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Identification tags for archival documents based on oxides of transition and inner transition metals – influence on paper supports

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Abstract: Theft of archival documents constitutes a serious problem for archives. A possible solution to this problem lies in labelling these documents with codes that are invisible to the naked eye. A possible method could involve use, e.g. of the oxides of lanthanum, dysprosium, samarium, gadolinium and niobium, which have good responses in the XRF spectrum and are normally not present in archival materials. This study is concerned with the impact of these oxides on the properties of lignocellulosic materials. The identification tags were printed on three different kinds of paper supports (Whatman No. 1 filter paper, paper according to ISO 9706 and sulphite pulp). The colour change, average degree of polymerisation, the pH values of an aqueous extract and selected mechanical properties after application of the tag and artificial ageing were studied on all the samples. The measurements showed that the studied oxides do not have a negative effect on the monitored properties of the paper supports and do not affect their long-term ageing behaviour.

Keywords: archival materials, protection against theft, identification tags

1 Introduction

Theft of archive documents and rare copies of books (e.g. manuscripts or incunabula) is a problem for archives and libraries. In the environment of libraries and

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especially archive institutions, the theft of archival materials constitutes a serious security risk. If the stolen documents are found and the perpetrator is caught and charged, it is very difficult to demonstrate ownership if the documents are not labelled. Usual current practice in archives and similar institutions is to label documents with the imprints of metal or rubber stamps with the necessary information. This procedure is cheap and undemanding on time and technology, but the tag is visible and reduces the aesthetic value of the document. In addition, commonly used stamp dyes based on aryl methane compounds are unstable and can be relatively easily removed. Thus, in the past few years, other methods of designation are being sought that would remedy these inadequacies.

The expansion of digital technologies has led to the increasing use of electronically readable identification elements (1D and 2D codes) or purely electronic identification elements (RFID elements and various types of contactless-read chips). However, these systems are not primarily intended for identification of archival materials and when found, can be easily removed from the document. Thus, there is a need for tags that are not apparent in normal perusal and thus escape the attention of the thief; however, if a document is found, the code can be read and the original owner ascertained. There are a great many technical principles and approaches (Dejneka et al. 2003; Paunescu et al. 2016), of which fluorescence is by far the most popular. Various conventional bar codes that are invisible when viewed under normal conditions become visible by fluorescence when irradiated with ultraviolet or infrared light (US patents 2001, 2013, 2017). This labelling method has various modifications based on the formation of short codes using quantum dots with a layered structure consisting of a number of fluorescing materials, where the actual code is manifested by various shapes of the emission fluorescence spectra (Finkel et al. 2004; Han et al. 2001; US patent 2014). Another method involves the use of microdots (US patent 1981), which can be located all over the document or only locally. If applied locally, it is necessary to supplement the labelling system with information on the location of the microdots. Another interesting labelling method is based on the identification of objects using elemental isotopes. Coding the information content is based on adjusting the specific ratios of the selected isotopes, while reading proceeds using mass spectrometry (US patent 1998) which, however, generally requires destructive pre-treatment of the sample for analysis and thus cannot be used for archival documents. This principle has been improved by using unnatural ratios of the isotopes of light elements leading to a change in the FTIR vibration spectra (US patent 2005). X-ray fluorescence (XRF) also seems to be a very promising method for contactless reading of codes based on the elemental composition of the tag. While this method cannot be used to distinguish between the isotopes of elements, but

only between different elements, it can provide sufficient capacity for the creation of short codes and their easy non-destructive reading. (Demirok et al. 2009; Dhara et al. 2010; Li et al. 2016; Sattayasamitsathit et al. 2007; Schramm and Kaiser 2005).

The identification tag for labelling archival documents developed in the context of project VI20162019037 supported by the Ministry of the Interior of the Czech Republic combines the negligible visibility to the naked eye (Figure 1) and the reliable sensitivity of XRF spectrometry (Figure 2) leading to low risk of undesirable persons discovering the label. The principle of the labelling is based on the presence and mutual ratio of the selected transition and inner transition metals, which do not occur naturally in archive materials. A thin layer of the coding mixture of oxides with a suitable binder can be printed directly on the document by various techniques (e.g. inkjet, screen printing, tampography). The applied label is visually indiscernible. Thus it is combined with a localisation label (up-conversion pigment), which is also visually indiscernible but becomes visible through fluorescence emission following excitation by an infrared laser. In the area of cultural heritage, emphasis is generally placed on the long-term stability of the employed materials and exclusion of undesirable effects on the object as such. The use of selected transition and inner transition metals in the form of their non-reactive oxides could suppress their catalytic effect on the degradation of lignocellulose materials, which are most frequently encountered in archive documents. Thus the development of methods for designating archival materials also included the necessity of evaluating the effect of the employed compounds on the long-term stability of lignocellulose materials.

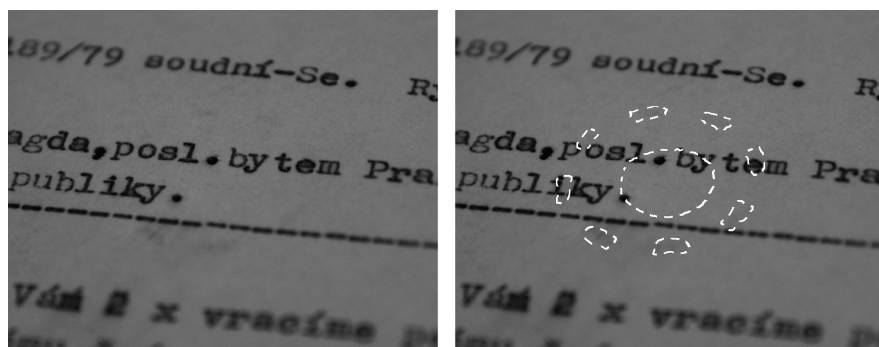


Figure 1: Detail of a document with applied protective tag (on the left) and its highlighted outline (on the right).

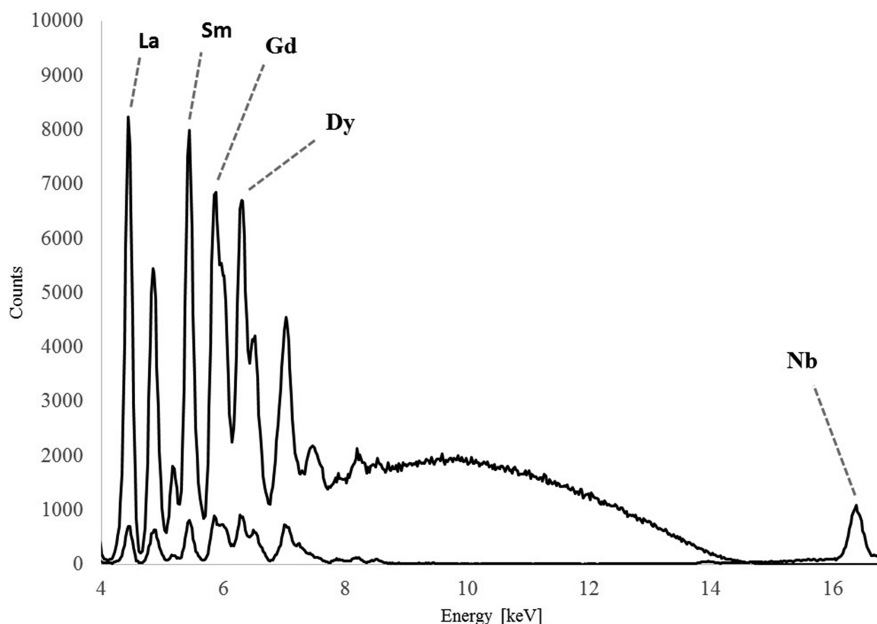


Figure 2: X-ray fluorescence spectrum of a tag applied to a document by inkjet.

2 Material and methods

2.1 Preparation of model samples

Model samples were prepared to verify the long-term stability of the lignocellulosic materials with XRF identification tags. Three types of paper were chosen as supports. These were Whatman No. 1 filter paper (pure cellulose, basic weight 87 g/m², supplier: VWR International, Czech Republic), sulphite bleached pulp (mixture of softwoods, basic weight 80 g/m², supplier: Vian-Paskov, Czech Republic), and paper for documents (according to ISO 9706, basic weight 80 g/m², supplier: Neograph Štětí, Czech Republic).

The following compounds were used in the printing ink: Samarium (III) oxide (99.9 %, Sigma-Aldrich), Gadolinium (III) oxide (99.9 %, Sigma-Aldrich), Dysprosium (III) oxide (99.9 %, Sigma-Aldrich), Niobium (V) oxide (99.9 %, Sigma-Aldrich), and Lanthanum (III) oxide (99.9 %, Sigma-Aldrich). First, a concentrated stock dispersion was prepared as follows: 60 g of Dowanol

PM (2-methoxypropanol) was mixed with 40 g of dry oxides (the particle median diameter was less than 200 nm) and 4 g of Disperbyk 103 dispersing agent. This concentrated stock dispersion was subsequently employed for mixing the printing ink. The ink was formulated using a recently reported oligomeric siloxane binder, which proved to be useful for bonding oxide nanoparticles as well as having suitable rheological properties for inkjet printing. The ink was prepared by mixing 4 mL of stock siloxane binder solution (20 wt % in anhydrous ethanol) with 4 mL of the oxide dispersion (40 wt % in Dowanol PM solvent) and 8 mL of isobutanol. The oxide layers were printed with a Fujifilm Dimatix 2831 experimental inkjet printer. The amount of oxides printed per 1 cm² was: 0.180 mg La₂O₃, 0.150 mg Sm₂O₃, 0.113 mg Gd₂O₃, 0.09 mg Dy₂O₃ and 0.03 mg Nb₂O₅. These amounts were chosen to achieve sufficient response for the handheld XRF analyser, while maintaining minimal tag visibility by naked eye.

2.2 Study of the stability of paper supports

2.2.1 Artificial ageing

The model samples with the printed oxides were subjected to three types of artificial ageing: dry heat (105 °C, 28 days, ISO 5630–1) in a Memmert UFE 500 chamber, moist heat (80 °C, 65 % RH, 28 days, ISO 5630–3) in a Memmert CTC 256 chamber and light (artificial daylight with increased UV component, light intensity 5.2 klx, energy of the UV component 12 W/m², temperature 38 ± 2 °C, 15 ± 3 % RV, 14 days, based on ISO 5630–7).

2.2.2 Total colour difference

The colour was measured on a white light-stable support in the CIELAB colour area using a Minolta CM-700d spectrophotometer (Konica Minolta, Japan). It was always measured at five identical points on each sample before and after applying the tag or after artificial ageing. The total colour difference was then calculated from the measured values according to equation (1).

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

where L^* is the specific luminescence, a^* is the green-red colour axis and b^* is the blue-yellow colour axis. The resultant value is the average of 5 measurements.

2.2.3 pH value of an aqueous extract

The pH of a cold aqueous extract was determined using an inoLab 7310 pH meter and a Sentix 41 glass electrode (WTW GmbH, Germany) according to standard ISO 6588. Because of the small amount of sample, the weight of the paper for the individual determinations was reduced to 0.5 g. The volume of distilled water was also proportionately reduced. The resultant value is the average of 2 determinations.

2.2.4 Average degree of polymerisation

The average degree of polymerisation was determined viscometrically according to standard ISO 5351. Two parallel measurements were performed on each sample. Printed and unprinted samples of Whatman No. 1 paper and sulphite pulp were measured. The average degree of polymerisation of the ISO 9706 paper samples could not be determined by this method because the sample was insoluble in the solvent employed. The average degree of polymerisation was calculated according to equation (2), where $[\eta]$ is the determined limiting viscosity number:

$$DP^{0.85} = 1.1 [\eta] \quad (2)$$

2.2.5 Mechanical properties

Of the mechanical properties, the tensile strength at zero measured length of the strip (i.e. zero-span), elongation (%) and the breaking length (km) of samples in the longitudinal machine direction (MD) were determined. The zero-span tensile strength was determined for the Whatman No. 1 paper, paper according to CSN ISO 9706 and for sulphite pulp paper using the LabTest 5.030–2 (Labortech, CR) universal testing instrument with special jaws. The remaining mechanical properties (elongation and breaking length) were determined only for the Whatman No. 1 and ISO 9706 paper samples on the Alvetron TH1 (Lorentzen Wettre, Sweden) tearing instrument according to standard CSN ISO 1924–2.

The results of the measurements were treated statistically and the interval of reliability of the average was calculated according to the reliability level $\alpha = 0.05$. The intervals of reliability are indicated in the individual graphs by error bars.

3 Results and discussion

3.1 Overall colour change

Total colour difference caused by the printed XRF identification tags did not exceed the reliability level 0.5 for all tested paper supports. The greatest total colour change ΔE^*_{ab} following artificial ageing by dry and moist heat and by artificial daylight was exhibited by the paper for documents (according to ISO 9706). In contrast to Whatman No. 1 paper and the samples prepared from sulphite pulp, this paper is sized with alkyl ketene dimers and filled with calcium carbonate. However, the measured colour of all the studied samples (printed with the siloxane binder alone and with the studied oxides) following artificial ageing did not demonstrate any negative effect of either the siloxane binder or the tested oxides on the paper support. Figure 3 depicts the total colour change ΔE^*_{ab} for all three kinds of paper following ageing by moist heat. For other types of artificial ageing, the ΔE^*_{ab} of the Whatman No.1 paper samples did not exceed 5, the ΔE^*_{ab} of the sulphite pulp samples did not exceed 6 and samples of the paper for documents did not exceed 7.

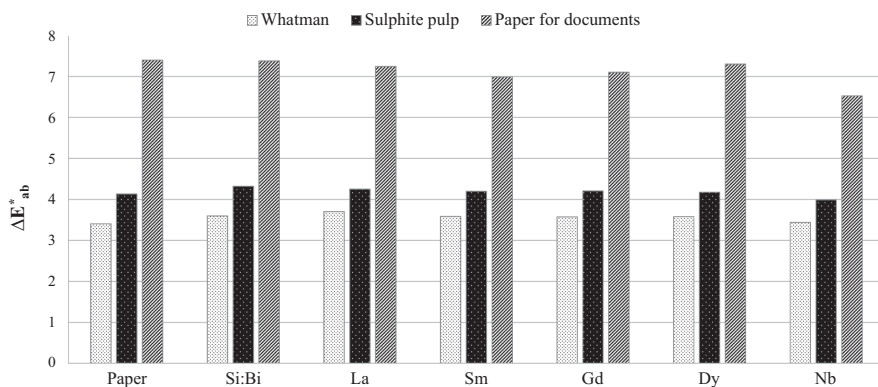


Figure 3: Total colour difference of Whatman No. 1 paper, paper for documents (ISO 9706) and sulphite pulp following application of the binder (Si:Bi), the tags and artificial ageing by moist heat.

3.2 pH value of aqueous extracts

As standard ISO 9706 requires, aqueous extracts of papers with an alkaline reserve have pH values of approximately 8.0, while the pH values of aqueous

extracts of Whatman No. 1 paper and sulphite pulp lie in the slightly acidic region. The artificial ageing did not lead to substantial changes in this parameter for any of the individual paper supports. Similar to the measurement of colour changes, measuring the pH values of a cold aqueous extract did not demonstrate any negative impact of either the siloxane binder itself or of the studied oxides on any of the studied paper supports. This is valid for all the tested types of paper supports and all types of artificial ageing. An example of the results of measuring the pH values of the extracts is depicted in Figure 4.

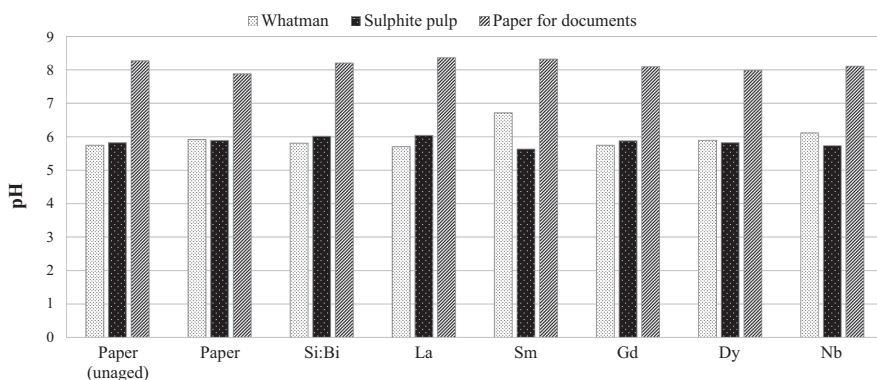


Figure 4: pH values of an extract of Whatman No. 1 paper, paper for documents (ISO 9706) and sulphite pulp following application of the binder (Si:Bi), the tags and artificial ageing by moist heat.

3.3 Average degree of polymerisation

Artificial ageing of Whatman No. 1 paper and bleached sulphite pulp by moist (Figure 5) and dry heat led to a reduction in the average degree of polymerisation by 40 to 45 %. Ageing by artificial daylight led to a reduction in the average degree of polymerisation of bleached sulphite pulp by 25 %, while no reduction was found for Whatman No. 1 paper. Changes in the average degree of polymerisation are not affected by the application of the siloxane binder or the studied oxides. The oxides of lanthanum, dysprosium, samarium, gadolinium and niobium did not catalyse the decomposition of the cellulose macromolecules. The average degree of polymerisation of paper for documents was not evaluated because of its insolubility in solvent used for viscometric measurements.

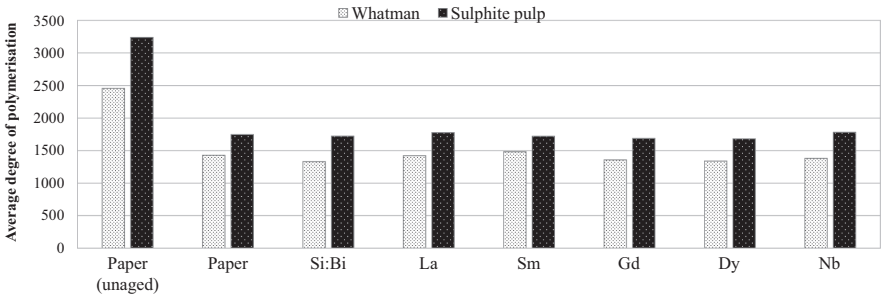


Figure 5: Average degree of polymerisation of Whatman No. 1 paper and sulphite pulp following application of the binder (Si:Bi), the tags and artificial ageing by moist heat.

3.4 Mechanical properties

Figures 6 to 8 depict the results of measurements of the zero-span tensile strength (kN/m), elongation (%) and breaking length (km) of samples in the longitudinal machine direction (MD) following artificial ageing by moist heat. Artificial ageing of most paper supports led to a slight decrease in the values of the monitored mechanical properties of the aged samples, but the application of the tested printing mixtures did not increase these differences. Neither the tested oxides nor the employed binder has any negative effect on these mechanical properties and also do not reduce the resistance of the samples to ageing. These conclusions correspond well with the results of determination of the average degree of polymerisation (Figure 5).

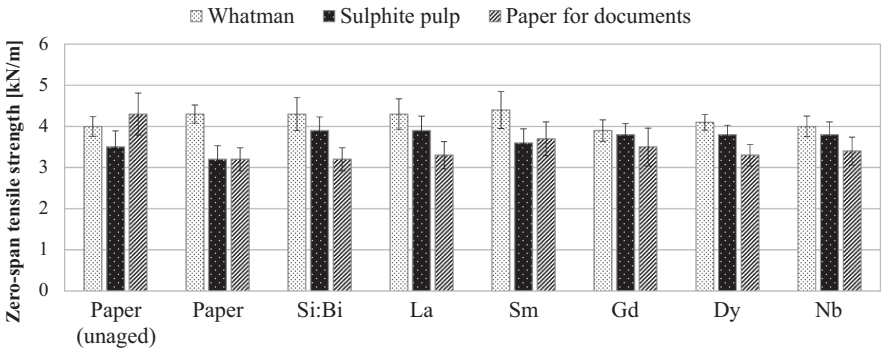


Figure 6: Zero-span tensile strength (kN/m) of samples of Whatman No. 1 paper, paper for documents (ISO 9706) and sulphite pulp following application of the binder (Si:Bi), the tags and artificial ageing by moist heat.

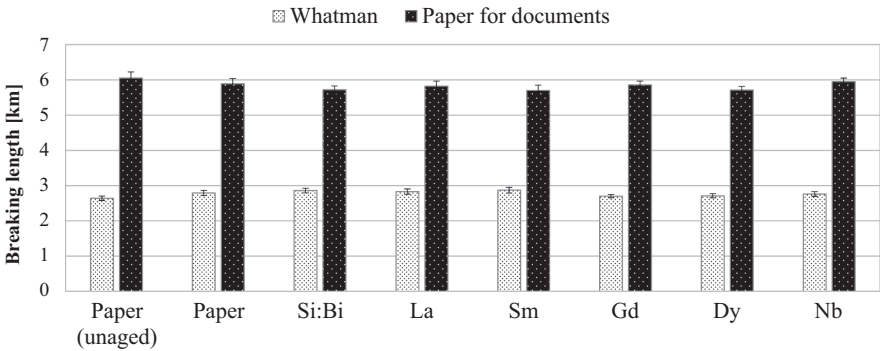


Figure 7: Breaking length (km) of samples of Whatman No. 1 and ISO 9706 papers with the applied binder (Si:Bi), tags and artificial ageing by moist heat.

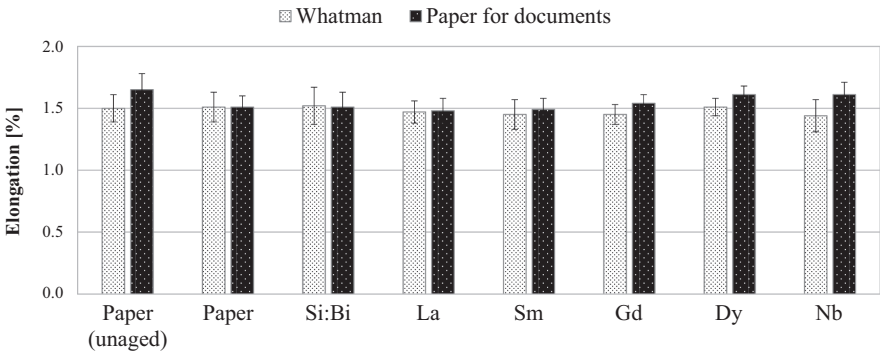


Figure 8: Elongation (%) of samples of Whatman No. 1 and ISO 9706 papers with the applied binder (Si:Bi), tags and artificial ageing by moist heat.

4 Conclusion

The use of the oxides of lanthanum, dysprosium, samarium, gadolinium and niobium, which have a good response in XRF spectra and simultaneously do not occur commonly in archive materials, is a promising approach to their use for unambiguous identification of documents. This study is concerned with the effect of these oxides with siloxane binder applied by inkjet printing on Whatman No. 1 paper, paper for documents (ISO 9706) and sulphite pulp paper on the overall colour change ΔE^*_{ab} , pH value of a cold aqueous extract, average degree of

polymerisation and selected mechanical properties (zero-span tensile strength, breaking length and elongation) following artificial ageing by dry and moist heat and by artificial daylight. The individual measurements unambiguously confirmed that the studied oxides do not have a negative effect on the monitored properties of the paper supports and do not affect their resistance to ageing. Thus, their use for printing protective codes does not seem to constitute any risk for documents printed on lignocellulose supports, while keeping the identification level satisfactory by means of an handheld XRF analyser. This study is a part of an extensive research which deals also with the long-term stability and reading of the XRF identification tags (Benetková et al. 2020).

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Zusammenfassung

Identifikationsmarkierungen für Archivdokumente auf der Basis von Oxiden von Übergangsmetallen und inneren Übergangsmetallen - Untersuchung ihres Einflusses auf die Eigenschaften des Papierträgers

Diebstähle von Archivdokumenten sind ein ernstes Problem für Archive. Eine mögliche Lösung besteht darin, diese Dokumente mit Codes zu kennzeichnen, die für das bloße Auge nicht sichtbar sind. Eine der Möglichkeiten besteht darin, z.B. Oxide von Lanthan, Dysprosium, Samarium, Gadolinium und Niob zu verwenden, die in XRF-Spektren eine gute Reaktion zeigen und gleichzeitig in Archivmaterialien nicht häufig vorkommen. Diese Studie befasst sich mit der Wirkung dieser Oxide auf die Eigenschaften von Papier. Identifikationsmarkierungen wurden auf drei verschiedene Arten von Papier gedruckt (Whatman No. 1 Filterpapier, Papier nach ISO 9706 und Sulfitzellstoff). Alle Proben wurden nach Aufbringen von Markierungen und nach künstlicher Alterung auf Farbveränderung, durchschnittlichen Polymerisationsgrad, pH-Wert des Extrakts und ausgewählte mechanische Eigenschaften untersucht. Die Messungen zeigten, dass die untersuchten Oxide auf die geprüften Eigenschaften der Papierträger keine negative Wirkung haben und deren Alterungsbeständigkeit nicht beeinflussen.

Résumé

Les marqueurs d'identification pour des documents des archives basés sur des oxydes de métaux de transition et de métaux de transition internes - étude de leurs effets sur les propriétés du papier

Le vol de documents d'archives est devenu un sérieux problème pour les archives. Une possible solution est de signer ces documents avec des codes invisible à l'œil nu. Les possibles marqueurs sont par exemple des oxydes de lanthane, dysprosium, samarium, gadolinium et niobium; ceux ont une bonne réponse dans les spectres SFX et au même moment ne sont pas habituellement présent dans les matériaux d'archives. Les marqueurs d'identification ont été imprimé sur trois types différents de support de papier (papier de filtration Whatman 1, papier selon la norme ISO 9706 et des spécimens de pâte au sulfite). Le changement de couleur, le degré de la polymérisation moyen, le pH de l'extrait et des propriétés mécaniques choisies ont été suivi juste après l'application de marques et ainsi qu'après le vieillissement artificiel. Les mesures démontrent que les oxydes étudiés n'ont pas d'influence négative sur les propriétés contrôlées des supports en papier et n'affectent en rien leur résistance au vieillissement.

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Michal Ďurovič graduated at the University of Chemistry and Technology Prague (UCT Prague) in 1983, with a focus on chemistry of conservation of works of art, such as paper, parchment, leather, photographic and cinematographic materials. He defended his doctoral thesis at the UCT Prague in 1995, and in 2013 he was habilitated at the same university. After finishing his master's studies, he started to work at the National Library in the conservation department. From 1989, he worked at the National Archives in Prague as researcher in the Preservation Department, from 1995 to 2013 as head of the department. He has cooperated with the UCT Prague (Department of Chemical Technology of Monument Conservation) for long time and since 2014 he is head of this department.