



TEST FOR COMPATIBILITY WITH ORGANIC HERITAGE MATERIALS – A PROPOSED PROCEDURE

FULL PAPER

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To evaluate the compatibility of conservation and storage materials with heritage objects of organic origin, a new test method is proposed.

The test is performed in closed vials at 100 °C for 5 days with the tested material and a reference paper in the vial. Volatiles off-gassed from the tested material may cause degradation of the reference paper and lead to a decrease in its degree of polymerization. This is determined using viscometry. The optimal vial type is proposed, leading to reproducible results with a standard deviation for three parallel experiments typically under 2%. The selected reference material, Whatman No. 1 filter paper, being made of purified cotton linters, is susceptible to volatiles promoting both hydrolytic and oxidative degradation, and its response to tested materials is thus likely to be relevant to a wide variety of heritage materials and objects of organic origin.

The case studies show possible uses of the proposed method, and a pronounced pro-degrading effect of ground-wood containing paper on the reference paper is shown, a variety of combinations of rag, groundwood and recycled papers were studied and a number of cardboards used for wrapping or for boxes were evaluated.

The new test is proposed as a repeatable, inexpensive and rapid method of assessment of compatibility of materials used for housing or display of heritage objects of organic origin, thus enabling conservators, providers of conservation materials and collection managers to make better informed selection of appropriate housing or display materials.

1 Introduction

The deterioration of museum objects by gases concentrated inside showcases and storage enclosures was first described by Byne in

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1898.¹ The concept was slow to diffuse into the museum community and only received broad appreciation after Oddy's paper in 1973.² In that paper the simple accelerated corrosion test suggested by Werner, and developed by Oddy was described. It involved cleaning coupons of three metals (silver, copper and lead – the major metals of antiquity that had been found to be susceptible to such corrosion). The coupons were enclosed in a glass tube with the material to be tested and some water to provide an atmosphere of nearly 100% relative humidity (RH). The sealed tube was kept at 60 °C for twenty eight days and the degree of corrosion on the coupon used to assess the suitability of the material for use in display and storage enclosures. The test accelerates the degradation of the material being tested and the corrosive gases are mainly degradation or secondary products.

Initially this was a simple pass or fail test, but the large number of short term exhibitions led to the introduction of a temporary (use for up to six months) classification. The variability in results reported between different users was assessed in 1993,³ and photos and descriptions were disseminated to help standardize the visual assessment of coupons and a second standard method published. An improved method that takes less time to set up the tests was published in 2003.⁴ Alternative methodologies have been published.^{5,6} The necessity for standardization of the methodology and unexpected results from small changes were recently underlined with significant problems encountered with the reaction vessels recommended in one of these modifications.⁷ The improved test recently published by Chen et al.⁸ makes use of silver nanoparticles.

Several alternative spot tests have been developed to produce results faster than the twenty eight days required for the Oddy test,^{9,10} but these are not as comprehensive and a risk remains of corrosion even if materials have passed these tests. The Oddy test is not normally undertaken with ferrous metals as the high RH induces significant corrosion without any test material and it is often impossible to distinguish a greater effect from a test material by eye than from the blank control test which is always run alongside. If the corrosion is quantified, for example by chemical stripping¹¹ then corrosive materials can be identified and excluded from use in storage and display.

The Oddy test has led to increased protection of metals on display and in storage for over forty years and where it has used, there have been no corrosion issues. Results are often extrapolated to other inorganic materials; glass, ceramic, stone

and shell. A material that has passed the Oddy test with lead will certainly emit only very low levels of acetic acid, formic acid and formaldehyde. The concentrations of volatiles developing in storage situations will be well below the no observable adverse effect levels collated for these materials by Tétreault and elucidated further in recent research.¹²⁻¹⁴

However, organic materials are probably susceptible to deterioration from a different range of pollutants than metals, and chemical damage is likely to occur well before any visible change is noticeable. From among the ten most abundantly VOCs emitted from paper (and hence probably from many archival paper storage products) seven were reported to accelerate the degradation of cellulose.¹⁵ Acetic acid has been shown to contribute to degradation of colour photographs.¹⁶

The development of a test analogous to the Oddy test, but determining deleterious effects of off-gassed volatiles on organic materials would be of great benefit to conservation practice. The first preliminary report on this development was published in 2007,¹⁷ and parallel research has been carried out in other groups,¹⁸ demonstrating that there is keen interest in development of a standard testing procedure. In this contribution, we report on the development of a test based on paper as a reference material, both because of its ubiquity and because of its susceptibility to a wide variety of volatiles. Its degradation however, cannot be assessed visually, and the simple (and standardized) method of determination of DP after accelerated degradation is proposed as a method of measurement.

2 Experimental

2.1 Materials

Whatman filter paper No. 1 (Wh, Whatman, Maidstone) is proposed as the reference material. The selection of a standard paper for the test is analogous to the standardized metals recommended for the Oddy test. For papers, as for a particular metal (lead, silver or copper), the composition determines the reactivity and different compositions would give different results. Therefore, the purified cellulosic material, susceptible to a wide variety of volatiles promoting both hydrolytic and oxidative degradation, is proposed for routine use.

The following materials were tested in the case studies:

- P3: STEP project paper P3, alum/rosin sized, pH 5.4, 80% groundwood, 20% cellulose¹⁹
- A1, A2: Two contemporary hand-made papers,

80% groundwood, supplied by Nationaal Archief, The Netherlands

- UL1, UL2, UL3, UL4: four 19th-century rag papers of European origin, 100% cellulose
- Wrapping paper, beige (chamois), produced and supplied by Wijsmuller en Beuns (Wormer, The Netherlands)
- Wrapping paper, blue, produced and supplied by Wijsmuller en Beuns (Wormer, The Netherlands), according to the 'ICN kwaliteitseis no. 1 (2002)'
- Box – cardboard in use at Nationaal Archief (The Hague, The Netherlands) until 1990, i.e. before "Amsterdamse doos" (old) was made available
- "Amsterdamse doos" (old) – first produced for Gemeentearchief Amsterdam in late 1980s, made of acid-free corrugated cardboard according to the 'ICN kwaliteitseis no. 4 (1993)', produced and supplied by Wijsmuller en Beuns (Wormer, The Netherlands)
- "Amsterdamse doos" (new) – made according to the 'ICN kwaliteitseis no. 4 (2002)', produced and supplied by Wijsmuller en Beuns (Wormer, The Netherlands)
- "Amsterdamse doos" (medium) – made in 2002 according to the 'ICN kwaliteitseis no. 4 (1999)', produced and supplied by Wijsmuller en Beuns (Wormer, The Netherlands)

ICN kwaliteitseisen are quality standards produced by the Centraal Laboratorium voor Onderzoek van Voorwerpen van Kunst en Wetenschap (Amsterdam, The Netherlands), which changed its name into Instituut Collectie Nederland in 1997 (ICN, www.icn.nl). The three "Amsterdamse doos" cardboard guidelines did not differ in terms of the prescribed composition: The outer layer of the cardboard should not contain more than 20% groundwood, while the inner layer should be cotton, linen or bleached pulp with an alkaline reserve of at least 0.4 mol/kg (ISO10716). The outer layer of the cardboard should have a minimal pH of 6.5, and the inner one between 7.5 and 9.5, as measured using the cold extraction method (ISO6588). The inner layer should not give a positive reaction to the phloroglucinol test for the presence of lignin (ASTM D1030).

The pH of paper test samples used in the study was determined using cold extraction of microsamples²⁰ in the following way: to 20-50 µg of sample, 5 µL of deionized water was added and left overnight. pH was determined in the extract using a micro-combined glass electrode (MI 4152, Microelectrodes, Bedford, NH).

2.2 Vials

Several vial types were studied, including those proposed in ASTM D6819-02:²¹

- Type A: Schott (21 801 24, retrace code: 00797355) – non-standard 100 mL (Figure 1)
- Type B: Cole Parmer (CZ-13247-45) – non-standard 150 mL
- Type C: Corning (7995-150) – non-standard 150 mL
- Type D: Kontes (K736500-3515) – standard 150 mL

All volumes reported above are nominal. To determine the actual volume of a vial, the weight of water filled to the top of the vial was determined in controlled conditions. The total volume of Schott vials was determined to be 0.132 L in average (N=3). For experiments with very small amounts of paper, 7-mL vials (Supelco 27150-U) were used, with the total volume 8.84 mL.



Figure 1: A Schott (Type A) vial with samples.

2.3 Degradation Experiments

The standard ASTM D6819-02²¹ conditions were used: 100 °C, 5 days. In all cases, 0.0275 g/mL of material was used per vial, regardless of the various ratios between the tested material and the reference paper studied.

2.4 Determination of DP

For determination of the degree of polymerisation (DP) of cellulose in paper, the standard viscometric method was used (ISO 5351/1:1981).²² DP was calculated from intrinsic viscosity using the Mark-Houwink-Sakurada equation:²³

$$DP^{0.85} = 1.1[\eta].$$

Calculation of DP is not strictly necessary, as intrinsic viscosity could be used for evaluation of the results.

2.5 Solid Phase Microextraction Experiments

In order to investigate the emission of VOCs from different materials, the samples were subjected to a thermal degradation pre-treatment in a closed reaction vessel (150 mL) with a PTFE cap,

equipped with sampling valves (Bohlender, Grünsfeld). The sample weight was 4.2 g, and it was degraded for 6 days at 80 °C.

Extraction of the VOCs from the atmosphere inside the reactor was performed using a SPME device with a DVB/CAR/PDMS fibre for 60 min at room temperature. After this, the SPME was transferred to the GC/MS, where desorption, injection and analysis took place.

An Agilent Technologies 7890A gas chromatograph, coupled to an Agilent Technologies 5975C quadrupole mass spectrometer equipped with a Gerstel cooled injection system CIS 4 was used heated to 250 °C. A 60-m Restek RTX-20 column, I.D. 0.25 mm and 1- μ m stationary phase thickness was used. The mobile phase used was helium (99.999%) at a flow of approximately 0.9 mL min⁻¹ (retention times are not constant as the flows in different runs differ slightly). The following oven temperature program was used: 1 min at 40 °C, then heating to 280 °C at the rate of 10.0 °C min⁻¹, after which the temperature was kept constant for 40 min.

Ionisation was performed using standard EI mode applying 70 eV at 230 °C. The interface was heated to 270 °C and the quadrupole mass analyser to 150 °C. The detection was initially performed using total ion current, and after the identification of the most abundant volatiles was performed using the NIST mass spectra library.

2.6 Proposed test for compatibility with organic heritage materials

1. Take Schott (21 801 24) 100 mL vials with Teflon-wadded Polybutylene terephthalate (PBT) caps. If other vials are used, the caps need to have Teflon-lined seals, which is the only material to be in contact with the atmosphere inside the vial. The total volume of the vial needs to be determined in order to always use 0.0275 g of materials per mL of the vial volume.
2. Insert 1.21 \pm 0.01 g of Whatman No. 1 filter paper (Wh), folded.
3. Insert 2.42 \pm 0.01 g of material to be tested.
4. Close the vials at room conditions and insert into a ventilated oven at 100 \pm 1 °C for 120 \pm 0.5 h (ASTM D6819-02²¹).
5. Determine the DP of Whatman after the experiment, following ISO 5351/1:1981.
6. Express the effect in DP_x/DP₀ in %, where DP₀ is a control experiment with Wh in the vial only.
7. Perform the test in triplicate.

3 Results and Discussion

3.1 Optimisation of Experimental Parameters

In development of the procedure, the following was optimized: (i) test vial type, (ii) duration and environmental conditions during the experiment, (iii) amount of sample to be tested vs. amount of reference paper. While the test vials described under 2.2. vary in size, the amount of test material can be adjusted so that the mass/volume ratio is the same (0.0275 g/mL).

Under the standard ASTM D6819-02 conditions (5 days, 100 °C, closed tube), statistically significantly different results were obtained for the four vials used (Figure 2). This result is of considerable interest, since if the amount of paper per vial volume is the same, similar results are expected. However, the DP after degradation differed for up to 10%, which is statistically significant. However, it is worth noting that the repeatability was best using Type A vials.

In closing the vials, no particular tools have been used. The good repeatability of results presented in Figure 2 is at odds with previous reports suggesting that hand tightening might be a considerable source of error.²⁴

Since the only material in contact with the atmosphere inside the vial, beside glass, is the cap, it was therefore of interest to investigate the emissions from the materials of which the caps are made. According to producer specifications, they are made of: Type A – polybutylene terephthalate, however, the cap additionally contains a silicone rubber septum with a Teflon layer, which is the only material actually in contact with the atmosphere within the vial; Types B, C and D –

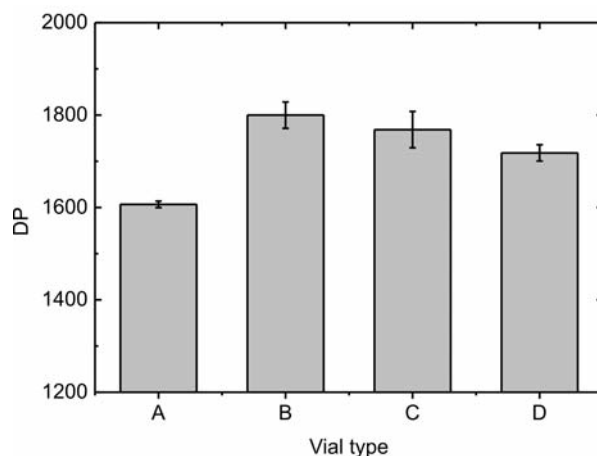


Figure 2: DP of Wh after 5 days of degradation in closed vials of four different types. The error bars represent standard deviation, N = 4.

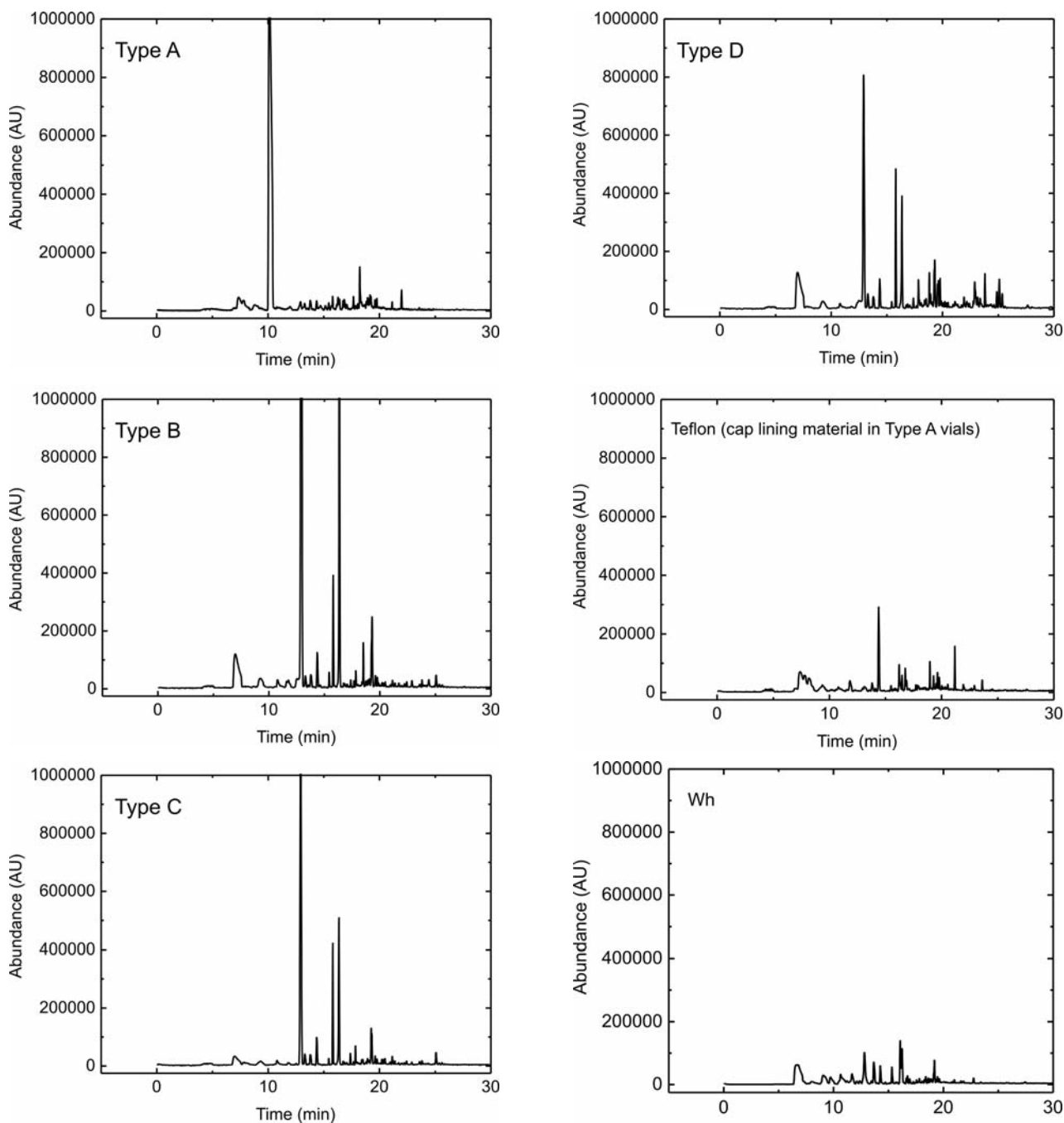


Figure 3: A comparison of total ion chromatograms of VOCs emitted from various cap materials used on vials in the study. For comparison, VOCs emitted from Wh are shown.

polypropylene caps with silicone O-rings. To investigate the emissions from these materials, they were inserted into 150-mL reaction vessels with a Teflon cap equipped with a valve and a Teflon septum, through which SMPE extraction of the emitted VOCs could be performed after a period of degradation. The results of this screening are shown in Figure 3. While a quantitative analysis of the emissions was not of interest, it is immediately apparent that caps can themselves emit high quantities of volatile organic compounds (VOCs), and that their composition can be very different. The effect of these VOCs on paper degra-

dation inside the vial is unknown and can be either positive (if e.g. stabilizers are emitted) or negative (if e.g. acids are emitted). For comparison, the emissions from Wh are shown.

Considering the above, the choice of an appropriate vial therefore appears to be almost arbitrary, however, on the basis of the low emissions from Teflon and satisfactory reproducibility of experiments performed in Type A vials (Figure 2), these can be recommended.

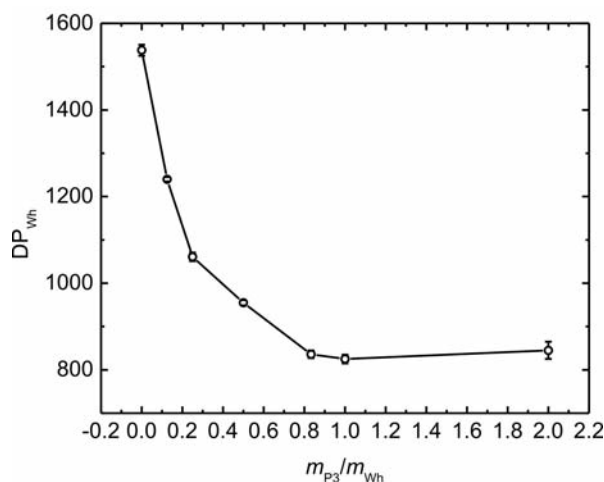


Figure 4: DP of Wh sample degraded in the same vial as P3 paper, in different ratios. Error bars represent standard deviations, $N = 3$. Average standard deviation was 1%.

Subsequently, the amount of tested material vs. the amount of Wh had to be determined. The tested material in this case was a groundwood-containing paper (P3), for which it is known that it emits high concentrations of VOCs.²⁵

During a typical degradation experiment, we studied the effect of various combinations of P3 and Wh. In Figure 4, we represent 7 experiments with various ratios between P3 and Wh, the total amount of material always being 3.62 g. After the experiment the DP of Wh was determined. It is evident that the amount of P3 in the vial has a very strong effect and in order to exaggerate this effect, the ratio 2:1 is proposed – meaning 2.42 g of the tested material per 1.21 g of Wh.

To calculate the effect in relative terms for comparative purposes, DP_x/DP_0 can be calculated. Pure cellulose retains only 55% of its DP if degraded in the vicinity of acidic groundwood containing paper. This is often the case in archival folders with mixed materials, and the result may provide a benchmark for classification, as discussed in section 3.4.

From the experiment in Figure 4, it is evident that a paper high in lignin content could have a potentially very strong negative effect on the degradation of other paper at room temperature. This is sometimes evident in collections: e.g. cardboard-based book covers affecting the degradation of paper in close contact. While it is known that acids and aldehydes are among the most abundant VOCs emitted from groundwood paper,²⁵ it is not clear how they affect the stability of cellulose either individually or in combinations. The proposed test therefore represents an attractive and rapid test making such evaluations possible.

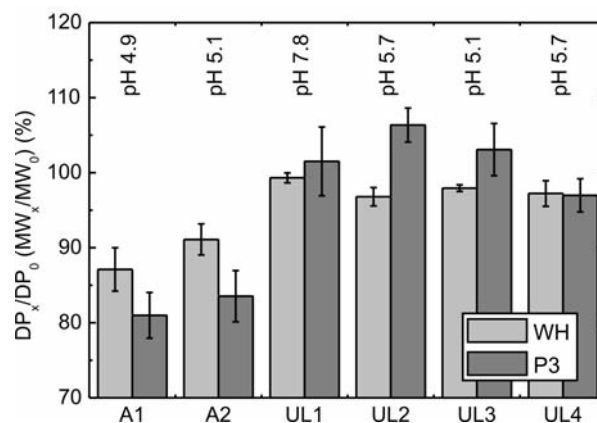


Figure 5: DP of Wh or P3 reference samples degraded in the same vessel with different tested papers, as indicated, vs. the DP of the same reference sample, degraded in a control experiment. Error bars represent standard deviations, $N = 3$.

The effect is not necessarily negative, however, if the tested material acts as a VOC absorber. This will be further explored in the following case study.

3.2 Case Study 1: Effects of Different Paper Types on Each Other

To show that papers of various compositions could have protective effects on each other, we studied various combinations of groundwood and rag papers with the standard Wh test paper, but also with P3 as a test paper. Due to the lack of materials, particularly historic rag papers, this study was performed in 8.84 mL vials (nominal volume 7 mL).

The DP of Wh (or MW of P3) degraded in the presence of another paper compared with the control experiment (Wh or P3 in the vial only), enables us to evaluate the potential effects various papers can have on each other. From Figure 5 it is evident that the effects can be negative, if the test paper promotes the degradation of the reference paper, but can also be positive, if the test paper is an effective absorbent of VOCs and thus contributes to their removal and as a consequence, inhibits the degradation of the reference paper.

The effect of the two groundwood-containing hand-made papers (A1, A2) on the degradation of Wh is negative. On the other hand, various rag papers have no or only a very slightly negative effect on the degradation of Wh. The negative effect of A1 and A2 papers on P3 is pronounced, while the effect of rag papers is either neutral or even slightly positive. The alkali reserve in rag papers must be a good absorber for VOCs emitted from P3 and thus contributes positively, even if only slightly, to its less pronounced degradation.

A similar study on the effect of iron gall ink documents on degradation of paper in the vicinity was

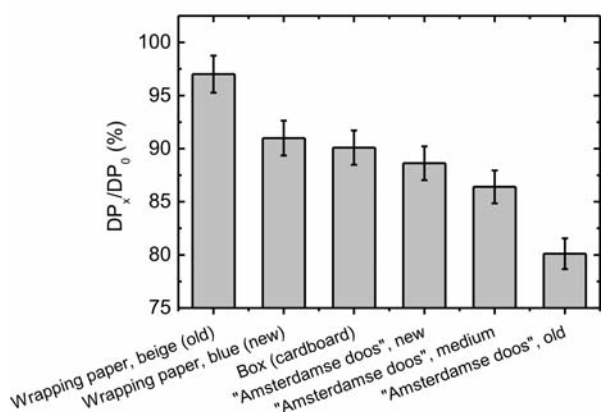


Figure 6: DP of Wh degraded in the same vessel with different materials, as indicated. Error bars represent standard deviations, N = 3.

recently published, demonstrating a significant effect of emissions of reactive oxygen species (hydrogen peroxide) from ink-containing paper.²⁶

3.3 Case Study 2: Boxing and wrapping materials

In this case study, we studied various boxing and wrapping materials (various types of cardboard), in line with the proposed methodology (section 2.6). In all cases, 2.42 g of the material was used against 1.21 g of Wh in the vial, and the degradation was carried out at 100 °C for 5 days.

In Figure 6, the effects of degradation of test materials on the ageing behaviour of cellulose are comparatively assessed. The lower the DP of Wh after the experiment, the more the emissions from the test material accelerate the degradation. It is evident that all materials studied affect the degradation of Wh negatively, and do not offer protection against degradation.

It is also of interest that the three "Amsterdamse doos" cardboards give different results, despite being produced according to the same material specification. The outer layer of this material could contain up to 20% groundwood, and could be slightly acidic, and considering the variation allowed by the specification, the different results obtained for the different types of the same wrapping material are perhaps less surprising.

3.4 Further Considerations

The proposed test for compatibility with heritage materials of organic origin is rapid and easy to per-

form, and can be employed to survey conservation materials in close contact or proximity to heritage objects. The negative (or positive) effect, which is evaluated using this test, is only related to *emission* (or *absorption*) of volatiles, however, and not to *migration* of non-volatile compounds from one material to another in close contact.

The choice of Wh as the reference paper is based on the observation that it is a widely available, well-studied²⁷ paper type and that its emissions are low in comparison to other heritage materials. In most combinations, it will therefore act as an absorbent. Being neutral and containing no alkaline reserve, it is also susceptible to both hydrolytic and oxidative degradation, so that emissions of various types of volatiles will affect its stability. This is particularly useful as Wh can thus serve as a good reference for various heritage materials degrading either hydrolytically or oxidatively.

However, it may turn out for the chosen temperature of 100 °C to be too high due to melting or rapid decomposition of some materials – e.g. certain waxes or glues. In such cases it may be necessary to perform the experiments at lower temperature to prevent such physical phenomena from affecting the chemistry of emission. Namely, the absence of constraints in molecular movement in melted materials (or plastic materials above the glass transition temperature) leads to faster degradation processes than below the phase transition temperature, and in such a case the test would give an overestimated value. In any case, it is important to note that the tests performed at 100 °C not necessarily compare with the behaviour of the tested materials at room temperature, as emission and absorption of volatiles are temperature-dependent phenomena.

A particularly useful feature of the test is the measurement method giving a range of values instead of a pass/fail decision. This allows for storage/display materials to be classified in various categories, from considerably protective to considerably aggressive, once a larger database of material performances is made available. However, the effect will always be relative to the amount and function of the off-gassing material present in a real situation. Since off-gassing is a function of time, it is likely that test materials may categorise better after certain time has passed after production. Not only materials, but also other strategies of environmental modification could be classified this way, e.g. the use of anoxic environments, VOC scavengers or other protective measures.

Thus, the effects of various tested materials or protective measures (removal of oxygen) on the standard Wh paper can be either *negative* (the emissions from the tested material lead to faster degradation of Wh than in the control experiment) or *positive* (the tested material or protective measure increases the longevity of Wh compared to the control experiment). Using the proposed test for compatibility with heritage materials of organic origin it is foreseeable for a database of evaluated materials to become available in due time. It is feasible that on this basis, the proposed test could become a standardised test and a classification system for conservation materials in close contact with organic heritage materials could be developed, e.g. from very beneficial to neutral to very negative.

Thus would enable the users (conservators, collection managers, companies) to make the right choice when selecting appropriate housing, display or conservation products.

4 Conclusions

A new test for compatibility with heritage materials of organic origin is proposed, based on accelerated degradation of a reference paper (Whatman No. 1 filter paper) in the presence of the material under evaluation, in a closed vial at 100 °C for 5 days. The degradation of the reference paper is assessed in terms of DP decrease, and compared to a control experiment. It is proposed that vials with Teflon-lined seals are used, e.g. Schott (21 801 24), 100 mL. These vials gave highly reproducible results and the standard deviation of DP of the reference paper for three parallel experiments was typically under 2%.

The selected reference paper is sensitive to volatiles promoting both hydrolytic and oxidative degradation, and its response is thus likely to be relevant to a wide variety of heritage materials of organic origin.

Several case studies are presented. A very pronounced negative effect of groundwood containing paper on the reference paper is presented. In an assessment of a variety of combinations of rag, groundwood and recycled papers, a high variety of interactions is presented: both protective and pro-degrading effects are possible if two materials are aged in close vicinity. A number of cardboards used for wrapping or for boxes were also evaluated.

Using the new test, the effects of volatiles emitted during degradation (or drying) of materials used for housing or display can be studied systemati-

cally and made available to users (conservators, producers of conservation materials, collection managers), thus allowing for better informed decision making.

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