Long-term effect of disinfection on collodion light-sensitive layer

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Cellulose nitrate in the form of collodion has been used as a light-sensitive layer since 1851. As such, collodion photographs are often found in cultural institutions. Because of its organic structure, it is susceptible to microbiological contamination and, therefore, a need for disinfection may occur. In such cases, the disinfection method must be effective and non-destructive towards the material and restorer. Since all tried disinfection methods were proven effective by cooperating microbiologists, the non-destructivity against material became the primary concern. Model samples were prepared, disinfected, and artificially aged; to observe any possible change in properties on a long-term scale. The properties measured were: change in colour, change in the content of nitrogen and change in the degree of polymerisation obtained by viscometric measurements. From the results, we could select a disinfection method that did not pose any measurable threat towards the collodion light-sensitive layer and, therefore, can be used in practice by restorers.

INTRODUCTION

Collodion photographs present an inseparable section of cultural institutions' collections. The first use as a binder of a light-sensitive layer was published in 1851 in the journal Chemist by Sir Frederick Scott Archer. In the following years, the collodion process underwent a dynamic evolution, and its main use can be set mainly between 1870 – 1930 [1].

The term collodion is used for cellulose nitrate with a degree of substitution close to 2 (amount of nitrogen ca 11.1%) in a mixed solution of alcohol and ether. As well as any other organic material, collodion is susceptible to microbiological contamination and degradation. While the effect of disinfectants on paper support was extensively investigated in the past [2-4], collodion and other light-sensitive layers are still at the beginning of the systematic studies [5].

In our work, we focused on two main types of cellulose nitrate degradation: release of nitro groups from the saccharidic chain, also known as denitration, and cleavage of the β-D glycosidic bond between glucopyranose units (Fig. 1). Denitration is caused by the cleavage of O–NO_2 bond. Consequently, NO_X is released, enhancing a whole spectrum of secondary reactions and bringing deterioration into an autocatalytic point [6-9]. The decrease in the degree of polymerisation caused by the cleavage of the polymeric chain is traditionally studied by viscometric measurement. In the case of cellulose nitrate, the viscosity behaviour is influenced not only by the length of the polymer chains but also by the degree of substitution [10-12]. To characterise the degradation of cellulose nitrate, it is, therefore, crucial to combine viscometric measurements with methods for determining the degree of substitution. The degree of substitution can be calculated, for example, by the response of the nitro groups in the polysaccharidic macromolecule using infrared spectroscopy or through the ratio of nitrogen and carbon atoms in the sample (elementary analysis, NMR) [7, 10, 13-15].

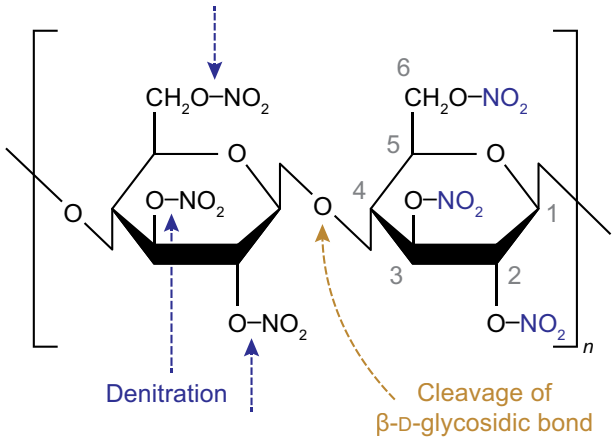

Fig. 1. Schematic picture of cellulose nitrate with all three possible positions nitrated

This work focuses on the degradation of collodion by exposure to disinfectants commonly used in practice. The main objective is to identify effective and material-safe disinfection methods for use in cultural institutions.

MATERIALS AND METHODS

Samples

Thin foils of collodion were prepared by free evaporation under laboratory conditions from a 4% solution of cellulose nitrate in the mixture of ethanol (30% w/w) and diethyl ether (>60% w/w) – type ÖAB (Fagron, Czech Republic). The thickness of the foils was approx. 23 µm. These were artificially aged for 28 days at the elevated temperature of 70°C and 70% relative humidity (modified standard ISO5630-3) in a Memmert CTC 256 chamber. After the artificial ageing, the samples were disinfected and aged under the same conditions [Fig. 2].

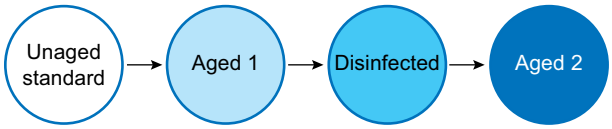

Fig. 2. Sequence of treatments of collodion samples

Material properties were tested after every step of the procedure and correlated respectively.

Three disinfection methods were selected after the consultation with photography restorers from the National archives of the Czech Republic. All of them are commonly used in the practice of cultural institutions.

The list of tested disinfectants:

Bacillol AF

Submersion of collodion samples into mixed alcohols solution Bacillol AF (Bacillol AF, Hartmann-Rico, Bode Chemie GmbH, Germany) for 5 min under laboratory conditions. Main active substances: propan-1-ol, propan-2-ol and ethanol.

Butanol (ButOH)

Exposure of collodion samples to saturated vapours of 96% aqueous solution of butan-1-ol (p.a., Lach-ner, Czech Republic) in a plastic laboratory desiccator under laboratory conditions for 48 h.

Etoxen

Exposure to mixed gas Etoxen (10% of ethylene oxide + 90% of CO_2, chamber MATACHANA, National archives, Czech Republic) for 6 h at 30°C and 220 kPa. The consequent ventilation lasted for 6 days at 30°C.

Colourimetry

The change of colour was measured by the spectrophotometer Konica Minolta CM-700d in the CieLAB colour space. The total colour difference was then calculated according to Equation (1).

$$\Delta E_{ab} = \sqrt{(L_2^* - L_1^*)^2 - (a_2^* - a_1^*)^2 - (b_2^* - b_1^*)^2} \qquad (1)$$

Nine measurements for every disinfection method were made – foil folded to quarters for changes to be evaluable against colour-stable underlay.

Organic elemental analysis (OEA)

The elemental analyser Elementar Vario Cube with thermal-conductivity detection was used for the measurements. For one measurement, 4 mg of sample were taken and preconditioned at 30°C and 50% RH. The amount of detected elements was calculated in relation to the mass of the sample. The total dry weight of each sample was measured and calculated on drying laboratory scales DBS60-3 (Kern, Germany) and used as a reference for weight percentage calculations to eliminate the influence of fluctuations in relative humidity and, therefore, the final result.

Fourier-transform infrared spectroscopy (FTIR)

FTIR analysis was performed using Nicolet iN10 with iZ10 module and single-reflection ATR diamond crystal, MCT-A liquid nitrogen cooled detector. Parameters of measurement: the spectral range of 4000-650 cm^{-1}, the spatial resolution of 4 cm^{-1}, spectral accumulation of 64, apodisation N-B strong. Spectra were consequently evaluated using programs Omnic 32 and Opus 8.1.

Nine parallel measurements were performed for every sample type. Nitrogen content was calculated according to the methodics published by Nunes et al. [13]. The calculation is based on the ratio of peak intensities corresponding to the glucopyranose ring vibrations and nitro group vibrations, namely 1060 cm^{-1} (stretching vibration of C–O–C in the glucopyranose ring) and 1636 cm^{-1} (anti-symmetric stretching vibration of $–NO_2$). The baseline was set between 1190-930 cm^{-1} and 1800-1525 cm^{-1}, respectively. The published calibration enables an assignment of the ratio of intensities to the number of nitro groups in the macromolecule. Thus, it assesses the amount of nitrogen even in the unknown sample [13].

Viscometry

The changes in the chain length were determined from viscometric measurements. Due to the limited amount of sample, reduced viscosity was used instead of the intrinsic viscosity.

The reduced viscosity was calculated using a 0.05 g/mL solution of dry-weight collodion sample in acetone (p.a., Penta, Czech Republic). Two parallel measurements were carried out at 25°C using micro-Ubbelohde's viscometer with an inner diameter capillary of 0.4 mm (K = 0.009789 $mm^2\ s^{-2}$). The reduced viscosity was calculated using the following Equation (2):

$$\eta_{red} = \frac{t - t_0}{t_0 \cdot c} \quad (cm^3\ g^{-1}) \qquad (2)$$

where η_{red} stands for reduced viscosity, t is capillary flow time for the selected sample, t_0 is the capillary flow time of pure solvent, and c marks the concentration of the selected sample.

RESULTS AND DISCUSSION

Colourimetry

Collodion samples were colourless, thin films with highly glossy surfaces, which led to a wide dispersion of values. This left the changes in colour within the range of the measurement's error interval without any observable trends or exceedings.

Organic elemental analysis (OEA)

The samples were measured by OEA after every step of the preparation process. Even though the difference in nitrogen content between not disinfected and disinfected samples is visible, the changes between samples disinfected by different methods were under the limit of experimental error of 0.1% (Figure 3).

The decrease of nitrogen content in all disinfected samples suggests that with every disinfection, the objects' surface is partially disturbed and, therefore, prone to easier degradation. However, the nitrogen content after disinfection and ageing is still very high, and at least for our samples, the degradation rate of cellulose nitrate did not show high differences for the tested disinfectants.

Fourier-transform infrared spectroscopy (FTIR)

The results from FTIR did not show any changes exceeding the standard deviation (Fig. 4). The FTIR method can be therefore recommended for more degraded objects, where the change in the nitrogen content can be observable and significant – the limitation of the method is the change in the composition of at least 0.5% as specified by the method specialists [16].

Viscometry

From the viscometric measurements, the samples before the second ageing disinfected by Bacillol AF showed a decrease, exceeding the standard deviation. After the second ageing, the decrease is not as eminent as before. However, a slight decrease indicates the possible risk in using this disinfection method (Figure 5).

Another disadvantage of using Bacillol AF is that the chemical composition is not stated from all 100%.

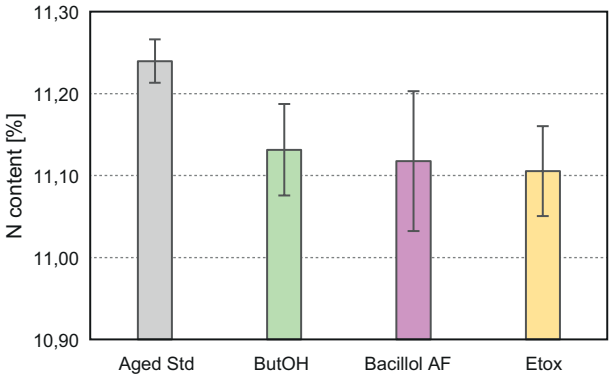

Fig. 3. Plot of nitrogen content in collodion samples after ageing, disinfection and second ageing; measured by OEA

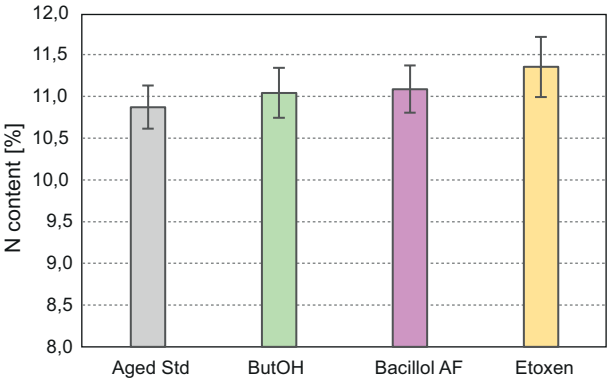

Fig. 4. Nitrogen content as calculated from absorbance intensities from FTIR spectra

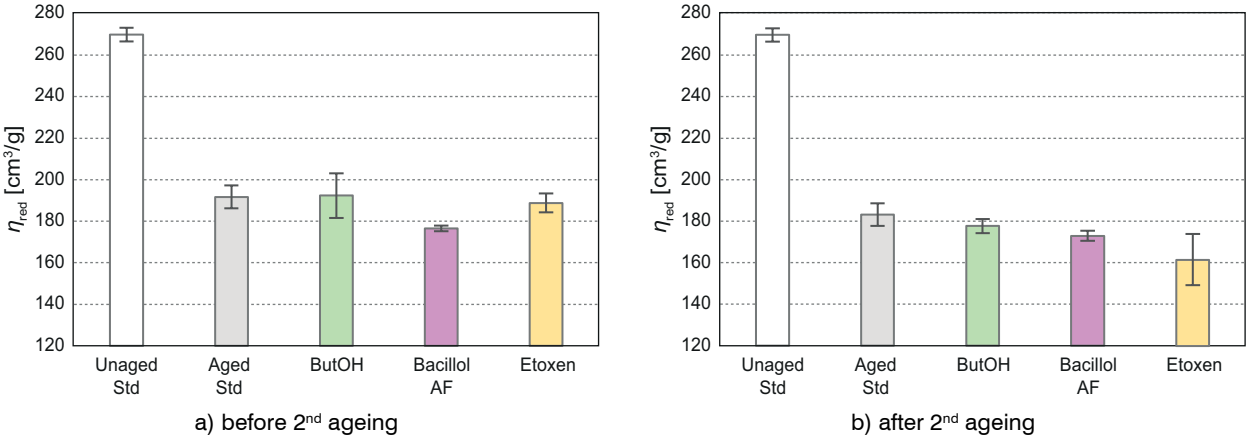

Fig. 5. The change in reduced viscometry after disinfection, before and after the second ageing; the decrease in reduced viscosity is visible for the samples treated with Bacillol AF; the samples treated by Etoxen were not fully soluble after the second ageing (therefore, the results cannot be considered)

Apart from the main active compounds, the mixture contained up to 10% of unidentified compound/s, one of which needs to be water for the disinfection to proceed. The combination of water and ethanol may be dangerous for cellulose nitrate use. As stated by Romanova et al. [17], the re-alkylation of the chain may occur together with many degradation paths of the cellulose nitrate macromolecule. One of which is the cleavage of the β-D-glycosidic bond.

After the second ageing, the samples disinfected by Etoxen were only partially soluble. Therefore, the results are not evaluable. The possible explanation may lie in crosslinking properties of ethylene oxide. However, Size exclusion chromatography with multi-light scattering detection (SEC-MALLS) needs to be performed to determine the gyration radius of macromolecules to ensure this hypothesis.

CONCLUSION

From the results obtained from all measurements, it is safe to assume that denitration does not occur to a measurable extent after any of the selected disinfection treatments. On the other hand, the decrease in reduced viscosity for samples disinfected by Bacillol AF indicates the cleavage of the β-D-glycosidic bond and, therefore, the degradation of the polysaccharidic chain. This fact, together with the unspecified part of the chemical composition of this commercial product, leads to not recommending its' use in practice until further disproved. The use of Etoxen seems to cause crosslinking of the polysaccharidic chain in the long term and needs to be further examined since it is one of the most commonly used methods for mass disinfection of archival objects. As a safe disinfection method, the exposition to vapours of 96% butan-1-ol was selected. This method is widely used and known among the restoration community and was not found to endanger cellulose nitrate in any measurable way.

Acknowledgements

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