The Oddy test

What works and what doesn’t
The Oddy test

Time and again we receive anxious inquiries regarding the significance of the Oddy test results. The Oddy test is used to roughly estimate the suitability of materials used in display cases, cabinets, museum showrooms and packaging.

When it comes to the significance of the information provided by the Oddy test, the opinion amongst the experts varies greatly. We have, therefore, requested Prof. Dr. Gerhard Banik to outline the scope and limits of the Oddy test.

In the KLUG Technical Knowledge folder no. 5 we are publishing his report on the Oddy test, accompanied by a comprehensive bibliography. With this we hope to provide you with more clarity regarding the Oddy test and we are happy to advise you any time personally, in order to help you find the most suitable material for your display cases, cabinets, exhibition spaces as well as for the cases and boxes used for long-term archiving.

Michael Kühner

Peter Lang
Prof. Dr. Gerhard Banik

Application of the Oddy test – a commentary

Gerhard Banik, who was the Director and Professor of the “Konservierung und Restaurierung von Graphik, Archiv- und Bibliotheksgut” course at the Staatliche Akademie der Bildenden Künste Stuttgart until 2008, has closely studied the use and application of the Oddy test.

Scope and limits

The Oddy test was first proposed by Antony Werner in 1973. In 1975, Andrew Oddy, who was working in the British Museum’s scientific department at the time, developed it into a replicable testing method to detect volatile contaminants (VOCs*) presumed to offgas from materials used for preparing display cases. Toxic materials could then be excluded from display cases used for museum exhibits (Oddy 1975). The Oddy test is a corrosion test in which contaminants induce corrosion of three indicator metals (silver, copper and lead) exclusively via the gas phase, at a relative humidity of 100%. The indicator metals should be evaluated after a treatment period of 28 days at 100 % relative humidity and 60 °C.

*VOCs = Volatile Organic Compounds
The testing method is described in a 1979 publication by Lee and Thickett, in which the authors expressly point out that: “The following recommended method should be followed exactly”. According to this method, two grams of the sample material are cut in small pieces and placed on the bottom of a clean glass container, such as an Erlenmeyer flask. The purified indicator metal is suspended on a nylon thread above the sample, and, in order to adjust the relative humidity, a glass vessel filled with distilled water is also placed at the bottom of the flask, which is then hermetically sealed with an appropriate plastic or glass seal. After that, thermal treatment is conducted over the predefined treatment period of 28 days in a drying cabinet at a constant temperature of 60 °C. An improved and simplified procedure can be found in a more recent publication by Robinet and Thickett (2003), which is also the version taught in training courses on the Oddy test offered by HTW Berlin (see References).

Despite the fact that the authors strongly emphasise strict adherence to test design and methodology, not least for the purpose of comparability of findings, about 20 different protocols are currently in practice, most which are conducted at museum laboratories or by freelance conservators. As a consequence, it is important to stress that results that have been obtained and occasionally published are neither comparable nor reproducible and in many cases fraught with considerable inaccuracies.
The reason that the Oddy test is subject to considerable uncertainty, is primarily due to the following facts:

1) Corrosion of test metals at 100% relative humidity (RH) is substantially different from corrosion under "normal" relative humidity conditions (50% RH).

2) Corrosion of test metals in direct contact with tested materials is substantially different from corrosion due to a mere gas phase reaction with the substances (VOCs*) offgassed from these materials.

3) Corrosion of test metals is crucially dependent on how the surface of the metals has been prepared for the test. This includes the precision of, both, how the surface is ground and how it was subsequently cleaned. In any case, for comparability of results and interpretation of any corrosive change in at least one of the test metals, it is essential that the indicator metals must be ground and cleaned with absolute accuracy. To this end, Lee and Thickett’s directions as well as those from other publications (Zhang et al. 1994, Robinet and Thickett 2003) are applicable.

4) Corrosion of the three test metals, silver, copper and lead, is in most cases due to three substances (VOCs*) offgassing from tested materials: hydrogen sulphide or other volatile sulphides (in the case of silver), acetic acid (copper) and again acetic acid (lead). Albeit, the exact mechanisms of each individual corrosion process are barely assessable on visual inspection in the case of mixtures of offgassed contaminants.

5) In addition, intensive colour changes occur on the surfaces of copper and lead due to the formation of oxide layers, which manifest themselves by distinctly obscuring the metal surfaces.

6) Comparison of the changes that occur in the metal surfaces according to steps from "no corrosion" via "slight corrosion" to "strong corrosion" is subject to the observer’s subjective impression. Therefore, it cannot and must not be regarded as a reproducible and unambiguously interpretable scientific measurement result for assessing tested materials.

7) Sampling, manipulation and storage of the materials to be tested in workshops and laboratories can substantially affect the test result, which, in case of storage, is due to contaminants present in the air that the materials may absorb.

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Accordingly, the Oddy test is an analytical instrument that is not precise enough to interpret the causes of corrosion phenomena or discolouration of indicator metals. Its use has been, and still is, a topic of controversial debate (Grzywacz 2006), despite its broad use in museum world. The test is only and exclusively suitable in detecting whether contaminant gases are emitted from certain materials under the respective experimental conditions. It cannot be used to inform about any deducible risks affecting other materials which are in any contact with the test materials during prolonged periods of time. Direct transfer of data is only permissible, although with restrictions, for the test metals and realistically should be restricted to silver (turns black to form silver sulphide in the presence of contaminant gases containing sulphidic sulphur) and lead (white crystalline deposits as basic lead carbonate and/or lead acetates is generated upon release of acetic acid). More details on lead corrosion in the presence of acetic acid can be found in Tetreault (1998).

More recent studies from the years 2003 and 2011, all listed in the References section, refer to slightly more precise testing methods, such as an optimized Oddy test (Robinet and Thickett, 2003) and a modified design with more precise analytics (Strlič 2011).

The method proposed by Strlič appears to be particularly apt to measure the level of risk for cellulose-based materials more accurately. However, this test requires a significantly higher degree of analytical effort.

As for the examination of cellulose-based materials like paper and board that are used for permanent storage of cultural possessions, one can find a number of pointers in Strlič’s work. These, however, are in need of further verification. It is known fact that gaseous contaminants have an affect on the durability of paper, although the magnitude of the risk depends on the composition of the paper and the particular compounds present in the contaminant. It is worth mentioning that, while gaseous acids have a considerable impact on paper, aldehydes may also cause paper to degrade, as they can oxidize into acidic components. Acetic acid is emitted by lignin-containing papers as they age, but based on current research results, (Di Pietro and Ligternik 2012, Potthast et al. 2012) their occurrence has little effect on the stability of paper. In addition to acetic acid, formic acid and other compounds, whose impact is still barely assessable, may also be present (Meyer et al. 2014). It is especially important to note that all board and paper based artefacts also emit acetic acid as they age, and naturally this accumulates when they are encased in containers.
It is remarkable how the DIN ISO 16245:2011-04 standard does not specify any criteria pertaining to materials used to encase gaseous contaminants and their accumulation in containers. Collectors could consider modifying their respective standards. The reason for this is that in addition to boxes and assembling materials, all of which emit acetic acid and other substances (VOCs*) at least to a limited extent, collected artefacts within containers may also emit acetic acid. The extent of the damage that could result or has already resulted due to accumulated acetic acid concentrations is hard to assess. Of course, if there were to be major damage, it would be clearly visible in a number of collected objects, particularly if colourations are acid-sensitive.

Likewise, museums should also contemplate on whether to uphold the existing version of the standard pertaining to materials that are used to encase collected items (DIN ISO 11799: 2005-06), even though current research results suggest that the detrimental effect of acetic acid on cellulose is negligible. In the existing standard, the threshold value is set to < 4 ppb for the concentration of acetic acid and to < 4 ppb for formaldehyde.

References


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