be drawn. A considerable decrease of thermooxidation stability was indicated for the sample IGI 11 after all kinds of aging. The decrease of the thermooxidation stability for bister does not seem high for all kinds of thermal aging; in the case of light aging, any value from the range <0;1 > can be obtained. A surprising result was obtained for the samples with sepia. Within the 95% confidence interval, the values of $R > 1$ for thermal aging and thermal aging with 100 ppm NO₂ have been found. This finding can be accounted for in the only way – during thermal aging with and without NO₂ a compound preventing thermo-oxidation was formed.

The results indicate that thermooxidation represents only a minor reaction path in the aging of paper/ brown-gray ink systems during the thermal methods of aging, except for iron-gall inks where the thermooxidation

Table 2 Values of the depolymerisation rate constants of model samples at the maximum time of light, thermal and thermal aging with NO₂

Sample	Depolymerisation rate constant [10 ⁻⁶ s ⁻¹] at the maximal aging time of		
	Light ageing	Thermal ageing	Thermal ageing with NO ₂
W	0.89 ± 0.10	2.25 ± 0.26	2.45 ± 0.23
B	1.25 ± 0.33	1.87 ± 0.31	2.89 ± 0.58
S	0.72 ± 0.19	0.81 ± 0.28	0.88 ± 0.26
IGI 11	3.09 ± 0.77	1080 ± 250	1550 ± 280
IGI 12	2.24 ± 0.53	490 ± 109	860 ± 150

Table 3 Estimated residual stabilities (R) with their standard deviations and 95% reasonability ranges of R at the maximum time of light, thermal and thermal aging with NO₂

Sample	Residual stabilities (R) and 95% reasonability ranges of R					
	Light ageing		Thermal ageing		Thermal ageing with NO ₂	
	R (23°C)	R 95%	R (23°C)	R 95%	R (23°C)	R 95%
W	0.85 ± 0.49	0-1	1.8 ± 1.2	0-1	5.2 ± 3.4	0-1
B	1.7 ± 0.9	0-1	0.79 ± 0.19	0.42-1	0.79 ± 0.23	0.34-1
S	2.4 ± 2.1	0-1	4.8 ± 1.6	>1	300 ± 124	>1
IGI 11	0.49 ± 0.16	0.18-0.80	0.18 ± 0.07	0.01-0.71	0.36 ± 0.18	0.01-0.71

might become the prevailing degradation reaction path. Moreover, considering the results of rate constants of depolymerisation, the iron-gall inks accelerated both reaction paths, i.e. thermooxidation and depolymerisation. In the case of the light aging, depolymerisation was the prevailing degradation reaction way.

FT-IR spectra

Changes of FT-IR spectra of aged inks on paper measured by ATR-FT-IR were imperceptible. We therefore decided to study the changes of powder dyes/pigments by transmission technique in KBr pellets. The most significant changes in the FTIR spectra were observed with IGIs. We found, in particular, a loss of vibration of SO₄²⁻ (1200–970 cm⁻¹) [33] from the excess of ferrous sulfate and changes in position of vibration of –OH and –C=O groups at 1700–1600 cm⁻¹ during the thermal aging (Figure 4). We observed conspicuous changes in the vibration range of the chemical bonds of aromatic ring [34] of iron gall inks at 1500–1200 cm⁻¹ during the light aging (Figure 5): shifts of peaks at 1452 to 1426 cm⁻¹, 1337 to 1320 cm⁻¹ and emerging of the new peaks at 1484, 1281 a 1268 cm⁻¹. The considerable changes in the FT-IR spectra confirming formation of

the degradation products of IGIs were related directly to the stage of the cellulose depolymerisation. Changes in FT-IR spectra of bistre and sepia were imperceptible, or none.

Conclusions

After assessing chemical, optical and mechanical properties of the historic brown-gray ink on the paper support, we concluded that the most stable appears to be the sepia ink, followed by bistre. Iron gall inks are the least stable of all. Degradation of paper pad depends on the ratio of Fe in the iron gall ink, the most noticeable is at Fe: GAL = 1: 1. The influence of light on stability of brown-gray inks on paper support is less significant than the influence of temperature and pollutants (in the studied time intervals); the most dangerous combination is high temperature with increased relative humidity and presence of air pollutants. Both degradation reaction paths – thermooxidation and depolymerisation in the aging of paper/gray-brown ink systems are noticeable and depend on the way of accelerated aging and the kind of applied ink. The acquired knowledge can be useful for conservators in securing optimum conditions of storage and accessibility of pieces of art.

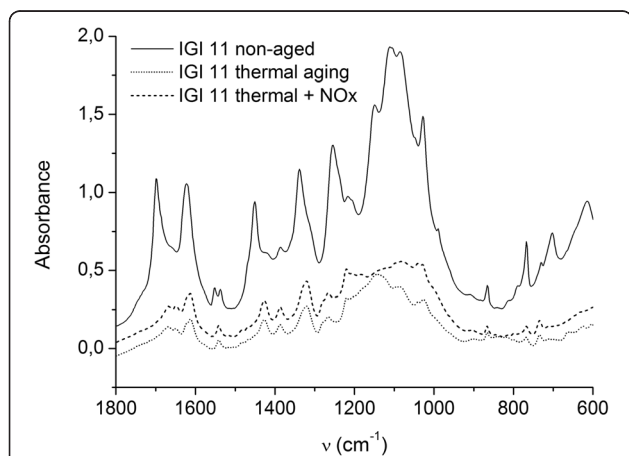


Figure 4 Changes in the part of FT-IR spectra of IGI 11 at the maximum time of accelerated thermal aging.

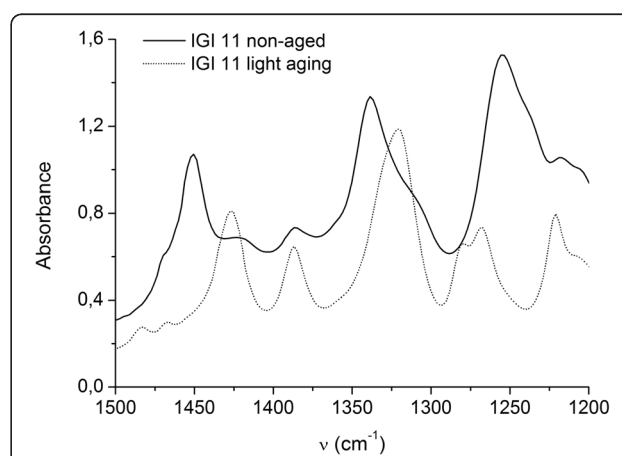


Figure 5 Changes in the part of FT-IR spectra of IGI 11 at the maximum time of accelerated light aging.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

MR conceived the study and made substantial contributions to conception and design. MC managed the research in the field of historical brown-gray inks and contributed to their identification. KV made data acquisition and interpretation. AP performed analysis of thermooxidative stability. MH performed the field work. DS participated in coordination and helped to draft the manuscript. All authors read and approved the final manuscript.

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