The Cole Course Protractor - Building of Whisker Crystals through Interaction of Copper Alloy and Cellulose Nitrate. Or: How to Conserve a Self-Destructing Composite Object?

Extract from the Bachelors Thesis at the University of Applied Sciences Berlin, 2018.

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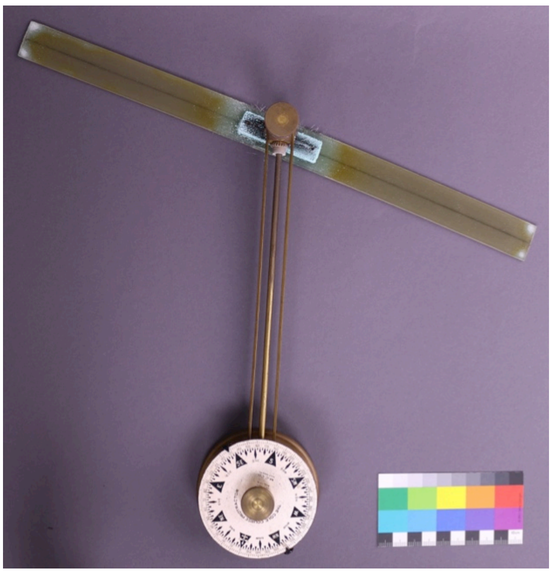
Abstract

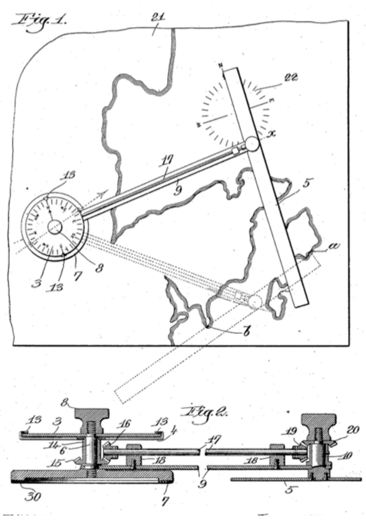
A great range of objects of everyday use as well as films and art works has been produced out of cellulose nitrate between the end of the nineteenth to the first third of the twentieth century. These today present a challenge to museums and conservators because their harming potential towards other objects in storage and exhibition areas is elevated, especially in closed vitrines or when in direct contact with other materials. Since the degradation process is autocatalytic, objects made out of cellulose nitrate are like a time bomb and also a danger to themselves!

In this case study of a nautical orientation instrument, the processes showed a new phenomenon, whose causes and effects were investigated and a long-term solution for storing elaborated in a bachelor's thesis at the University of Applied Sciences of Berlin.

The object: A "Cole Course Protractor"

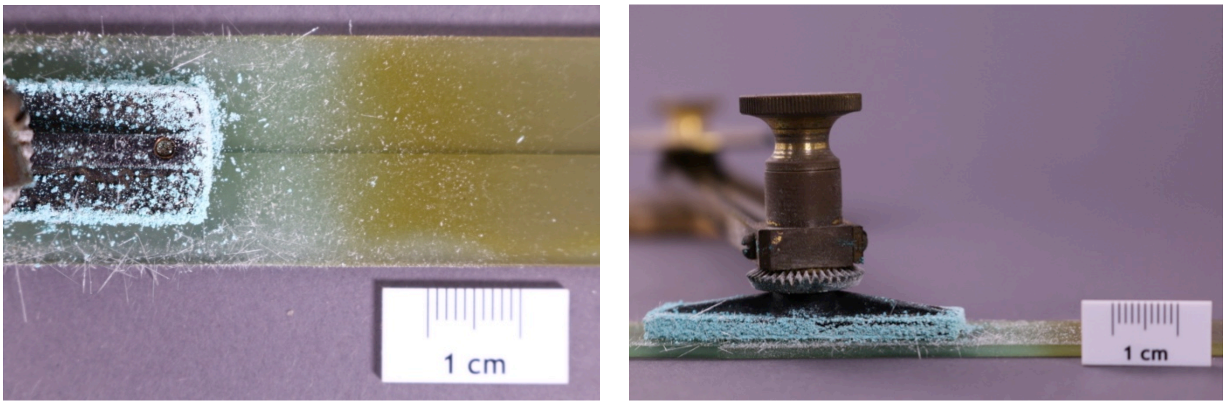


The object before treatment (picture taken by the author, 09/2017).

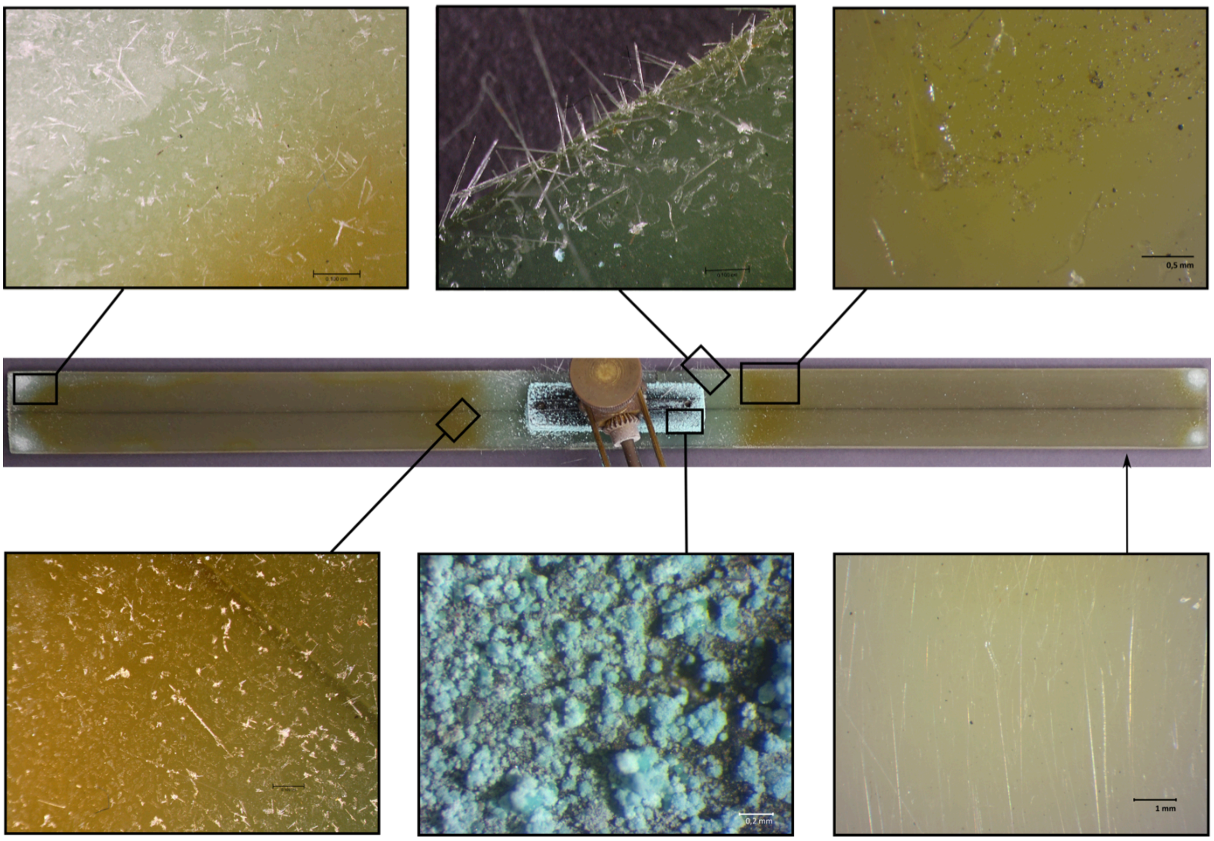


Detail from the front page of the 1907 patent, showing the application and the single parts of the Protractor (source: https://patents.google.com/patent/US8689069).

As a means for drawing courses of ships onto maps, the Protractor was produced in the 1920ies in Bryantville, Massachusetts (USA). It combines a compass with a ruler element to help find the direction of a chosen course on a map quickly and to be able to draw them at the same time using only one instrument. Its inventor John F. Cole patented this first version of the "Cole Course Protractor" in 1907 and a second, more flexible one in 1919. Nonetheless, both were fastly replaced by more efficient instruments and represent a rarity in nautical collections. The Protractor here treated had been acquired in 1989 by the German Technical Museum of Berlin and did not show signs of ageing until 2017, where it began to fail dramatically. Not only did the ruler elements' colour change rapidly, also fine transparent needle-shaped crystals formed on its outer rims.



Details of degradation phenomena on the object (pictures taken by the author, 09/2017).



Microscopic views of degradation phenomena of the Protractor (pictures taken by the author, 10/2017), up left to down left:

1) Opaque, discoloured, yellowed and uneven surface of the plastic with crystalline particles.

2) Needle-shaped crystals and uneven, inhomogeneous surface with transparent, fluid particles.

3) Oily brown-yellow stain on the plastic's surface of unknown provenience.

4) (Center) Course Protractor, detail with location of the microscopic photographs.

5) Partially elevated yellowing of the cellulose nitrate in vicinity to the blue-green discoloured areas.

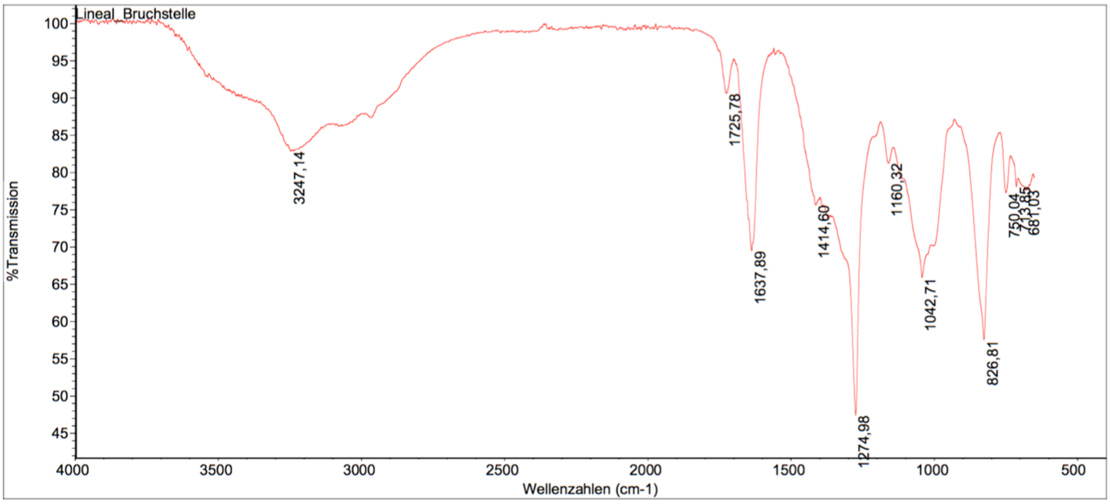
6) Corrosion products on the surface of the metal connecting piece.

7) Parallel, very fine scratches on the downside of the ruler.

An investigation of the composite object and the causes and processes of its degradation became urgently necessary, starting with the analysis of the materials presented in the next lines.

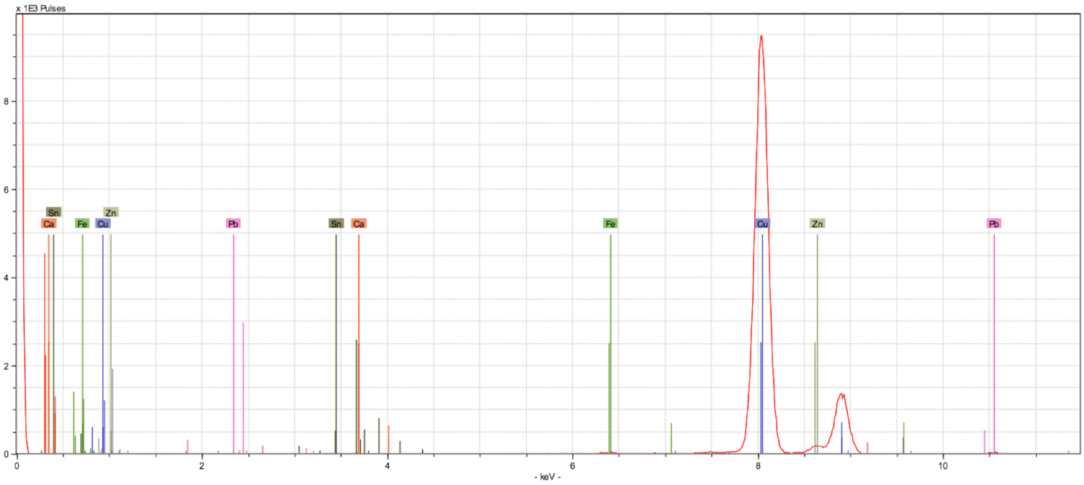
Analysis and materials

The time of production, the appearance and the degradation phenomena of the plastic part gave indication on the material to be possibly either cellulose acetate or cellulose nitrate. An FTIR (Fourier-transform infrared spectroscopy) analyses confirmed that it is cellulose nitrate, but unfortunately it did not help identify a plasticiser nor the nature of the crystals.



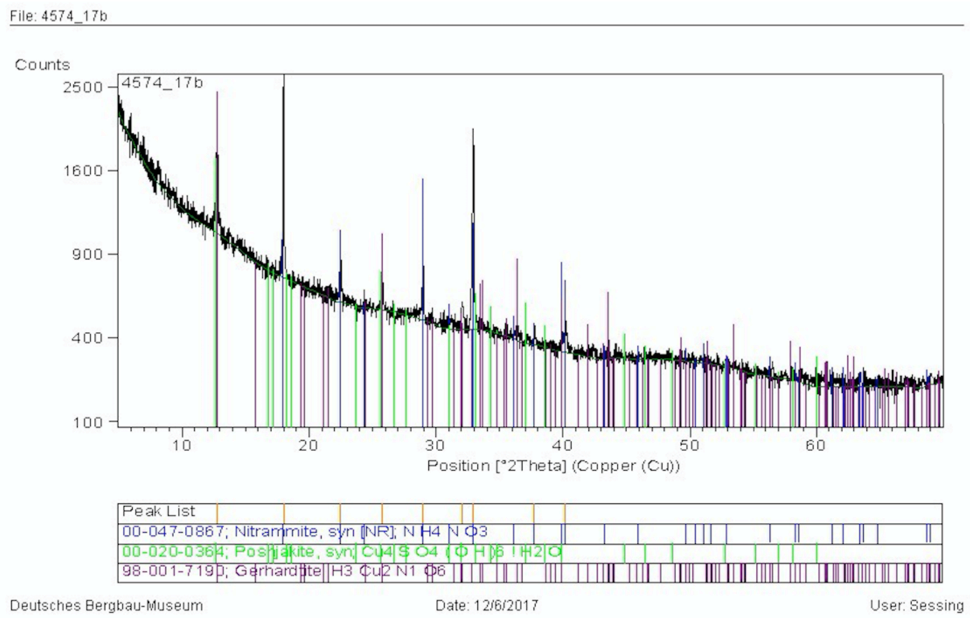
FTIR spectrum of the ruler (taken at the University of Applied Sciences Berlin).

Through an XRF (x-ray fluorescence spectroscopy), the metal parts could be specified as an alloy of mostly copper and zinc.



XRF-graph of the metal connection part to the ruler element (taken at the University of Applied University Berlin).

An XRD (x-ray diffraction) analysis of the needle shaped degradation products on the outer rims and edges of the ruler identified them as composed by copper nitrate, copper sulphate and ammonium nitrate[1].



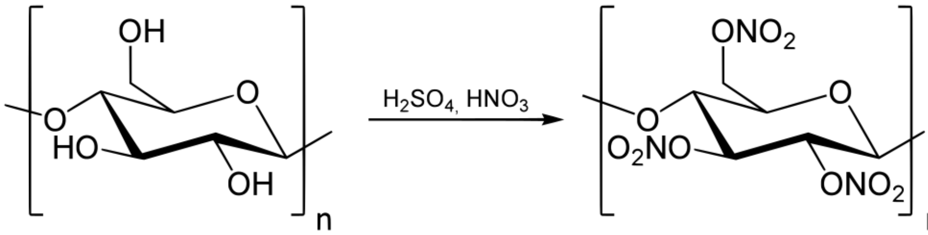
XRD graph of the needle-shaped crystals (taken at the Deutsches Bergbau-Museum Bochum).

Thus the conclusion was drawn that an interaction between the metal and the plastic part had taken place. To understand how the two materials could react chemically with each other, both materials were studied regarding their production and degradation processes.

[1] The presence of ammonium nitrate was first believed to be a consequence of a darkening technique of the brass. During cleaning, though, the dark surface revealed itself as an organic varnish. Thus further analysis and research is requested to clear where the ammonium comes from.

Cellulose nitrate

To obtain cellulose nitrate out of its raw materials cellulose from cotton, nitric acid and sulphuric acid (the latter acting as a catalyst), the OH-groups of the cellulose molecule are being substituted by NO_3-groups:



[2]

The addition of plasticizers, such as camphor or phthalates helped the product becoming workable and less brittle.
But these modifications of the cellulose are reversible, and with time the material reforms the raw products it is based on: cellulose, nitrogen dioxide - that with humidity of the surrounding air turns into nitric acid, some sulphuric acid, and only physically bound plasticizers. Besides for this degradation process known as de-nitration, physical and chemical factors can lead to the breakdown of chain molecules. The loss of plasticizer weakens the structure of the material and leaves gaps that can fill with water from air humidity. Once induced, thermal, photochemical and hydrolytic reactions cannot be stopped, but only slowed down. The most harmful influence on cellulose nitrate is the contact with water and humidity, since volatile nitrogen gassing off will form nitric acid on the surface and thus create an acidic environment causing further breakdown.

Copper zinc alloy (brass)

The degradation of metal is based on various forms of corrosion, induced by chemical or electrochemical processes. Electrons from the metal cloud are exchanged with protons from the environment through an electrolytic solution (e.g. a solution of a salt) and oxygen. But also the contact with metals of a different voltage potential, resulting in an anode-cathode-reaction, can be the cause. Copper alloys, as other metals, build up a stabile oxidation layer on their surfaces that generally prevent them from further corrosion.
The combination of the two materials brought about additional degradation mechanisms, that are explained in the next paragraph.

[2] https://de.wikipedia.org/wiki/Cellulosenitrat#/media/File:Synthesis_Nitrocellulose.svg

Interaction of materials: catalysis and capillary condensation

In the case of the Cole Course Protractor as a composite object, it was not only the single degradation processes of the materials that caused parts of it to fail.

Since the degradation products of cellulose nitrate form a salty solution with air humidity, they provided the condition for corrosion of the copper alloy. On the other hand, copper ions from the metal element in direct contact with the cellulose nitrate accelerated its breakdown through catalysis and reacted with the nitrate and sulphate forming the needle-shaped transparent so called Whisker-crystals. The reason for their appearance only in the outer areas of the ruler might be that during exhibition in the last 15 years, the ruler was placed on a plastic film in the same size to isolate it from the underlying paper map. Thus, every time the climate changed inside the vitrine, humidity couldn't diffuse to the bottom side and instead wandered, with the help of capillary condensation forces, to the borders and edges of the ruler, most likely along the extension direction of the cellulose chains. There it resulted in crystals by the evaporation of the transportation liquid.

After the identification of the operating factors, it became clear that the two materials had to be separated to stop their harmful interaction. The restoration and conservation treatment of the object according to this understanding is described in the following.

Restoration and Conservation

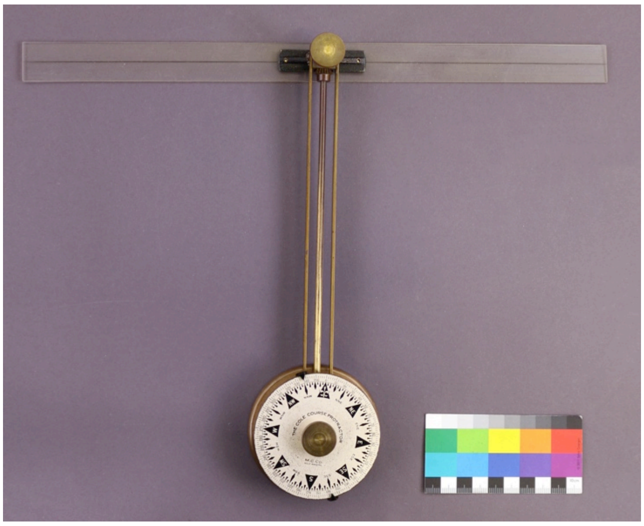
The first step to prevent further damage was clearly to dismantle the object. The two parts were held together by two screws on the bottom side of the ruler that were additionally glued into the thread inside the metal element. Thus it was impossible to simply screw them out without causing further damage to the sensible cellulose nitrate ruler. They had to be drilled out, losing the screws.

The bottom side of the connecting metal element was thickly covered in light blue-green copper corrosion products. These were taken off mechanically with different brushes, erasers and an ivory scalpel, also on other affected spots of the object. Dust and corrosion particles were removed from the ruler's surface with a latex sponge. The remaining degradation products were cleaned off with cotton swabs and white spirit.

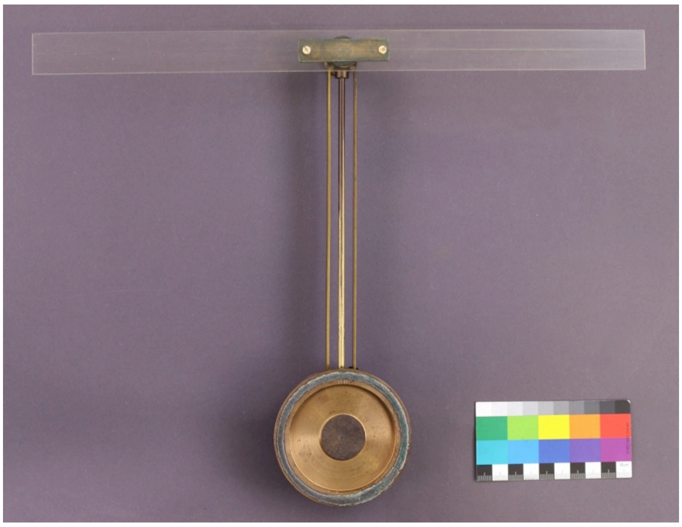
Even though the museum climate is adequate for metals (humidity levels at around 40 % rH), the metal parts were conserved by applying a layer of microcrystalline wax to protect them from possible contact with bare hands during handling.

In the case of the cellulose nitrate element, the conservation was more complicated to decide on. Even during the short period of this study (6-7 months), the condition of the plastic had undergone some visible change. Due to the unavoidable but forced dismantling, a few new cracks had formed, one of which led to the break up of a fragment. This fragility will very likely increase with rising age and the hazardous effects of volatile degradation products on the object itself as well as other materials had to be taken into consideration. For this reason it was decided on a separate storing of the cellulose nitrate, in a dark, cool and isolated environment. A storage box out of acid free cardboard was built in a way that the ruler fitted exactly inside, without the possibility to move when the box is being moved. The plastic is also wrapped in a layer of activated carbon textile to absorb off gassing nitrogen and nitric acid which has to be exchanged periodically.

The object, as part of the permanent exhibition of the Deutsches Technikmuseum Berlin, was supposed to return to its place in the vitrine. Therefore it needed a replacement for the plastic part to keep its function understandable to the museum visitors. This was created in Plexiglas, adding the central line through milling and colouring with a pencil. The replacement then was screwed into the metal connecting piece with two new brass screws. Its transparent and modern appearance in contrast to the rest of the object was diminished by a slight yellowing of the plastic applying several layers of shellac onto its bottom side with a brush.



Object (frontside) after treatment, including replacement ruler (picture taken by the author, 03/2018).



Object (rearside) after treatment (picture taken by the author, 03/2018).