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The investigation of dye aging dynamics in writing inks using Raman spectroscopy

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ABSTRACT

The durability against light and aging dynamics of heteroatomic aromatic dyes and pigments containing nitrogen atoms used in writing inks was studied using Raman spectroscopy. The mechanisms of their thermal and photo-decomposition were proposed and the rates of these processes were determined. According to Raman spectroscopy, it was found that depending on the presence of one or another colorant, there are three main types (Type A, Type B and Type C) of blue dye inks used in ballpoint, gel and capillary pens which were studied in this work. Each type is characterized by a certain set of signals in Raman spectra. Time dependencies of Raman signal intensities for each type revealed the dynamics of the processes occurred with colorants included in the studied inks from the moment when they were printed on paper. Thus, the results obtained in this study can be used for the age estimation of the paper documents up to 15 years.

1. Introduction

Despite the rapidly developing digital technologies, paper documents remain the primary source of information in many areas. A common way of document falsification is counterfeit the signatures, inscriptions and dates with ballpoint, gel and capillary pens. In some cases, in order to conceal the fraud the paper, documents are heated or irradiated by artificial and natural light sources. However, the identification of the date when a writing ink was printed on paper is one of the most difficult tasks in the field of criminology. Therefore, the study of the artificial and natural ink aging is an important criminalistic, judicial and social problem, which deserves particular attention and efforts. In order to create high-quality technique that meets all the requirements dictated by the specifics of the area under investigation, one should provide the detailed studies of all processes responsible for the property changes of ink components in time. The main components of writing inks are shown in Fig. 1. Here, the most interesting objects are dyes because they are least susceptible to temporal degradation among other components of writing inks. The proposed approach opens the possibility to identify documents up to 15 years due to the fact that the degradation of a dye is a long process.

When ink is applied on paper, a series of processes simultaneously occur: ink drying due to the solvent evaporation, solvent absorption on the surface of the paper and solvent diffusion inside the paper [1], ink fading due to degradation of colorants and ink solidification due to polymerization of resins [1–4]. The degradation of dyes is much slower than many other processes. This process may take several years under natural conditions due to photochemical reactions that occur during the absorption of visible or ultraviolet light. The absorption of a photon by an organic molecule leads to the formation of the electronically excited state, which results in the subsequent dye photodegradation [5–7]. Deactivation of the excited states of dyes is induced by the interaction with the environment because many radicals involved in the degradation reaction are formed from solvent or substrate upon light irradiation [8]. The photodegradation of a dye may occur due to several competing reactions:

a) N - demethylation. The methyl group of a dye is sequentially replaced by hydrogen when exposed to light [9] (Fig. 2).
b) Photooxidative cleavage of the central C–phenyl bond occurs probably via singlet oxygen resulting in benzophenone and phenol formation [9,10] (Fig. 3). It is known that the photolysis of triarylmethane dyes leads to formation of singlet oxygen not only in solution but even on paper [8,9,11]. As a result, in the

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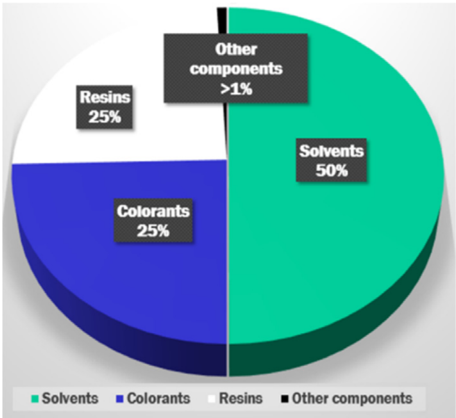

Fig. 1. The main components of writing inks [2].

absence of air under these conditions only leucobases are formed (colorless or weakly colored reduced forms of many organic dyes) [12].

c) Photoreduction of the excited dye cation to colorless leuco form. Here, the photoreduction of the excited dye cation is achieved by the addition of an electron to dye photoexcited states or by photochemical hydrogenation of a dye [9,13].

It is necessary to note that dyes such as crystal violet and methyl violet are not stable and can decompose not only upon light irradiation but also in the dark due to oxidation by atmospheric oxygen. All these processes can occur at the same conditions and compete with each other. The writing inks usually consist of complex mixtures with various additives, solvents, resins. Moreover, materials of paper documents can also be very different in their structure and chemical composition. Therefore, it is quite important to study in detail the aging process of dyes taking into account all aforementioned factors [13].

2. Experimental

2.1. Materials and samples

All writing inks of various grades used in this work were commercially available and their types are presented in Supporting Information (SI, Table S1). We obtained the database of blue ink strokes of 1-cm length printed on paper at different time intervals (2000–2015 year). All samples were stored under the following conditions: temperature was kept at about 20 ± 5 °C; the relative humidity was held at 70–95%; atmospheric pressure was 730–780 mm of Hg; without direct exposure to light, UV radiation and chemicals.

In order to study the influence of environmental factors on ink aging two groups of samples were prepared. In the first group, the ink strokes with a length of about 1 cm were drawn on paper. In the second one, the strokes of solution of colorant in dimethyl formamide (DMFA) were drawn on paper by a glass rod. The choice of DMFA was based on its high dissolving capacity and suitability for spectroscopic studies in the near infrared region. Then all of these samples were subjected to heat and light exposure.

We used the following colorants in powder form: fat-soluble purple K, alcohol-soluble phthalocyanine blue, direct purple, basic purple K, acid purple, acid bright blue, pigment phthalocyanine blue, victoria blue, crystal violet, methyl violet, rhodamine G, basic blue lacquer K.

For spectrophotometric measurements the piece of a paper the sizes of 3 × 10 mm was stroked by the aforementioned inks. Also approximately the same paper area was stroked by the DMFA solutions of colorants using a glass rod.

For thin-layerchromatography (TLC), plates of Silufol (PTSH-AF-15 × 15) on the aluminum substrate were used. The chromatographic separation was carried out in the next solvent system: ethyl acetate-isopropyl alcohol-water-acetic acid in a volume ratio of 30:15:10:1. The about 1 mg of each individual colorant was placed in microvial and dissolved in the 2 ml of DMFA for 2 h at the room temperature. The resulting dye solutions were transferred to the starting line on chromatographic plate using a microcapillary pipet. Before the chromatographic measurements, the TLC was stored at room temperature for 24 h. The zone detection was carried out visually in visible light.

2.2. Instrumentation

Raman spectra were obtained using a Senterra Raman spectrometer (Bruker Optics) equipped with three lasers with excitation wavelengths of 488, 532, 785 nm, a laser module confocal

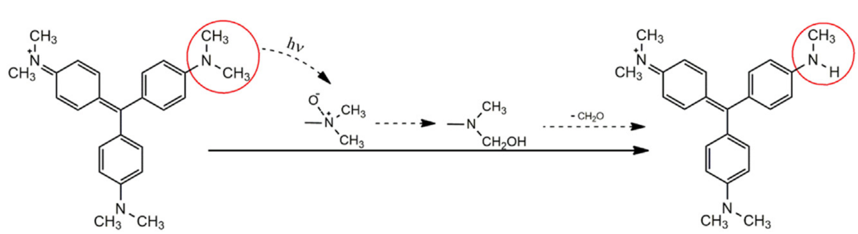

Fig. 2. The mechanism of N-demethylation.

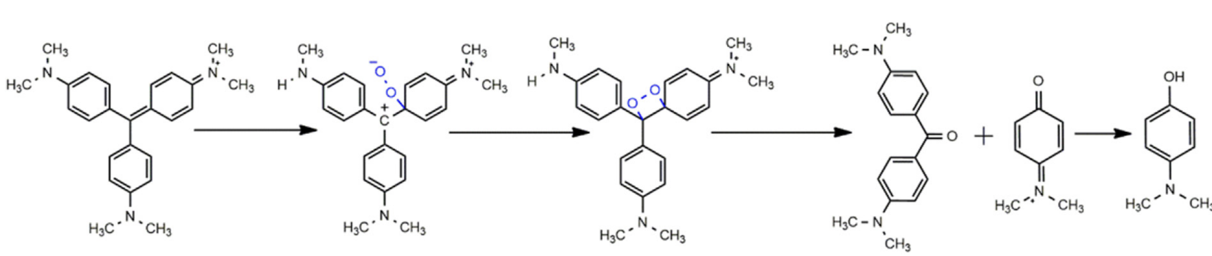

Fig. 3. The mechanism of the degradation of methyl violet through the attack of singlet oxygen.