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The effect of disinfection methods on the stability of photographic gelatin

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ABSTRACT

The influence of disinfection methods on paper-based archival and library materials has been well documented and, thus, these methods are commonly used in paper conservation. However, little is known about the effect of these methods on the emulsion layer of photographic prints, which is often formed by photographic gelatin. In this paper, we examine the stability of photographic gelatin after disinfection by three methods: γ-radiation, ethylene oxide and butanol vapors. The degree of gelatin degradation and its possible mechanism were determined by monitoring its molar weight (by measuring its intrinsic viscosity), primary structure (by amino acid analysis), and secondary structure (by FTIR spectroscopy and XRD). The smallest risk to the material was posed by butanol vapors, which suggests that this is a promising disinfection method for photographic prints based on gelatin.

1. Introduction

Gelatin is a natural proteinous material based on collagen. Its primary structure consists of polypeptide macromolecules with various molar weights (20,000 g/mol to 250,000 g/mol) [1–3], formed by condensation of 18 various amino acids mutually connected by peptide bonds. In general, this protein is formed of approx. 24% glycine, 17% proline, 14% alanine, 10% hydroxyproline, 7% glutamic acid and other amino acids [1]. While gelatin macromolecules assume a random arrangement in solution (grouped into micelles by intermolecular bonds), the secondary structure of the gel is formed by laevorotatory α-helices. The tertiary structure consists in three mutually intertwined helices that are grouped together at the supramolecular level to form coarse and fine networks with crystalline areas at their nodal points [1]. The exact chemical structure of gelatin depends on its manner of production and thus it is not a clearly defined chemical compound [3,4]. For photographic purposes, particularly gelatin of type B is used; this is obtained from animal bones by the alkaline method (using a lime suspension) [1,2].

Because of its useful physical and chemical properties, photographic gelatin has become the most important emulsion medium used in the history of photography and is thus a component of many types of photographic materials (negatives as well as printed-out or developed-out prints, transparencies and high-grade prints) [5,6].

Of these materials, the most common in archive and library collections are apparently silver gelatin prints on paper [4]. These prints consist in layered material formed of a paper support, a substrate layer of barium sulphate and a sensitive layer with a light-sensitive substance (silver halogenides) finely dispersed in an emulsion medium (gelatin layer) [5–8]. Nonetheless, gelatin is an organic hygroscopic substance that can become a substrate for the growth of microorganisms when it is stored for a long time under unfavorable conditions; this risk applies also to an organic hygroscopic paper support. Gelatin is most frequently attacked by molds of the *Aspergillus* and *Penicillium* genera, and also *Cladosporium cladosporioides*, *Alternaria alternata*, *Mucor racemosus*, *Phoma glomerata* and *Trichoderma longibrachiata*. Members of the *Bacillus* and *Staphylococcus* genera are amongst the most common bacteria attacking gelatin [2,4,9,10].

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Attack of gelatin by microorganisms can lead to serious damage. This generally occurs (depending on external conditions) by one of two basic mechanisms of degradation of proteinous materials: acid hydrolysis or oxidation, which can take place independently at all structural levels and which complement each other in a real environment [11]. Enzymes and organic acids produced by microorganisms cause polymer chain scission (liquefaction) in gelatin and thus decomposition of the photographic image. Other metabolites of microorganisms can act as oxidation agents and cause oxidation damage to the attacked substrate or locally increase its moisture content [2,12,13]. In addition, unsightly growths and green, pink or brown spots appear on the surface of the materials [4,5,12,13]. The level of cross-linking of the gelatin does not have any effect on the degree of its biological damage [10].

The best means of protection against microorganisms is preventative conservation ensuring such storage conditions that are unfavorable for the growth of microorganisms [2,4]. If attack does occur, it is necessary to rapidly isolate the affected material and commence removal of the microorganisms by a suitable disinfection method [4]. For archives and libraries, it is useful to employ disinfection methods that can be applied collectively to a large number of affected items. Of chemical disinfection methods, this purpose can be served, e.g., by butanol vapors or ethylene oxide and, of physical interactions, for example, by γ-radiation [4,12–14]. In order to select a suitable disinfection method, careful evaluation has to be made, not only of the nature of the treated material and its current condition, but also of the effectiveness of this disinfection method and its health risks for humans [4,12].

The effects of the individual disinfection methods are well known in case of the paper support [12,14–19]. Thus, photographs are frequently disinfected using methods employed in conservation of paper archive materials despite their effect on the individual layers of the photographic material (including the light-sensitive gelatin layer) has not yet been studied adequately and in sufficient detail. Of individual bits of information, it is known, for example, that the gelatin viscosity decreases with the increasing dose of γ-radiation, indicating a decrease in its molar weight [20]. Ethylene oxide, containing a strained epoxide ring, can easily split and react through various mechanisms with archive materials; amongst other things, it reacts with the amino-, thio- and carboxy-groups of the amino acids methionine and histidine, which are contained in small amounts in gelatin, and could thus theoretically damage the sensitive layer of the photograph [1,4,21]. Although ethylene oxide is desorbed quickly from baryta paper photographs and, thus, it does not leave significant residues in this material, its direct effect on photographic gelatin has not yet been studied [4,22]. No information about the effect of butanol on photographs is, in fact, available at the present time and thus it is necessary to proceed with care.

This work was performed to assess the effect of these disinfection methods (γ-radiation, ethylene oxide, butanol vapors) on the stability of photographic gelatin. The results of this study (together with the results of related research) will be used as a basis for choice of a suitable disinfection method for non-destructive disinfection of a specified photographic material in relation to its individual components.

2. Methods and materials

2.1. Gelatin samples

The samples were prepared using photographic gelatin from FOMA Bohemia, s.r.o., Hradec Králové hardened with commercial hardener from the same manufacturer. It was dissolved in water with a maximum temperature of 40 °C to prepare a 7% w/w aqueous solution, which was then poured in 150 mL aliquots onto polymethylmethacrylate plates. After drying, the gelatin formed a continuous film of the thickness about 0.04 mm, which was removed and cut into pieces of the same size. These samples were then stored in polyester foil and polyethylene bags.

2.2. Methods of disinfection

2.2.1. γ-radiation

The gelatin samples were irradiated in the irradiation chamber of the Central Bohemian Museum in Roztoky near Prague with the ^{60}Co radionuclide. The radiation dose, subsequently evaluated using alanine dosimetry, equalled 2.2 kGy.

2.2.2. Ethylene oxide (EtO)

Disinfection using ethylene oxide (hereinafter EtO) was carried out by the procedure used in the National Archives in Prague: the gelatin samples were spread out in paper boxes and placed in a MATACHANA (type 1.3100 LGE-2) disinfection chamber with a total volume of 6.4 m^3. The disinfection was carried out using Etoxen gas (a mixture of 10% EtO and 90% CO_2), in which the samples were disinfected for 6 h at a temperature of 30 °C and pressure of 220 kPa. Then, to reduce the EtO concentration below 1 mg/m^3, the samples were aired for 6 h in a ventilation tunnel with countercurrent air heated to 30 °C. At the end of the whole cycle, the concentration of EtO remaining in the samples was measured by gas chromatography for 24 h in closed air-tight chambers.

2.2.3. Butanol vapors (ButOH)

Disinfection of the samples by butanol vapors (hereinafter ButOH) was carried out in a disinfection chamber, where the samples were distributed on metal screens. The butanol vapors were obtained by evaporation of 600 mL of a 96% v/v butanol solution from an open vessel. Disinfection was performed for 48 h at 26 °C and 64% relative humidity in the disinfection chamber [16].

2.3. Methods of monitoring structural changes in gelatin

2.3.1. Viscosity measurement

It was found in previous works [2,23] that the values of the intrinsic viscosity obtained from the Schulz-Blaschke $[\eta]^{S-B}$ Equation (1) are sufficient for comparison of the decrease in the gelatin viscosity:

$$[\eta]^{S-B} = \frac{\eta_{red}}{\left(1 + k_{SB} \cdot \eta_{sp}\right)} \quad (1)$$

where η_{red} is the reduced viscosity, η_{sp} is the specific viscosity and k_{SB} is the Schulz-Blaschke constant, which was found to be 0.28 for the given photographic gelatin – water system [9]. The viscosities of solutions of disinfected and undisinfected gelatin were thus determined by this method.

The viscosity was measured using an Ubbelohde 536 10/I capillary micro-viscometer (SI Analytics GmbH, Germany) with a 0.4 mm capillary diameter. The measured solutions have a volume of about 3 mL. A digital chronometer with a precision of 0.01 s was used to measure the flow-through time of the solutions and pure solvent between the marks. The measurements were performed at a temperature of 37 ± 0.01 °C maintained using a thermostatic bath. Prior to the actual measurement, all the solutions were stored in an oven at a temperature of 35 °C.

The exact concentrations of the solutions were calculated by determining the content of dry material in weighed gelatin samples in Petri dishes before and after drying in an oven at 105 °C to