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COMMENTS ON THE BARROW DOUBLE METHOD FOR DEACIDIFICATION

I was asked to make some comments on the use of the Barrow double method for deacidification of archival material of paper.

After some research, I introduced the method in the Danish National Archives in the autumn of 1967, but for technical reasons we were not able to work in the method until at the beginning of 1969. Since then the method has been in daily use so my experience in that field only counts eight years.

The three main reasons for deterioration owing to acidity in paper are the following:

First the "built in" deteriorater alum. In the 19th century there was a rapid increase in consumption of paper. The paper manufacturers used any raw material of which they could make paper, and owing to lack of knowledge of chemical and physical influence of the raw materials used in the manufacturing of paper, restorers around the world to-day have very many problems to get the enormous amounts of archival paper material (deteriorated by acids caused by deposits of alum from the manufacturing process) restored and saved from further deterioration. Until two years ago, almost all conservation from all over the country was made here in our workshop in the Danish National Archives, and we therefore had materials of all sorts. To-day all the workshops of the four provincial archives are able to do their own deacidification.

But back to reasons. Because of access to so different materials as churchrecords and a lot of official documents of all sorts, I was able to do some research on products from

several small paper manufacturers, and by this research I found support for my suspicion of the alum as a "built in" deteriorater. At that time as well as to-day, the manufacturers had to report monthly to the customs about import of raw materials and the amount of production sent to the market. We therefore know that in the year 1835 the paper manufacturer P.C. Deichmann in Copenhagen used 21 barrels of alum in the production of about 2,5 - 3,5 million sheets of paper, and unfortunately this paper was mostly used in the central administration for churchrecords and other official documents.

P.C. Deichmann made a nice hard paper to write on which gave a suitable low friction between the paper and a goosepen. Paper was expensive and Denmark was poor, so the smoother the paper, the more writing the church ministers could do on a sheet of paper.

It is a well known fact that high relative humidity and a high temperature activate the alum to decompose into sulphoric-acid and aluminium. To-day we can show many typical examples of the P.C. Deichmann paper from about 1830 - even paper that has never been touched by a pen, and still it is completely deteriorated.

Our next problem in the row of deteriorater by acidity is the oxidation by iron-inks. Much has been said about the possibilities of restoring the material after attack by ink-acid, but everybody knows that if paperfibres have once been broken down, there is so to speak no way back - the cellulose is decomposed and the fibres have become hard and brittle - a material that easily disintegrates to dust.

What we can do is to stop a further migration of the ink-acid to the healthy surroundings i.e. fibres not yet being in contact with the ink. This can be done in two ways: The first

one is to keep the material as much chemical inactive as possible until treatment. The temperature must be kept at a low level - (about 15° Celcius) - and the relative humidity must be kept at about 50% ± 5%. The second way is to deacidify and to create a buffer to prevent a further breakdown.

The third problem of acidity in paper arises from the pollution of the surroundings. To illustrate that, I have made a test to show how easy it is to get archival material polluted by the surrounding air without any visible signs at the moment when it occurs. I collected 50 sheets of non-written papers for census lists from 1872. Each sheet was divided into five test strips marked a1-a2-a3, and so on. All strips were tested for pH-value before any other treatment was made. Each set of strips, for instance a1 - a50 was treated according to the Barrow double method, b1 - b50 was treated with barium hydroxide, and so on. a, b, and c 1-12, and a,b and c 26-37 were stabilized by methyl-cellulose, some of the strips were bleached while others were not, following the same order. Set no. e 1-50 was kept as zero test strips. All strips were divided into halves having the dimensions 150 x 25 mm. Half of the material was kept in acid-free packing material in one of our storage rooms for 60 days, and the other half was exposed to ordinary office-air for 60 days - the same way in which very much of our archival material is kept in the historians' workrooms - sometimes for a very long time.

All strips were tested for pH-value just after the first treatment and again after 60 days. The material was also submitted to several physical tests, but time was too short, and no real differences in strength turned up. It will be too much to describe the whole test in this context, in order to give the figures of the pH-values after 60 days. Before any treatment had been effected, all the strips showed a pH-value

of about 4,3 without much variation. After the first treatment the pH-value was about 8,2 - the pH-value of the strips treated with bariumhydroxide was a little higher, while the pH-value of the strips treated with calcium was a little lower. After 60 days the material which had been kept in an acid-free packing showed a pH-value of about 7,7 - the pH-value of the material treated with barium was a little higher and the pH-value of the material treated with calcium a little lower. The material which was exposed to open air showed a pH-value of about 6.7 - 7.1, and there were no differences as to the different treatments. I am not completely convinced by a short test as this one, but it showed one thing: the pH-value fell more rapidly in exposed material than many restorers expected. As the test mentioned has only been running for 60 days, we now make a test in our laboratory that will run three to four years.

How we conduct the Barrow double method.

After having received archival material to conservation we point out the treatment for the material and afterwards the pH-value is measured. If the material has to pass a deacidificationprocess, we decide which type of deacidification to make. If the Barrow double method is chosen, the procedure is as follows, Theory: It is well known that calcium as a member of the second main group of the periodical system gives a strong base and neutral salt with a strong acid.

$$Ca(OH)_2 + CO_2(g) \rightarrow CaCO_3 + H_2O$$

With the Calcium hydroxide we get a strong base, and to stabilize the pH-value of around 7,0, we therefore use a weak acid:

$Ca(HCO_3)_2$ Calcium bicarbonate

To make $Ca(HCO_3)_2$ we bubble $CaCO_3$ washed out in water with CO_2 in twenty minutes:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

Practice: Dissolve 1,5g of $Ca(OH)_2$ per litre H_2O + extra 0,5g of $Ca(OH)_2$ per litre to react with the free CO_2 (Carbondioxide) normally dissolved in water.

Material to be deacidified is submerged in this solution in twenty minutes. Afterwards excess fluid is pressed out, and the material is ready for the next bath.

Wash out 2,0 g of $CaCO_3$ per litre H_2O and bubble this solution with CO_2 in twenty minutes to make $Ca(HCO_3)_2$ (Calcium bicarbonate). After the first bath the material is submerged in the next bath - this is the reason for the name Barrow double method. The material remains submerged for another twenty minutes, and then the thoroughly wet material is taken out of the bath and placed sheet by sheet on dryingshelves to dry and thereby establish a neutral carbonate.

200 sheets are under preparation at the same time. Each sheet is placed on a sheet of filterpaper. All 200 sheets are submerged in the first bath,and the excess solution is pressed out in one operation by means of a graphic rubber roll.

It is of the greatest importance to have a well equipped drying place especially when large amounts of material have to be prepared. It has been said that the Barrow double method has too heavy an influence on the ink. It may by true as to paper and inks from the last half of the 19th century and later, but it is our experience that material from earlier periods comes out brighter and that the paper regains some of its old strength.