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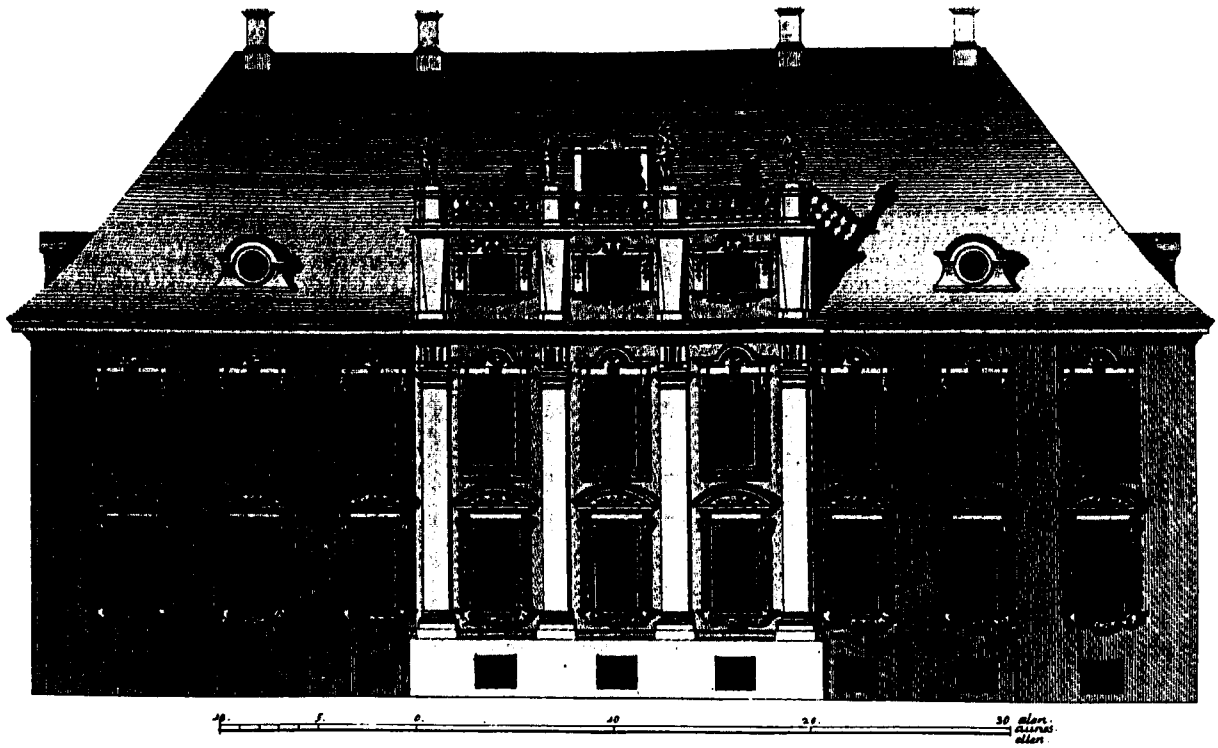

The *Moltkes Palæ*, Copenhagen, engraving from *Hafnia hodierna* by L. de Turah, published 1748

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CONSERVATION OF WATERLOGGED ORGANIC MATERIALS: COMMENTS ON THE ANALYSIS OF POLYETHYLENE GLYCOL AND THE TREATMENT OF LEATHER AND ROPE

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PART I BATAVIA TIMBERS: AN UPDATE

Since 1976 a large section of ships timbers from the wreck of the *Batavia* (1629) has been undergoing treatment in Polyethylene Glycol 1500 at the Conservation Laboratories of the Western Australian Museum. In order to follow the progress of the treatment it is useful to know the extent of the polyethylene glycol penetration.

The use of infrared spectroscopy in the quantitative analysis of polyethylene glycol was first suggested in 1981 by Dr. J.T.T. Pang (Pang, 1981) who has since left the W.A. Maritime Museum.

Unfortunately, Dr. Pang left behind insufficient information for us to properly assess his work in this particular area and we were therefore obliged to start our investigation virtually from scratch.

The Analysis

Effective use of infrared spectroscopy in quantitative analysis (Afremow et al, 1961) requires the elimination of a number of possible sources of error which would not normally be considered in qualitative analysis. A scanning speed must be selected which will allow the instrument to accurately record the true intensity of an absorption band. This speed is determined by scanning at successively slower speeds until there is no further increase in the recorded band intensity; in this particular analysis a speed of 3800cm^{-1} (from 200 to 4000cm^{-1}) per hour was found to be satisfactory.

Background absorption was compensated for by using a reference as close as possible in composition to the sample, in this case by using a reference cell (optically matched to the 0.2mm path length sample cell) filled with benzene, the solvent used in the PEG extraction stage.

In practice it is not necessary to record the entire spectrum of each sample and two smaller scanning ranges were chosen, namely 1000-1250cm^{-1} and 2650-3050cm^{-1}. These ranges include the two largest absorption peaks (Pang, 1981), the 1105cm^{-1} symmetrical ether carbon-oxygen-carbon bond stretch and the 2870cm^{-1} asymmetrical methylene carbon-hydrogen bond stretch, and the limits were chosen so that the lower limit of each range lies on an area of relatively low and constant absorption to enable consistent adjustment of the zero absorbance position for the machine and the upper limit allows the recording of the entire peak so that the baseline can be more accurately determined (using the tangent line technique).

The instrument used was the SP2000 spectrophotometer at Murdoch University and all spectra were recorded in the linear absorbance mode which enables direct measurement of peak absorbance.

Results and Discussion

Fifteen standard polyethylene glycol solutions in benzene (caution - benzene is highly carcinogenic and should only be used under the supervision of a qualified chemist), covering a range of concentrations (5 x 10^{-3} g/ml to 25 x 10^{-3} g/ml) and molecular weights (200 to 6000) were made up and their spectra recorded under the conditions outlined above. The concentration range covers all PEG concentrations possible where core samples (max 200mg) are extracted in 10ml of benzene. These spectra were analysed by plotting both peak height (which assumes Gaussian peak shape) and peak area (integrated intensities method) against concentration. It should be noted that while peak height data may not be transferable to another spectrophotometer, the integrated intensities data should be so transferable. The results are shown in Figs. 1 and 2 below and can be summarised as follows.

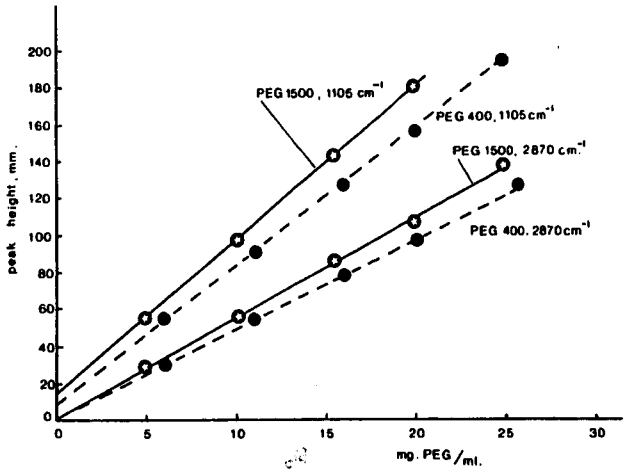

Figure 1. Peak height versus concentration. For the SP2000 Spectrophotometer absorbance = peak height (in mm) x 5 x 10^{-3}.
For details - Appendix I.

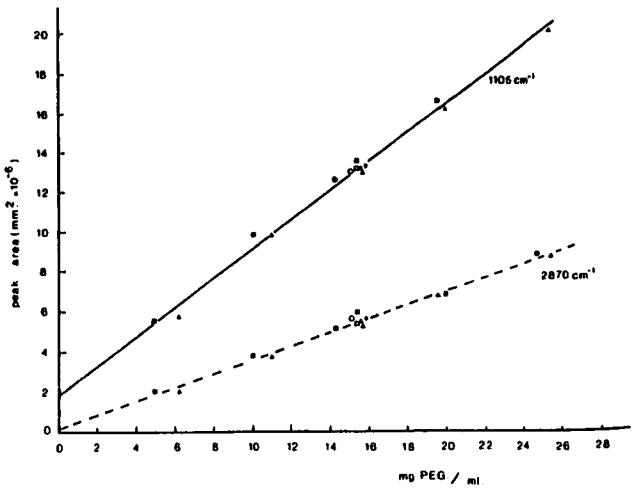

Figure 2. Peak area versus concentration.
△ PEG 200; ▲ PEG 400; □ PEG 600;
$ PEG 800; ■ PEG 1500; ● PEG 4000;
○ PEG 6000.
For details - Appendix I.

The different results obtained by using both peak height and peak area as measures of absorbance are related to the peak shape. In the higher molecular weight PEGs, the absorption peaks are sharply defined while in the lower molecular weight PEGs the peaks are broadened due to the increase in the influence of the terminal hydroxyl groups.

Table 1.

	Identification number	Impregnation solution (% wt/wt)	Shrinkage* (after freeze-drying)	Condition
a)	First set			
	SC 13	control	20%	poor, too dry
	SC 47	5% PEG 1500	11%	fair, relatively inflexible
	SC 47	10% PEG 1500	9%	fair, relatively inflexible
	SC 47	15% PEG 1500	5%	poor, wax-covered
	SC 47	10% PEG 1500/1% Luviskol	none	fair, virtually inflexible
	SC 47	10% PEG 1500/2% Luviskol	none	fair, virtually inflexible
	SC 29 TB6	10% glycerol	none	good
	SC121	15% glycerol	none	poor, too moist
	SC149	20% glycerol	none	poor, too moist
b)	Second set			
	SC 13	painted with 10% PEG 1500/ 1% Luviskol	no change	poor, no change
	SC121	soaked in water	11%	poor
	SC149	soaked in water	13%	poor
c)	Third set			
	SC 13	10% glycerol/5% PEG 1500	5% (from initial state) =17% expansion	good
	SC149	10% glycerol/1% Luviskol	6% (from initial state) = 7% expansion	fair to good (due to initial condition)

*Shrinkage is calculated with respect to the maximum (waterlogged) dimensions.

Treatment of Leather from the *Vergulde Draeck*

The *Vergulde Draeck* was outward bound for the East Indies from the Netherlands in 1656 when she struck a reef near Ledge Point on the western coast of Australia. The wrecksite was rediscovered in the early 1960s and several expeditions have been undertaken since then resulting in the recovery, among other things, of numerous leather artifacts.

Following the success of the 10% glycerol solution in treating the *Sydney Cove* leather a number of leather items from the *Vergulde Draeck* were treated similarly. This resulted in leather of reasonable appearance and strength but with shrinkages ranging from 4% to 22%. See Table 2-a.

Further experiments were then carried out as summarised in Table 2-b and 2-c. From these results it can be seen that considerable improvement has occurred since the initial treatment. As well as shrinking less on drying out the leather now has improved flexibility; strength and appearance were unaltered and still satisfactory.

A number of leather items from the *Vergulde Draeck* had previously been treated with toluene/lanoline. These were considered unsatisfactory due to the considerable excess of sticky lanoline which readily picked up dust particles during storage.

The lanoline was first removed from these by immersion in toluene and the removal was considered complete when no further dry weight loss was noted for the leather pieces (about four hours).

On placing the pieces in 10% glycerol rehydration immediately began, resulting in an expansion in area of 25% in a few minutes. This corresponds to the reversal of the maximum shrinkage we have noted for waterlogged leather on freeze-drying without any treatment.

Table 3 summarises the results of the experiments carried out on three pieces of this leather.

Table 2

	Identification number	Impregnation solution (% wt/wt)	Impregnation time (days)	Shrinkage* (after freeze-drying)	Condition
a)	First set				
	GT 4088 (1)	10% glycerol	13	8%	leather appears dry and somewhat inflexible
	GT 4088 (2)	10% glycerol	13	12%	
	GT 4127 (thicker leather)	10% glycerol	27	13%	
b)	Second set				
	GT 4088 (1)	15% glycerol	14	10%	no improvement
	GT 4088 (2)	15% glycerol	14	7%	improved
	GT 4127	20% glycerol	14	9%	improved
c)	Third set				
	GT 4088 (1)	25% glycerol	21	4.2%	satisfactory
	GT 4088 (2)	25% glycerol	56	1.2%	satisfactory
	GT 4127	30% glycerol	continuing		

*Shrinkage is calculated with respect to the maximum (waterlogged) dimensions.

proposed that all the waterlogged leather in the W.A. Maritime Museum could be treated by impregnation in 30% glycerol followed by freeze-drying. Previously treated unsatisfactory leather could also be successfully retreated in aqueous glycerol using a similar method to that outlined above for GT 4074. See Table 3.

The leather would first be sorted into groups depending on size, thickness and extent of contamination with salts and metal corrosion products. Cleaning of waterlogged leather items will not be discussed at length here although it does appear at present that the safest approach is to clean these by hand every few weeks until a satisfactory condition is reached.

At various times after the start of the glycerol impregnation treatment pieces from each group would be freeze-dried then weighed and measured in order to determine the optimum length of time for each group. These sample pieces could then be replaced in the treatment solution with no adverse effects. If a sample piece was found to contain excess glycerol (shown by a moist surface) then the leather pieces from its group would simply be placed first in water for a few days to completely reverse the treatment and then retreated in a lower concentration of glycerol.

Data on the condition and composition (Jenssen, 1983) of the leather before treatment (dimensions, especially thickness; surface and extraction pH's; results of analyses for protein, moisture, fat, ash, non-hydrolysable matter, tannins, minerals and other contaminants; and animal species if this can be determined etc.) and on the environment of the wrecksite (date of shipwreck, water temperature, whether aerobic or anaerobic, current strength, general chemistry and biology of site, metals in close proximity etc.) could then be considered in conjunction with the impregnation times found to be required for successful treatment. This would indicate which are the most important factors affecting the treatment and would then allow the determination of approximate impregnation times before treatment and the elimination of most of the sample freeze-drying trials.

For example, the better state of preservation of the *Sydney Cove* leather with respect to the *Vergulde Draeck* leather, indicated by the lower glycerol concentration and shorter impregnation time required, could be due to a shorter immersion time (180 rather than 320 years) and a lower water temperature on the wrecksite. The average water temperature at the *Sydney Cove* site is 15.2±1.7°C while the *Vergulde Draeck* site is 21.3±1.7°C. (Ministry of Defence, USSR, 1974) Presumably the characteristics of the leather should also be considered.

Although the glycerol treatment can yield excellent results the following should be taken into account.

Glycerol provides an excellent substrate for microbial growth. This can be prevented by the use of a biocide either in the impregnation solution or during storage and the regulation of temperature and relative humidity during storage.

Glycerol enhances the corrosion of iron. If the artifact to be conserved contains both iron and leather, glycerol should preferably not be used. The substitution of low molecular weight polyethylene glycols is under active investigation at our laboratories.

In some cases glycerol has been observed to gradually settle out in the treatment solutions. This can be avoided by occasional but thorough stirring and should not be significant in view of the relatively short periods (at most a few months) required for impregnation.

Treatment of Waterlogged Rope

Waterlogged rope and matting have been treated very successfully at the W.A. Maritime Museum by impregnation in an aqueous 5% glycerol/5% Luviskol (plus a biocide) solution for periods of time ranging from one to three weeks followed by either freeze-drying or slow dehumidification at 10°C. This treatment yields rope of good flexibility and strength, and very natural appearance. Shrinkage is minimal but the rope pieces should be quite closely bound with fine nylon netting to avoid distortion due to unravelling.

Where there is considerable iron present in the rope, 20% PEG 1500 can be used with similar results.

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Appendix I

For Figure 1

PEG	peak (cm^{-1})	ρ	slope ($mm.ml.mgPEG^{-1}$)	intercept (mm)
1500	1105	0.99997	8.37	13.89
400	1105	0.99975	7.34	11.22
1500	2870	0.99896	5.41	2.08
400	2870	0.99995	4.97	-0.09

For Figure 2

PEG	peak (cm^{-1})	ρ	slope ($mm^2.ml.mgPEG^{-1}$)	intercept (mm^2)
all grades	1105	0.99551	0.729×10^{-6}	1.90×10^{-6}
all grades	2870	0.99267	0.342×10^{-6}	0.16×10^{-6}