

AN ANALYSIS OF PAPER MADE FROM THE DUNG OF ELEPHANT, RHINOCEROS AND OTHER WILD HERBIVORES TO DEVELOP CONSERVATION GUIDELINES

by

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SUMMARY

Title of dissertation: An analysis of paper made from the dung of elephant, rhinoceros and other wild herbivores to develop conservation guidelines.

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Paper has been around from the 3rd century BC. From then on different kinds of paper were made but the original recipe remained the back bone of how paper is made today. In this study the different components of paper were discussed to understand what paper is, namely: Cellulose, hemicellulose and lignin. The food preferences of elephants and how their food is broken down in the gastrointestinal process showed why the artist could use elephant dung for paper making as shortcut in the papermaking process. The chemical processes to prepare the dung explained the bonding processes of the different components of paper to achieve good quality paper. Paper made from elephant, rhinoceros and other herbivores' dung were analysed to find out what the components of the paper are and if it will lead to deterioration of the paper. Experiments such as UV light exposure, pH, lignin test, hygroscopic test and tear resistance were carried out on eight different paper samples. The samples were of unsized rhinoceros dung fibre paper, sized rhinoceros dung paper, rhinoceros dung mixed with Sappi paper, only Sappi paper, Kruger elephant dung paper, white rhinoceros dung paper, Chinese artist paper, and newsprint paper. The results showed that because of the low lignin content of the paper, lignin might not have any detrimental effect on the paper. Discolouring of the paper under UV light exposure where possibly because of oxidation where bonds between hemicellulose and cellulose degraded. The alkaline pH of all



the paper samples except the newsprint paper, indicated the possible good quality and high durability of the paper. To conserve handmade paper, the guidelines of all the conservational institutions are an essential tool. The main degradation cause of paper is its inherent instability that will increase under heat and fluctuation of relative humidity. It is therefore essential to keep to the conservational guidelines to prolong the lifespan of paper.

KEY TERMS: Elephant dung, components of paper, paper making process, accelerated ageing, lignin, conservational guidelines.



DECLARATION OF ORIGINALITY UNIVERSITY OF PRETORIA

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DECLARATION

1. I understand what plagiarism is and am aware of the University's policy in this regard.

2. I declare that this dissertation is my own original work. Where other people's work has been used (either from a printed source, internet or any other source), this has been properly acknowledged and reference in accordance with departmental requirements.

3. I have not used work previously produced by another student or any other person to hand in as my own.

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Initial – Supervisor	ML



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CHAPTER 1: INTRODUCTION

1.1 Background

If paper was never invented humankind would have been much poorer. Oral traditions and stories would still be there to help us understand our world and give us valuable information, but someone would always have to tell you the stories. With the invention of paper and the written word, humans were now able to write down ideas, stories, fantasies and dreams, opening up a new world of creativity. Do not forget about drawing and painting that further broadened humankind's creativity (Ewins, 2001: 2).

For me, paper was always something that was readily available. Books were made of it, examination pads were for writing down notes, clean white sheets were for printing and for creating beautiful works of art. I never thought about actively preserving paper until I enrolled for the masters' degree in Tangible Heritage Conservation. When I started research into dung made paper, all the literature was about the conservation of ordinary paper made from wood or plant fibres. There was no specific academic research on paper made from dung to establish the conservation thereof and whether the composition will have an impact on the degrading of the paper. I mostly found research on how to make elephant dung paper, how it is bleached, why it is better for the environment and why it would be a potential alternative to conventional wood pulp sources for paper (Fasake, 2020, Rathnayake, 2019, Saleem, 2016). Research that was done, mainly focussed on how to make paper from dung and how to make it more user friendly (Saleem, 2016: 32-34).

That was why I was so intrigued with the birthday card my husband received from his aunt. It was handmade paper made from disinfected dung of elephant, rhinoceros and other wild herbivores. On the front was a picture of a buffalo in a field with long grasses and a dry tree. The picture was printed on the paper and signed by Sheila Collins. The card had some rough fibres, but the overall feel of it was smooth with no rough edges. On the back of the card was a sticker



from Scarab paper, explaining that the card was handmade from the bigger African herbivores' dung.



Figure 1: Card made out of elephant dung paper. Photo: Author (2022).

It is a beautiful card and I wondered about the cycle of making the card that is sort of resembled in the picture of grass, the animal and then the end product, the paper of the card. I did not really dwell much more on it. In May 2021, I accompanied my husband to Durban on a business trip and we stayed in a guesthouse on the Bluff. There I saw a painting of San/Khoisan sketches made by Sheila Collins on handmade paper of elephant dung. This started me thinking on the conservation process of such paper. I wondered if the composition of the paper will have an influence on the degrading of the paint pigments. Will the conservation or preservation guidelines for paper differ for this type of paper? How quickly will it disintegrate? When will you intervene to start the preservation? What technique will you follow?

I decided to find out more about Sheila Collins and her handmade paper. A search on Google took me to a website that briefly explained how she started making paper (Discover Sedgefield, 2010: 3). In 1985 she lived in Mooirivier and used pampas grass to make paper. When visiting Umfolozi Game Reserve, she saw a rhinoceros midden and thought that the digested grass could be an easier option for her papermaking. A friend brought her some white rhinoceros dung and she started to experiment with it. She also used black



rhinoceros and elephant dung. She noticed that the fibres in elephant and rhino dung are not fully broken down and because of their varied diet, such paper would be very unique (Wilson, 2021: 1). She then moved to Sedgefield and continued with her experimenting and even sought help from chemists at Sappi to help with the sizing of the paper (Collins, personal communication 2022, February 16). She eventually was happy with the end product, but continued to experiment with horse, kudu and zebra dung. She even used sea-grass and algae from the Swartvlei Lagoon.

It was a very labour intensive and time-consuming process and the paper did not sell very well. Her son suggested to paint or print on the handmade paper and then sell the paintings. That finalised her idea of making cards with her designs and selling it in her shop.

In 1998 the Wild Life Society decided to print more books of Margo Mackay's *The Knysna Elephants and Their Forest Home* (1983). They needed R40 000 for the project. Collins originally painted the Matriarch of the Knysna forest as front cover for the book and she offered to help by printing the Matriarch on elephant paper (Discover Sedgefield, 2010: 5). Foresters collected elephant dung to make up to 1000 sheets of paper. The finished painting was then taken to Cape Town where it was printed onto the dung paper. The television series, named 50/50 (aired in 1998), filmed the whole process of making the paper and of Collins painting the picture.

This fundraising and public awareness expanded her paper making from a double garage to a house where Scarab Paper, as business, was located. Here she used her own make-shift equipment for paper making – a pulping drum, pulping basins and a car-jack made into a press. Later she bought a 4 ton paper press and the Heidelberg Printing Press (Collins, personal communication 2022, February 16). The paper was rolled through the press numerous times for separate printing of colours creating a full multi-colour litho-print on handmade paper.

In 2002 Collins sold Scarab Paper and concentrated more on her painting.



1.2. Problem statement

The questions I asked myself in section 1.1 and the gap in research led me to address the research needs on handmade paper made from the dung of elephants and big herbivores. My proposed study focused on how to preserve this type of paper. Cathleen Baker (2004: 7) mentions that it is important to understand how an object was made and what it is made of. I researched the composition of the paper to understand and determine how the paper will degrade. I investigated how the paint pigments react to the handmade paper to determine any deterioration. Depended on the results of these investigations, I determined what conservation techniques and guidelines to follow that will add to the framework of academic knowledge on this subject.

1.3 Research questions

According to Mouton (2009: 53) my study is an emperical study with a real-life problem where new data and/or existing data are presented and analysed. The emperical research questions lead to resolving the data by analysing it according to scientific knowledge. Therefore, the following research questions were formulated to guide the study on conservation of elephant dung paper:

- What are the composition of elephant dung-made paper?
- How will the composition of the paper impact on the preservation thereof?
- What are the causes of deterioration?
- Will paint pigments effect the degradation of elephant dung paper?
- What are the conservation guidelines to follow to preserve elephant dung paper?



1.4 Aims and objectives

The general aim of the study is to provide guidelines to preserve handmade paper made from elephant dung. My objectives to achieve this aim were to do a literature study to understand what paper is, where it comes from, how it is made, what the causes for deterioration are and how to preserve it. I looked at existing data on the composition of paper and of elephant dung paper, compared it to industrial made paper to understand its composition. I contacted the artist, Sheila Collins who started the elephant dung paper project, to find out how she made the paper, how she refined the process and what results she obtained. I reproduced her recipe to understand the process and to record any data on making hand made elephant dung paper. I built an ageing chamber to accellerate paper samples to test tensile strength and micro-fading. I used analytical microscopic techniques to identify the ultra violet fading of the paper samples. And finaly, when all data were collected and analysed, I provided guidelines on elephant dung paper conservation.

2. Literature review

Existing academic literature that I consulted included books, journal articles, internet sources, interviews, standing working procedures and instructions. Some of the sources are:

Area, M.C. and Cheradame, H. 2011. Paper aging and degradation: Recent findings and research methods. *BioResources* 6(4): 5308-5337. Available: <u>https://www.academia.edu/25049536/Paper_aging_and_degradation_Recent_findings_and_research_methods?email_work_card=view-paper_____[2022, August 09].</u>

The complex components of paper, composed of cellulose, hemicelluloses and lignin, but also other additives like starch, synthetic polymers and minerals are discussed in this paper. How these components and other factors like hydrolysis play a role in the degradation of paper are also discussed. The paper provides an update



of new tools available for the study of paper deterioration that will be discussed in this study.

Baker, C., 2004. The importance of differing in perspectives in the conservation and preservation of paper-borne materials. *The book and paper group annual*, 23(1). <u>https://cool.culturalheritage.org/coolaic/sg/bpg/annual/v23/bpga23-</u> 01.pdf, [2021, November 21]

The author argues that different perspectives to view objects are needed for good decision making. Not only condition problems should be looked at, but also the technological, cultural, historical and material perspectives should be taken into account. These arguments will be delved into in this study.

Brückle, I. 2011. Effect of pulp processing on paper-water interactions. In *Paper and water: A guide for conservators*, edited by G. Banik & I Brückle. Oxford: Butterworth-Heineman.

Chapters in this book contain information on the chemistry of paper and water, the structure and properties of dry and wet paper, pulp processing, sizing of paper, drying of paper in the manufacturing process, and paper ageing which will be discussed in this study.

Carter, H.A. 1996. The chemistry of paper preservation: Part 1. The ageing of paper and conservation techniques. *Journal of chemical education*. 73(5): 417. Available: DOI: <u>https://doi.org/10.1021/ed073p417</u>. [2022, June 12].

This paper discusses the aging of paper and the conservation techniques of paper preservation, the chemical reactions responsible for the aging process and the chemistry of deacidification methods. Other techniques such as paper strengthening, bleaching, pest control and an introduction to alkaline papermaking are also discussed in this study.



Carter, H.A. 1996. The chemistry of paper preservation: Part 2. The yellowing of paper and conservation bleaching. *Journal of chemical education*. 73(11): 1068. Available: DOI: <u>https://doi.org/10.1021/ed073p1068</u>. [2022, June 12].

This paper discusses photo-oxidation of lignin-containing papers and the yellowing of paper. The basic principles of conservation bleaching where discoloration and stains are removed are described. The paper also explains the use of oxidizing bleaches and the chemistry of it. These arguments forms part of this research.

Crespo, C and Viñas, V. 1984. The preservation and restoration of paper records and books: A RAMP study with guidelines. Paris: Unesco. Available: <u>https://unesdoc.unesco.org/ark:/48223/pf0000063519</u> [2022, February 09].

This study has detailed chapters on how paper is made, the inks and graphics of documents, deterioration causes and effects, storage of documents, conservation and restoration. Explanations, methods and classifications are discussed to understand the deterioration of paper and provide guidelines for conserving paper.

Daniels, V. 2006. Paper. In *Conservation science: Heritage materials*. Edited by Jones *et al.* London: Royal society of chemistry. pp. 32-55.

This chapter in the book is about the properties of paper, the deterioration of paper, deacidification, bleaching and washing to remove discolouration, safe environments for paper, methods for monitoring the deterioration of paper and the characterisation of paper. Arguments in the book are discussed in this study.

Ewins, R. 2001. Talk presented to a meeting of the University of the Third Age(U3A).Hobart,Tasmania,15May2001.Available:https://www.justpacific/art/articles/paper/paperorigins.html [2022, May 10]



The author explains how paper was made, how scientists in the 20th century determined the scientific components of paper, namely: The molecular bonding of elements. These explanations and the story of paper making are discussed in this study.

Kamoga, O.L.M., Byaruhanga, J.K., & Kirabira J.B. 2013. A review on pulp manufacture from non-wood plant materials. *International Journal of Chemical Engineering and Applications* 4(3): 144-148. Available: DOI: 10.7763/IJCEA.2013.V4.281 <u>http://www.ijcea.org/papers/281-I10005.pdf</u> [2022, February 08]

In this paper the type of non-wood material, the methods used to determine the chemical composition of the pulp to make paper, the methods used to pulp plant material, and the bleaching techniques are observed.

Kumar, A., Gautam, A., & Dutt, D. 2016. Biotechnological transformation of lignocellulosic biomass into industrial products: An overview. *Advances in Bioscience and Biotechnology*. 7, 149-168. Available: https://dx.doi.org/10.4236/abb.2016.73014 [2022, July 27].

The explanation of cellulose, hemicelluloses and lignin were studied for this research.

Malachowska, E., Dubowik, M., Boruszewski, P. & Przybysz, P. 2021. Accelerated ageing of paper: Effect of lignin content and humidity on tensile properties. *Heritage Science*. 9(132):1-8. Available: <u>https://doi.org/10.1186/s40494-021-00611-3</u> [2022, July 25].

This paper studied the microscopic degradation of paper, specifically the role lignin plays. It has been believed that lignin is responsible for the destructive changes caused by hydrolysis. Findings in this paper were discussed in this study.



The effects of accelerated aged paper under different temperature and humidity conditions were studied in relation to the strength properties of such paper, where lignin is seen as responsible for the breakdown of mechanical bonds. The results of this study indicate that the impact of moisture on paper is a greater agent of deterioration than increased temperature. The aim of the study is to provide greater technical support to conservators.

Mayer, D.D. 2021. BPG spot tests. Book and Paper Group Wiki. American Institute for Conservation (AIC). <u>https://www.conservation-wiki-</u>.com/wiki/BPG_Spot_Tests [2022, February 22]

The different tests and sampling methods are discussed in the methodology chapter.

Petherbridge, G. Ed. 1987. Conservation of library and archive materials and the graphic arts. London: The institute of paper conservation and society of archivists, Butterworths.

Chapters regarding my research in this book are on the scientific developments of paper, conservation treatments, the storage of art on paper, and developing of a conservation policy.

Saleem, M., Yaqoob, N. & Rehman, I. 2016. Eco-friendly bleaching of soda-AQ chemical elephant dung pulp. IRA-International Journal of Applied Sciences. 4(1): 30-38. Available: DOI: <u>http://dx.doi.org/10.21013/jas.v4.nl.p4</u> [2022, February 28].



This paper studied the cellulosic fibres of elephant dung, the different colour of the dung depending on the elephant's diet, and what type of bleach to follow for high quality, aesthetically acceptable paper. This research is discussed in this study.

Zervos, S. 2006. Methodology and criteria for the evaluation of paper conservation interventions: A literature review. *Restaurator* 27(4): 219-274. DOI: 10.1515/REST.2006.219. Available:

https://www.researchgate.net/publication/240754602 [2022, February 20]

The methods to evaluate paper for conservation treatments are discussed in this paper where paper properties and different tests for treatments are discussed. The criteria for intervention are examined and discussed in this study.

Rod Ewins (2001: 7) compares the traditional making of barkcloth of the people of the Pacific with the development of paper making in China. Both discovered that they could pound certain plant fibers into a pulp, remove the impurities by hand and by washing it in water, strain it from custom made structures and let it dry into sheets of paper that was remarkably strong. The same processes that the Chinese used are still used today for making handmade paper. Added knowledge gained in the 20th century on understanding the properties of paper helps conservators to understand the dynamics of paper.

This is important because in conservation it is necessary to understand what an object is made of and how its properties will interact with each other and with the external environment (Baker, 2004: 5). The complex properties of paper, composed of cellulose, hemicelluloses and lignin, but also other additives like starch, synthetic polymers and minerals must be taken into account for conservation. How these properties and other factors like hydrolysis play a role in the degradation of paper conceptualise paper deterioration (Area, 2011: 5307).



Water plays a significant role in handmade paper when pulped wood fibers are washed and bleached. Sheila Collins used caustic soda (sodium hydroxide) to cook and wash the elephant dung. This process sanitized the pulp and prevented microbial growth that would damage the fibers, making it unfit to use as paper (Saleem, 2016: 3). It also broke the chemical bonds of the lignin to separate it from the cellulose fibers. Lignin acts as barier between the cellulose bonds to prevent them from forming stronger bonds. When the lignen is removed, the cellulose bonds strengthen and stronger paper is formed. The lignen also discolours the paper and by washing it out, a whiter colour of paper is achieved. Lignin will deteriorate easier over time and will also lead to paper being more brittle with a lower tensile strenght (Daniels, 2006: 51, Saleem, 2016: 5). The role water plays is seen in the absorption capacity of the pulped During pulping and bleaching the internal structure of lignin and fibers. hemicelluloses change which affects the water absorption of the fibers (Brückle, 2011: 140). As relative humidity is one of the agents of deterioration of paper, water is an important role player in paper. Cellulose molecules tend to bond with other cellulose molecules and not with water. In a high humidity environment the cellulose will absorb water and the dimensions of the fibers will change. Paper will deform and continious changes in relative humidity will lead to stress in the paper leaving it with permanent buckles or bends (Daniels, 2006: 37).

Another influence of paper deterioration is oxidation. Vincent Daniels (2006: 41) describes how the absorption of light changes the absorbing molecule's energy. This lead to discolouring of the paper. When inks used in the painting on paper oxidise, it can be so severe that the copper or iron in the pigments can cause losses in the sheet of paper.

Petherbridge (1987: 1) noted the increasing practice in conservation to restrict treatment to minimal intervention of an object. Characteristics (original and aquired) of the object should stay as unique as possible. With this in mind, Zervos (2006: 2) sugggested that treatment should include the evaluation of chemical properties (pH, alkalinity and colour change) and of physical properties (tensile properties, folding endurance and tearing resistance).



These treatments can be destructive but when making use of optical microscopes and infrared spectroscopy, chemical bonds can be detected non-destructively.

Vincent Daniels (2006: 55) concluded that the knowledge of the properties of paper and basic scientific knowledge thereof, empower the conservator to treat a paper object effectively. More research on non-destructive methods will improve knowledge on the effect of treatments on paper (Zervos: 2006: 19).

3. Theoretical framework and research methodology

With this in mind, I framed my research paradigm as an experimental design or laboratory study combined with a literature review. The literature review will explain what paper is, where it started, what it is used for and how the paper making process evolved, what paint pigments are, how it will impact on the degrading of paper, the causes of deterioration in paper and how to preserve paper.

The study is quantitative with a small number of case studies under highly controlled laboratory conditions. The relation between techniques, experiments and repeated measures are shown (Mouton, 2009: 155). Causal questions lead the experiments to show the assumptions about causality. Examples of questions are: What is the composition of the paper and how will the specific material lead to deterioration?

My research design can be described as methodological studies (Mouton, 2009: 173) where my research aims to develop guidelines for conserving elephant dung paper. I compared the existing guidelines to preserve paper, when confronted with causes of deterioration, to those made of elephant dung.

Sheila Collins, the artist whose handmade paper I studied, lives in Sedgefield in the Western Cape. She has agreed to the research according to the ethical guidelines of the university (see Appendix 3). She made samples of her elephant dung paper of different years (from 1992) and of different stages of



the paper making process available to me. I analysed paper made from elephant dung and other herbivores from a wide array of paper samples for fibre analysis using a Leica S9i microscope It was useful to detect the fibres of the paper and the pigments of the painted areas.

I conducted analysing experiments on the pH of the paper samples, the lignin content, hygroscopic absorption, ultra violet light exposure, and tearing resistance. The experiments enabled me to observe what the composition of the elephant dung paper is to generalise what the causes for deterioration might be and what guidelines for preservation should be implemented.

4. Delimitations, significance and feasibility of the study

For this study, I referred to commercially made paper and also to paper made from the dung of rhinoceros and other herbivores, but my main focus was on the composition of elephant dung paper. This type of paper was made in the Sedgefield area where the artist lived and where she had her business. Mainly foresters of the Knysna Elephant Park collected the dung for the paper making (Collins, personal communication 2022, February 16). I decided on using the elephant dung paper of Collins, because she has examples of it that is about 20 years old. Because of their age and possible degrading, analysis of these samples was used to reflect the change in composition that was expected. This was compared with the results of experiments mentioned in par 3. Sheila Collins, the artist, is a voluntary participant and is aware that she may withdraw at any point without any consequences. She has agreed that data collected will be for academic research purposes only and that the information will be stored for 15 years at the University of Pretoria School of Arts. No financial benefits will be involved and the research will be done according to the ethical guidelines of the university.

The 2021 run-away veld-fire on the slopes of Table Mountain in Cape Town that destroyed some of the buildings and part of the library of the University of Cape Town, made it clear that in the conservation environment more paper conservators are needed. More than 2000 volunteers helped to salvage



documents and books, but there was too much specialised conservational salvaged work to be done on the collections that needed the expertise of paper conservationists (Minicka, 2021: 14). This research will contribute to the pool of knowledge on more specialised paper conservation with clear guidelines. This will not only benefit South African conservationists, but also worldwide where more and more artisanal paper makers make use of dung as component for paper making (Collins, personal communication 2022, February 16).

5. Outline of chapters

Chapter one of the study provides a general introduction to the study. It includes the background, an explanation of the research problem, aims and goals, the research design and research methodology. The benefits, uses and value of the study are discussed and its value for future research is indicated.

Chapter two contains the discussing on the composition of paper, the composition of wood, the chemical processes of pulp for paper making and the composition of the elephant and rhinoceros' dung.

In chapter three the deterioration causes of paper is discussed as well as the major ageing processes of paper and the effect of paint pigments on paper.

In chapter four the different analytical techniques used on the paper to identify the composition of the paper are discussed. Data was compared to determine variations or to discover connections between concepts of the degradation of the paper.

The fifth chapter discusses the major agents of deterioration of paper-based objects. Clear guidelines for the conservation of such paper are presented.

The conclusion chapter contains the research problem, research questions, aims, goals and how it was presented in the chapters. The main arguments are summarised to show how it impacted the study. The benefits and value of the study are noted as well as the value for future research.



CHAPTER 2: THE COMPOSITION OF PAPER

2.1 Introduction

Nowadays you cannot imagine modern life without paper. Although electronic communication is now the norm, paper still has its place where the archived original paper document is necessary. In the art world, no electronic version of an artwork can take the place of the original work on paper or canvas. But how did we first start to put our ideas into visible form? Where did paper come from?

The earliest visible form of people's ideas is found in caves, where early humans made engravings on the stone walls (Marchant, 2016: 2). The pigment ochre was found in caves in South Africa dating as far back as 164 000 years. Jo Marchant (2016: 5) did research on cave paintings (hand stencils and animal images) in Sulawesi, an island in Indonesia, dating it to be around 39 900 years old. Similar stencils were found in Europe, in Chauvet in France and El Castillo in Spain. The same type of art was also found in Asia and Australia. This shows that the early humans needed to express their thoughts. The best medium they could find was the cave walls where they knew they could go back to it, and it would still be there.



Figure 2: Hand stencils in caves found in Indonesia (Marchant, 2016: 4)



Figure 3: Drawings of lions found in caves in Chauvet, France (Marchant, 2016: 2)









Figure 5: Detail of papyrus sheet (Shenoy: 2016: 341).

This idea of permanency might have given way to further development in writing methods. Around 3100 BC in Mesopotamia, clay tablets with wedge-shaped marks done with a reed were used to send messages and as a type of bookkeeping for products sold at markets (Shenoy, 2016: 338) (see Fig. 3). But this was cumbersome, and people were looking for a more portable product. Around 3000 BC in Egypt, people started making sheets for writing from the papyrus plant that grew on the banks of the Nile. It had a smooth surface, and they could use ink without it blurring or smudging (see Fig. 4). However, the only people who could make use of papyrus for paper making, were those living in Egypt and Sudan along the banks of the Nile River. Other civilisations started to use dried animal skin (parchment) as writing material (Ewins, 2001: 2, Shenoy: 2016: 340).

The earliest use of paper was around the 3rd century BC by the Chinese who made paper to use for wrapping. Then around 8 and 220 AD they used a recipe of treated plant and bast fibers, fishnets, old rags and other fiber-rich items to make paper.

Cai Lun can be acknowledged as the father of papermaking. He invented and stablised the recipe for papermaking in China around 75 - 105 AD. He improved the chemical mixture and started the process of wetting the fiber in hot water, then pressing the thin sheets with machines to remove all moisture and let it dry completely. He produced small notebook size paper as well as longer scrolls that were more expensive. This procedure was used for about one and



a half thousand years and was jealously guarded in China (Ewins, 2001: 1-4, Shenoy, 2016: 341). It was only after the Battle of Talas in Kyrgyzstan in 751 that the Arabs got hold of the secret and it spread to the rest of Europe. The Arabs advanced the techniques, making the paper sheets thicker for paintings and bookmaking up until the 10th century. From the 11th century paper mills spread throughout Europe, but paper remained expensive and rare. To mass produce paper a new method was introduced to pulp the vegetable material The Chinese paper makers used hand- and foot-operated more finely. machines to pound the pulp. The paper mills in Europe were mostly established along rivers or streams where wind or water mills were used to drive the stamping machines. The Dutch developed a cylinder-type machine (the Hollander) that cuts the pulp, ciculates and squeezes it, resulting in finer control over the pulp. Only in the 19th century the French improved the paper machine to produce a large roll of paper which was cut into smaller sizes. The world's paper making techniques are still based on the Fourdrinier machine of 1803 and most handmade paper makers still use the Hollander machine (Ewins, 2001: 4). It is very time consuming and not environmental friendly, because of large water volumes used, the energy effeciency of driers and the chemicals used. Nowdays bi-products of the agriculture industry are used for paper making because the cellulose, hemicellulose and lignin content are adequate. Products like bamboo, elephant grass, pinewood, poplar wood and sugarcane bagasse are used for papermaking. Other environmentally friendly options are now looked at for further use in the paper making industry (Kumar, Gautam & Dutt, 2016: 150).

To understand the paper making process, it is good to look at the different fibres that wood contains.

2.2 Wood fibres

To produce paper, wood must be beaten to break down the different fibres. It is a challenging process where mechanical and chemical processes are used because of the complex structure of wood. The three main components of wood are cellulose, hemicellulose and lignin (see Figure 5). But about five



percent of wood also contains wood extractives of organic compounds that must be removed to have a better pulp and paper quality. Because these compounds are organic, they can be removed by organic solvents or hot water. This process is seen as the pre-treatment for pulp and is an important part preceding the pulping process (Lehr, Miltner & Friedl, 2021: 888).



Figure 6: Wood structure. (Lehr, Miltner & Friedl, 2021: 887)

2.2.1 Wood extractives

The two main extractives are identified as lipophilic and hydrophilic extractives with the lipophilic extractives further categorised as aliphatic compounds and terpenes containing the fatty acids, various alcohols, esters, hydrocarbons and various resins. They serve as nutrients for the trees. The hydrophilic extractives are the phenols containing lignin, stilbenes, flavonoids, tannins and tropolones. These lignin containing extractives regulate moisture and protect the tree from insects and attacks by micro-organisms, brown rot, fungi and bacteria.

The location of wood extractives differs between two groups of trees, the softwoods and the hardwoods. It also differs between species, and single trees, based on the age of the tree, geographical site and season when the tree was cut. Usually older trees have more extractives, especially in the heartwood. The surrounded sapwood contains less extractives, with knots and bark



containing more. Studies by Phojamo et al. and Willför et al. noted by Lehr, Miltner & Friedl (2021: 889) showed that knots have denser, shorter and stiffer fibres. When cooked during chemical pulping, the fibres are not removed completely leaving dark spots and impurities in the pulp. It is thus important to remove the knots and bark from the wood and to chip the logs to prepare it for pulping (see Figure 6). In the wood yard the debarking, knot removal and wood seasoning are the first processes in the pre-treatment of pulp. The main purpose of a wood yard is to store the wood to decrease the extractives content. As soon as trees as felled, the chemical and biochemical reactions start in the degradation of the wood, including the hydrolysis of glycerides and other esters, oxidation of wood resin, and microbial degradation. To have some control over the microbial growth, different bacteria strains and fungi are used as biological treatment. This is known as bio-pulping. Experiments with fungi such as whiterot removed up to 51% of resin acids and up to 89% of fatty acids. Other experiments with yeast strains removed 78% of resin acids and up to 63% of fatty acids (Lehr, Miltner & Friedl, 2021: 889). However, this microbiological treatment should be carried out under controlled settings that can take up to several weeks, where mechanical or chemical pulping is much shorter and can take only hours.

2.2.2 Cellulose

Cellulose is the main structure and act as "skeleton" of the fibre (Brückle, 2011: 122). It is a type of glucose with many long carbon chains. Attached to the carbon atoms of the chains are hydroxyl ions consisting of oxygen and hydrogen, the same as in water. When the cellulose fibres are beaten in the water to make a pulp, it gets damaged and ravels out, exposing the hydroxyl ions. This process is called fibrillation. The oxygen in the water then attach to the exposed hydrogen ions in a process called hydration. When the water is removed from the pulp, another process namely hydrogen bonding takes place. In the drying process, the broken hydrogen bonds of the cellulose fibres and the oxygen of the different frays bond in a process called hydrogen bonding. The micro-fibrils of the beaten cellulose also intertwine that will form a very strong sheet of paper (Ewins, 2001: 3).



2.2.3 Hemicellulose

Hemicellulose consists of eight different polysaccharides or polycarbohydrates. They mix with cellulose and lignin to form different bonding situations: cellulosehemicellulose-cellulose and cellulose-hemicellulose-lignin (Brückle, 2011: 124). They are also carbohydrates but with different structures and functions. In hardwood, the major hemicellulose is xylan and in softwood it is glucomannan. They differ from cellulose by having a low molecular weight because of their short chain length; they do not have a clear structure and are non-fibrous; they swell more than unstructured cellulose; and they can easily dissolve.

Their interaction with water is important for papermaking. In dry conditions, hemicellulose polymers are very brittle. This is indicated by their glass transition temperature of Tg 150-220°C, cellulose is Tg 230°C and lignin is Tg 150°C. They easily absorb water that helps to improve fibre bonding when paper sheets are formed. They help cellulose fibrils to move freely in water, acting as a lubricant, and releasing internal stresses of the fibres. In conservation treatment, when paper is humidified, hemicellulose can absorb up to 30% of their dry weight in water. That is why paper with some hemicellulose can be made flexible in paper conservation. Hemicellulose can also contribute to the deterioration of paper because of their carboxylic acid content that can chemically break down paper.

2.2.4 Lignin

Lignin is an unstructured aromatic polymer, which can be described as large molecules forming bonds like a chain with links called monomers. These links form a large three-dimensional network of crosslinked ring-shaped structures with up to 20 monomers. It anchors to hemicellulose and so intermingle with the cellulose. Lignin is like a glue found more towards the outer cell walls of wood and in the middle lamellae. Its main aim is to keep the plant fibres stiff, therefore it is hydrophobic and prevent the plant fibres to absorb water (Brückle, 2011: 125). Lignin is seen as an antioxidant and protects the plant from



microbial and oxidative attacks (Kumar, Gautam & Dutt, 2016: 2). On the other hand, it can also contribute to the deterioration of cellulose when it reacts with oxygen forming acid by-products that deteriorate the cellulose (Brückle, 2011: 125). Good quality paper should be without lignin to enhance the quality and durability of paper.

2.3 Chemical processes of pulp for paper making



Figure 7: Wood yard procedures (Lehr, Miltner & Friedl, 2021: 900)

Paper making is a chemical process whether it is done on an industrial scale or by hand. To understand the whole process of paper making, the chemical process need to be explained. The aim of the chemical process is to remove unwanted material from the pulp, such as soiling, extractives and lignin. It is important to remove the lipophilic extractives, because the fatty acids and resin acids stick together to form pitch deposits that stick to the parts of the papermaking machines and equipment. They contaminate the pulp in the Kraft process, forming dark spots and streaks, leading to lower quality paper. Research noted by Lehr, Milner & Friedl (2021: 890) showed that especially polyphenols lead to wood becoming darker when exposed to oxygen and



sunlight. Although lignin and hemicellulose reactions also have an impact on darkening of wood, extractives intensify it.

There are four types of pulping techniques: Mechanical, thermal, semichemical and fully chemical (see Figure 6). Chemical pulping helps to break down the molecules of hemicellulose and lignin into water soluble molecules to wash it from the cellulose fibres. To do so, the pulp can be boiled with certain chemicals to whiten and sterilise it (Kamoga, Byaruhangu & Kirabira, 2013: 146). The pulping and bleaching process remove or convert lignin chemically, but still retain enough cellulose material to form paper sheets. Brückle (2011: 127) refers to the process of making paper as the controlled physical interaction between forces where bonds are broken and reformed to make something that is very different from the original raw material.

2.3.1 Pulping

Through chemical pulping wood and non-wood fibres are manupulated to reduce the lignin content. By removing the lignin, fibres are more flexible, interfibre bonding increases and paper sheets are stronger. When wood fibres are only mechanically beaten without any chemical pulping, the lignin still coats the frayed fibres, keeping them together. Small wood particles will then be part of the paper, decreasing the strength of the sheets. When mechanical pulping is combined with chemical pulping, the strength of the papersheet increases. The lignin and hemicellulose are broken down and the smaller particles can be washed away (Brückle, 2011: 128). In thermo mechanical pulping (TMP) the wood fibres are softened at high temperatures, but they are not as effective in forming hydrogen-bonds well with each other because they are coated with lignin. This process can be combined with chemi-thermomechanical pulping (CTMP) where the wood is treated with mild chemicals to enhance the extractive process. The high temperatures also degrade the cellulose and hemicellulose partially, dissolve saccharides in the water as well as fatty and resin acids. These composites are responsible for the toxicity of the mechanical pulping waters (Lehr, Milner & Friedl, 2021: 893).



Chemical pulping uses reactive compounds in the cooking process that breaks down the lignin to wash it away. The chemical mixture penetrates the pit apertures, lumen and pores of the wood fibres, increasing the absorbancy of the fibres resulting in an even dissolving of hemicellulose and lignin (Brückle, 2011: 129).

The two main chemical pulping procedures are Kraft, also called sulphate process, an alkaline process, and Sulphite/Bisulphide, an acidic process (refer to Figure 6). The Kraft process has replaced the older process where sulphurous acid was the main chemical ingredient. Kraft pulping now dominates as process to remove lignin through sodium hydroxide and sodium sulphide with a boiling temperature of about 175 °C for 2-5 hours. About 3% of lignin remains which is seen as acceptable. The use of sodium sulphide in the process helps to divide ether molecules and to decrease unwanted condensation reactions. The alkaline process darkens the pulp because the black concentrated liquor that the chemical process produces, converts the resin and fatty acids into soluble sodium soaps and glycerol that need to be washed out several times. This converting process is called saponification. However, by using the Kraft process the fibres are strong and the paper products are also strong (Holzapple, 2003: 1). Paper made by Sheila Collins will be examined to see if it complies to above-mentioned research that points to her methods of making elephant dung and rhinoceros' dung paper. If our theory holds that the gastrointestinal physiology of the elephant or rhinoceros helps with the pre-treatment of pulp by removing the fatty acids and resins her paper should be strongly bonded with a good longevity prospect.

The other pulping techniques as mentioned are briefly discussed here. Sulphite pulping is an acidic process where more lignin is removed, but the fibres are weaker. However, the paper is of a higher quality. Magnesium bisulphite and sulphur dioxide are used in the boiling process where the fibres are boiled at 175 °C for 6-12 hours. The result is a weak red liquor with about 2-3% sugar from the degraded hemicellulose (Holzapple, 2003: 2). In research noted by Lehr, Miltner & Friedl (2021: 893) the sulphate process removed double the



extractives than the sulphite process, but the alkaline Kraft process is seen as the better process for extractive removal due to saponification.

In a study that Kamoga, Byaruhangu & Kirabira (2013: 146-147) did, they found that by washing pulp made from elephant grass (*Pennisetum purpureum*) and alfalfa stems, good quality paper can be made. Sodium hydroxide and soda anthraquinone were used to wash the pulp, the same chemical process that Sheila Collins used in her paper making process. This is may again be an indication of the good quality of her paper.

Alternative extractive methods are more and more being used for their better extractive qualities and sometimes cost-effectiveness (Lehr, Miltner & Friedl (2021: 895) (see Figure 6). Organosolv pulping is also an acidic process where ethanol is preferred as solvent in the boiling process of about 2 hours. Different chemicals are used, such as: Hydrochloric adic, sulfuric acid, ferric chloride, ammonia, aluminum salts and urea. With the organosolv process hemicellulose is degraded through hydrolysis and lignin is dissolved into the solvent. According to Holzapple (2003: 3) organosolv as process is not as popular as the Kraft process. The lignin content are also reduced to about 3% which is acceptable for paper making, because a longer pulping process will reduce the cellulose significantly (Brückle, 2011: 129). Studies noted by Lehr, Miltner & Friedl (2021: 895-897) also confirm the higher cellulose content of pulp and the brighter and stronger properties of it. The main disadvantage is the high level of energy needed in the extraction method that is economically unfeasible.

Because of the environmental disadvantages and the increased costs of the organosolv process, more research led to the use of green solvents through the process of supercritical extraction (SCE) (see Figure 6). Supercritical fluids which are mixtures of organic co-solvents, water, and carbon dioxide, are used to remove wood extractives and to break down the internal bonds in lignin and hemicellulose. The fluids are highly dissolvable, have a high diffusivity, low viscosity and low surface tension. Advantages in using it are the following: It is


non-flammable, non-toxic, recyclabe, non-polar, and dissolves resin and fatty acids (Lehr, Miltner & Friedl, 2021: 896-897).

Another novel extraction method is steam explosion where wood is treated with hot steam under pressure, destructing the cell layers to easily turn the wood extractives into solubles. A disadvantage is that evaporation cannot always be controlled leading to the extensive degrading of hemicellulose. It can be used on a small scale but will be difficult on an industrial scale.

Another new approach is to use ultrasonic-assisted extraction (UAE) where ultrasonic waves degrade the cell walls of the wood to break the bonds between lignin, cellulose and hemicellulose. It has been proved as a successful method to remove wood extractives, but more research has to be done to use it on an industrial scale (Lehr, Miltner & Friedl, 2022: 899).

2.3.2 Bleaching

Wood pulp is bleached usually to increase brightness and to reduce the lignin content of the pulp. Chemicals used to treat the fibres are used to either remove the lignin (delignification) or to preserve the lignin (decolonisation) (Brückle, 2011: 129). It can also be used to clean the pulp from impurities that was not removed during beating. The Japanese used water from high mountain sources as bleaching medium because it contained ozone. Sunlight was also used as the earliest bleach procedure. Sheila Collins did not use a bleaching process. Only when the sheets were made, she put them out to dry in the sun.

In 1774 chlorine was discovered and from 1789 calcium hypochlorite was used. Delignification bleaches are chlorine based such as sodium hypochlorite, calcium hypochlorite, chlorine dioxide, oxygen and ozone. Chlorine-based bleaches break down lignin faster, but is much more degradative to cellulose. Chlorine-containing bleaches are used to decolonise lignin with a five-stage bleaching sequence: (1) Chlorine, (2), alkaline extraction, (3) chlorine dioxide, (4) alkaline extraction, (5) chlorine dioxide. The process form chlorinated lignin by-products and the pulp must be washed as alkaline treatment between



stages, because the lignin by-products are not completely removed in one step. Sometimes the pulp is cooked <u>and</u> bleached to remove the lignin. This can reduce the lignin content to less than 1% that is not traceable with the phloroglucinol test (Brückle, 2011: 130, Kamoga, Byaruhanga, & Kirabira, 2013: 147).

2.3.3 The effect of chemical processes on the fibre composition

The first step in Sheila Collins' recipe of making paper is the cooking of the dung in a sodium hydroxide mixture. The cooking process and temperature of the chemical processes influence the composition of the fibres in the pulp. Hemicellulose and lignin are gradually removed from the cell wall between the fibrils and the remaining cellulose chain length is shortened. Pores develop because there is still enough lignin left to keep the cell wall from collapsing. When most of the lignin is removed, the cell wall collapses, and the pores became smaller or close completely. This has an influence on the porosity of the paper. Bleached wood pulp retains less water than pulped but unbleached fibre. Fibre that can hold more water, has better and stronger hydrogen-bonds and the paper sheet will be stronger (Brückle, 2011: 130-140).

In Sheila Collins' next step she adds a sizing agent as internal sizing, but also as surface sizing to seal the paper to be printed and painted on (Collins, S. (sheila@magneticsouth.net) 06 June 2022. *Elephant dung paper*. E-mail to Marinda van der Nest (marindavdnest@gmail.com). Paper is sized to make it more water repellent. Sizing also changes the surface structure of the paper as well as the wet and dry strength of the paper (Daniels, 2006: 36). Sizing is a chemical process that prevents water from entering the paper surface so that it can be used for writing, painting and printing. The sizing agent prevents the interaction of certain polar groups on the surface of the paper with water molecules. Likewise, the pore openings of the fibres are blocked by the sizing agent to stop the penetration of water through this capillary system (Brückle, 2011: 148). Sizing strengthens the paper surface by acting as adhesive for fibre-to-fibre bonding and by flattening loose fibres to the paper surface (Kapur, 1963: 8). Sizing can be applied through two methods: internal when added to



the pulp or by surface application. Traditionally gelatine was used by hand paper makers in Europe as surface sizing. Collagen is the basis of gelatine, making it an organic medium. In the nineteenth century aluminium sulphate, or papermaker's alum, was added to gelatine to harden it to reduce its water absorbency. Sheets are dipped in a warm diluted solution of gelatine to cover the surface with a thin film. It improves the oil resistance of paper and prevents inks or dyes to bleed. As gelatine is a type of gel, it reduces water absorption and only let small amounts of water through to the paper. The gelatin layer can be broken down by acids from the environment or fibres in the paper. This can lead to oxidation that causes a slight yellow discoloration and when the paper is soaked in water to reduce the discoloration, some of the gelatin can dissolve leaving the paper surface vulnerable to degradation (Brückle, 2011: 150-155).

Rosin is another internal sizing agent. It is a natural resin obtained from pine trees. Rosin particles are evenly distributed in the water to attach to the fibre surfaces. Like gelatine, it prevents water to be absorbed by the fibres and prevents bleeding of inks and paints. For conservation purposes, it can be lifted with organic solvents. Added alum as part of rosin as sizing agent makes it more acidic. Aged rosin-sized paper has unstable compounds and oxidation may occur.

Internal sizing is when the sizing agent is added to the pulp in a process called wet-end or stock-sizing. Kapur (1963: 4) mentions that when starch is used as internal sizing agent the tensile, strength, tear, stretch and bursting strengths of paper sheets show a positive improvement. Sheila Collins used starch together with an alkaline reactive sizing agent in her paper making. Alkyl ketene dimer (AKD) was introduced in 1953 and alkyl succinic anhydride (ASA) in 1974 as new sizing agents when calcium carbonate fillers were introduced to the paper making industry. When added to the pulp, it is mixed with the fibres where it reduces the interaction between water and individual fibres (Brückle, 2011: 149-165). Because the sizing agents form part of the whole papermaking process, from the heating of the pulp to the drying, it is well cured, are bonded covalently and not removable. It is an alkaline agent and may not affect the aging of paper.



For my study the use of starch as surface agent is of importance as this was used for making the elephant dung paper. The Arabs used cooked rice or wheat starch to brush onto both sides of the paper sheets. After drying the paper surface was polished to form a water-resistant layer. It prevented bleeding of ink and of water colour paints. It is not used nowadays as sizing agent but to strengthen the surface of the paper by binding the loose fibres. Printing and photocopying of sheets are easier and no fibres interfere with the adhesion of ink and sheets are not caught in the photocopying machine. (Brückle, 2011: 149). Sheila Collins printed her artwork onto the elephant dung paper that was sized with starch. I also used starch and internal sizing agents as per Sheila Collins' recipe to make my test paper sheets as a control sheet.

When Collins decided to use elephant dung, she took a short cut by cutting out all the pre-treatment of the pulping process. To find out if elephant dung is a replacement for the pre-treatment of pulp, it is good to look at the digestive system of the elephant.

2.4 Elephant and rhinoceros' dung as fibre content for paper making

Elephants are classified as monogastric (one stomach), herbivorous, nonruminant, hindgut fermenters (Green, Dierenfeld & Mikota, 2019: 3). They weigh more than 1000 kg, and are primarily food-limited, meaning they are not predators. The African elephant (*Loxodonta africana*) and the black rhinoceros (*Diceros bicornis*) usually share the same food resources. Elephants feed on green grass, shoots, twigs, leaves of trees and shrubs and rhinoceros prefer succulents, pasture, and dwarf shrubs. Both these herbivores prefer lower quality food as long as there is an abundance of it (Landman, Schoeman & Kerley, 2013: 2). I include the rhinoceros' data here, because I used rhinoceros' dung as an experimental paper sheet for this study.

Collins used dung that was collected from the Addo Elephant Park as well as sites adjacent to the park. Landman, Schoeman & Kerley (2013: 2) did a study on elephant and black rhinoceros' diet preferences in these sites that presents



a good idea of the composition of their dung. The semi-arid region has a rainfall of about 260-530 mm annually during March and November with succulent thickets of 2-4 m high. The dominant drought resistant vegetation is the tree *Portulacaria afra*, low trees such as *Euclea undulata*, *Schotia afra*, *Sideroxylan inerme*, spinescent woody shrubs such as *Azima tetracantha*, *Capparis sepiara*, *Carissa bispinosa*, the genuses *Gymnosporia* and *Searsia*. In the undergrowth geophytes, dwarf succulents, pasture and couch grass (*Cynodon dactylon*) are plentiful.

For their study Landman, Schoeman & Kerley (2013: 3) collected fresh dung samples from August 2001 to June 2003 to cover all four seasons and different rainfall and temperature patterns. The dung was oven-dried for their experiments. They categorised plant species into grasses, succulents, woody shrubs, pasture, lianas, epiphytes and geophytes. They identified 90 plant species forming part of the elephants' diet, confirming that they are mixed feeders. Elephants frequented woody shrubs more, followed by succulents (preferably *Portulacaria afra*), leavy branches, grasses (*Cynodon dactylon*) epiphytes and geophytes. During the wetter months elephants grazed more on grasses and reduced their intake of grasses during the drier months to maintain their diet quality. They have a long feeding time, about 80% of their day, where they can consume 1,5-2% of their body weight.

A total of 87 plant species of the categorised species were identified in the diet of rhinoceros. They frequented grasses, followed by succulents, pasture, woody shrubs, lianas, geophytes and epiphytes. Both elephants and rhinoceros graze on grasses as part of their constant diet (Landman, Schoeman & Kerley, 2013: 7, Green, Dierenfeld & Mikota (2019: 11).

Because elephants are hindgut fermenters they ingest and process food fast. They always have six sets of molars that can be as long as 40 cm and can weigh over 5 kg. With these they can grind and shred their food into a pulp. They have a high content of saliva with amylase as enzyme to break down starch into sugars. The high urea content in the saliva plays an important role in the digestion of nitrogen containing composites of their food (Green,



Dierenfeld & Mikota, 2019: 2). Elephants have a short digestive tract. The oesophagus is short ending in the stomach that can hold up to 65 litres of ingested food. The small intestine ends in the caecum where most of the fermentation of the elephant's food takes place. The large intestine, colon and rectum complete the gastrointestinal anatomy. The elephant does not have a gall bladder but produces and discharge bile alcohols into the small intestine to help with lipid digestion and absorption. Because of their short digestive tract, the retention time of food is also shorter. Elephants digest about 60% of their food, leaving about 40% of plant fibre containing cellulose in their dung (Green, Dierenfeld & Mikota, 2019: 3).

By using their dung as the fibre content for paper making, the time-consuming and costly pre-treatment of wood products are eliminated. Collins used the Kraft process where the dung is cooked in a sodium hydroxide solution to soften and sterilise the fibre (Collins, personal communication 2022, February 11). She also explained that there was a difference in the colour of the paper made from white rhinoceros' paper. The paper was slightly green, because the white rhinoceros is a grazer. The paper grain was also finer and more even than the paper made from black rhinoceros' dung. Their paper had a reddish tint from the sap in the wood. These pulps were rougher with pieces of twigs and thorns that the paper makers took out, because the black rhinoceros browses bushes and shrubs. Both species bite the grass and woody shrubs into even-sized pieces of about one and a half centimetres long and with a 45-degree angle. These pieces are visible in the paper. The elephant on the other hand, eats a variety of fruit, leaves, bark, roots, branches, shrubs as well as grass, making the variety of textures in the paper greater. The pulp was also much rougher and they needed to remove or cut the bigger pieces before making the paper.

As the research of Green, Dierenfeld & Mikota (2019: 2-3) shows, the enzymes in elephants' saliva help to digest the sugars in the roughage and the bile alcohols break down the lipids. The gastrointestinal physiology of the elephant helps with the pre-treatment of pulp by removing the fatty acids and resins. Enough cellulose and hemicellulose remain, cellulose being one of the building



blocks for paper. There is also lignin left in the pulp that still needs to be removed to have good quality pulp.



CHAPTER 3: DETERIORATION CAUSES OF PAPER

3.1 Introduction

Museum, library, and archival communities laid down certain norms or standards for paper composition to ensure durability and permanence. Paper should be alkaline, include neutralising buffers and the lignin content should be less than 1%. Although these standards are in place, there are still a need for research on the stability and composition of paper. There is no assurance that paper will not degrade if these standards are followed (Area & Cheradame, 2011: 5309).

In their review on paper conservation methodology Zervos & Moropoulou (2006: 219) point out that paper conservation is a fairly new research field, and it is costly. The existing research methods were used by the paper industry for research on new paper products, to improve quality, and for performance of paper. They had the funds to keep their products competitive and to comply with market laws. Paper conservation on the other hand, are practised by public organisations and individuals with limited funds where testing is kept to the minimum and focused on specific outcomes.

Tests for performance and to identify change in the properties of paper are: tearing strength, folding endurance, tensile strength (fibre strength), viscosity, alkali solubility, oxidation, acidification, distribution of chain lengths, and peroxide formation to name a few. The outcome of all the tests is to see what happens when paper deteriorate. The accelerated ageing tests used are to predict the life expectancy and stability of paper. This is one of the tests that is rather important for paper conservators. Although extensive research was done on it, there was no agreement of the best procedure (Area & Cheradame, 2011: 5309). Whitmore (2012: 245) also mentions the difficulty to age paper naturally. He mentions that research where extreme temperatures, bright lights and high quantities of air pollutants are used, do not take the hydrolysis of natural ageing into consideration. Research that Shahani did where paper was aged in sealed containers are now more widely accepted (Whitmore, 2012:



245). He argues that the unstable properties of paper cannot escape and because they are acidic, they contribute to the degradation process. Because paper usually ages together in stacks, as pages of books or in files, the unstable properties are trapped. His sealed containers also trap the unstable properties as well as the inherent water of accelerated aged paper. According to Shahani, mentioned by Whitmore (2012: 245) this test imitates natural aged paper better than other experiments. Because of his finding, a new standard for accelerated aged paper was developed: ASTM D6819-02e2 (the American Society of Testing Materials) (Zervos & Moropoulou, 2006: 224).

Although accelerated ageing is seen as an important test for paper permanence, our laboratory is not equipped for these tests. I rather focussed on some of the other major ageing processes of paper as degradation markers as seen in the discussion below.

3.2 Major ageing processes of paper

According to Whitmore (2012: 248) the major causes for paper deterioration is water (humidity) and acid-catalysed hydrolysis. The causes can be internal because of the pH count, lignin amount, metal ions, and degradation products of paper. It can also be external because of the influence of humidity, heat, pollutant gasses and physical handling. As mentioned previously the intrinsic strength of fibres and inter-fibre bonding determine the paper strength. Cellulose deterioration starts when these fibre strengths deteriorate. It can be chemical through acid and enzymatic hydrolysis, which break the bonds, or it can be through oxidation with exposure to UV radiation, or high-energy radiation or through metal ions from pigments and ink. Acid-catalysed hydrolysis is usually the reason for the breaking of the cellulose bonds. (Area & Cheradame, 2011: 5310 and Whitmore, 2012: 248).



3.2.1 Acid-catalysed degradation

As paper ages it loses its strength and flexibility. The weakened fibres and broken cellulose bonds lead to the forming of small chain fragments and sugars. These small fragments further react to form acidic substances that will further break down the cellulose chains (Whitmore, 2012: 222). It was always presumed that the manufacturing process of paper where acidic alum-rosin sizing was used and the oxidation from the environment contributed to paper ageing and strength loss. Research mentioned by Porck & Teygeler (2000: 9) found that alkaline papers showed increased acidity as it aged, because of the reactions of broken cellulose bonding. The yellow discolouring of old paper is also a sign of the degraded cellulose. Acidity also causes an increase of crystallinity in the microfibrils. This reduces the flexibility of paper and its reaction to water, especially in conservation treatments. Hydrolysis is seen as a major cause of broken cellulose bonds. Is goes hand in hand with strength loss as many studies have shown (Whitmore, 2012: 225). Hydrolysis increases when there are contaminants in paper from the pulping process, such as alum in rosin sizing, metal ions from the water used, or in the pigments or ink. These contaminants increase the acidity of paper. Whitmore (2012: 226) indicates that the cellulose breakdown in paper with a pH of 4 is 1000 times faster than paper with a pH of 7. To keep the moisture content and the relative humidity conditions of stored paper under control, are essential. The same can be said for temperature control. Fluctuations in thermal energy initiate the reactions for chain breaking.

3.2.2 Oxidation

Oxidation is another degradative reaction of cellulose. It is usually a very slow process but can become more rapid when paper is exposed to specific triggers. Oxidizing bleaching treatments can reactivate a molecule to separate a hydrogen atom from the carbons that make up the glycose unit of the cellulose. The same reaction can occur when paper is exposed to bright lights or UV radiation. Certain metallic impurities such as copper or iron or iron gall ink, or metal tannate ink can also trigger the reaction. Gasses in the air can act as



oxidising agent to start the breaking down of bonds. Oxygen absorption by alkaline paper, produces changes of polymerisation in the cellulose that additionally leads to reactions to break cellulose chains (Area & Cheradame 2011: 5312-5313, Whitmore 2012: 231-232).

High alkali concentrations of pH more than 8 can lead to swollen fibres that break down the cellulose. This can happen during the pulping process or when testing the alkalinity of cellulose. The breaking down reaction is the same as with oxidation where the hydrogen atom is removed from the cellulose molecule. Here the alkaline reaction removes a hydrogen ion from the cellulose molecule, leaving it with a negative charge. This reaction leads to the breaking of cellulose chains and the degrading of oxidised paper (Whitmore 2012: 233).

3.2.3 Biological and mechanical degradation

The most common cause of biological degradation is insects and mold. Fungal attacks are more frequent in tropical and subtropical areas but can be found in any archive with high humidity. Usually, it is because of inappropriate storing conditions. Paper degrades through the enzymes that mold produces and its acidic waste that attack the cellulose and break its molecular bonds. Mold spores can be inactive for years and then start growing under favourable conditions such as high humidity or temperature changes. To control and prevent fungal growth, temperature control and humidity should be carefully monitored. To stop fungal growth, studies showed that ethylene oxide and spraying of disinfectants are efficient, but it is time consuming and costly. Gamma radiation was also studied, but more research is needed to understand the damage to the strength and appearance of paper products. Fungal attacks are still a problem for paper degradation (Area & Cheradame, 2011: 5314-5315).

High humidity can also cause foxing stains, that is the small, discoloured spots on paper. Causes can be metal impurities that create rust or salts or sugar formations that break down the molecular bonds of cellulose. Foxing can also be because of mold growth from the manufacturing process where



contaminated felts or other material were used. Just as with other molds, the enzymes and acids released by foxing, react with the cellulose molecules to break it down (Whitmore, 2012: 240).

3.2.4 Moisture content (relative humidity)

Both relative humidity and the temperature of the environment determine the moisture content of paper which is an important factor in degradation of cellulose. Numerous studies mentioned by Zervos (2010: 14) indicated that water is responsible for the swelling of paper, increasing the bond reactions and mobility of molecules. Just as in aqueous solutions, water is also responsible for the breaking of bonds in paper. To prevent paper degradation, the recommended relative humidity in archives, libraries, and museums should be between 25-60%.

3.2.5 Lignin and light

Mechanically pulped fibres usually have a high lignin content, where chemically bleached pulp fibres have a very low content as international standards require. The standards specify that paper should be alkaline, with at least 2% calcium carbonate (CaCO₃) content acting as alkaline reserve. These standards also require that the lignin content in paper should be minimal. It was implemented because the degradation of paper was thought to be because of the lignin Research done on UV radiation and visible light indicated they content. changed the structure of lignin (Area & Cheradame, 2011: 5316). The antioxidant properties of lignin, containing free phenolic radicals, are responsible for the degradation of lignin in the photo-oxidation process where molecules split off. A direct link was found between lignin content, oxidation, and yellowing of paper (Zervos, 2010: 17). More tests, however showed that paper yellowing does not infer that deterioration of paper will take place the same time. Studies done by Malachowska, Dubowik, Boruszewski & Przybysz (2021: 1-8) showed lignin contents below 28% do not contribute to the aged loss of mechanical paper properties. Their research concluded that the lignin content in paper made under neutral pH conditions had no impact on the



accelerated ageing conditions of the paper pH, or on the breaking length, or on the tear resistance, or on the bursting strength. Further research needs to be done to substantiate this.

The research found it was rather acidity that is a greater degrading factor than the lignin content. Alkaline lignin-containing paper is less stable than alkaline lignin-free paper. But if the pH value is between 7 and 10, and the strength and performance properties of the paper is good, then the lignin content should not be a problem. To ensure that the lignin content is restricted, the standard of 1% has been approved that will assure the optical stability of paper (Area & Cheradame, 2011: 5317).

3.2.6 Air pollution

The two air pollutants that contribute to the increased acidity of paper are sulphur dioxide (SO₂) and the nitrogen oxides (NO_x). Through oxidation and an increase in moisture content, strong acids form to deteriorate paper. Studies on pollution of mechanical pulped paper showed a greater absorption of pollutants and loss of brightness than lignin-free paper. The lignin only had an effect on the brightness, and not on the mechanical properties of the paper. The combination of nitrogen oxides (NO₃), ozone (O₃) and a high RH increase the absorption of sulphur dioxide (SO₂). This transfer of molecules was found to be the first step to react with cellulose, starting the degradation process of paper. Further studies confirmed that nitrogen dioxide (NO₂) is the most lethal pollutant that cause greater mechanical loss and more yellowness in paper (Zervos, 2010: 18, Area & Cheradame, 2011: 5316).

3.3 The effect of paint pigments used in the lithographic printing

Inks made of vegetable, mineral or animal ingredients have been used for millennia for writing purposes, or for art. The basic ingredients of ink are the pigments and dyes that provide the colour, solvents that dilute the ink to help its fluidity, adhesives that bind inks to the paper, mordants which are chemical ingredients used instead of adhesives and usually contain acid compounds.



Secondary ingredients are thickeners, humidifiers to regulate the drying process, anti-septics to prevent microbial growth, scents to give it a pleasant smell, brighteners to give ink a shine, penetrants to help with the absorption.

Inks are also classified as stable and unstable. Stable inks are not influenced by environmental variations and do not influence paper. Unstable inks contain elements that can alter or deteriorate paper. Usually ink that is known as permanent, has unstable chemical ingredients and can deteriorate paper (Crespo & Viñas, 1985: 11-13).

All coloured inks contain metallo-acid inks that are made up of a metal and an acid. The acid as well as the chemical ingredients of the mordant help the ink to adhered. These inks are seen as permanent, because they are not soluble in water, but they are chemically unstable and can cause considerable damage. The acid reacts with the iron to produce sulphuric acid as corrosion agent of the paper. Although the alkaline components of the paper and other ingredients of the ink can deter the corrosion, it does cause damage to the paper. Metallo-acid inks also contain alizarin and vanadium. Alizarin is a red dye that has an iron tannate base. By adding an acid, the diluted iron salt oxidizes on paper and the greenish-grey colour change into black. By adding sulphuric acid, the dye changes into indigo. Vanadium in an acid solution can produce a very deep black colour. These compounds are one of the corrosion causes in paper because of their acid content (Crespo & Viñas, 1985: 15, Viñas, 1988: 12).

Lithographic inks contain lampblack mixed with linseed oil and can contain wax, animal fat, grease, or olive oil, to help transferring the ink colour to the paper while preventing the ink to adhere to the plate. Lampblack inks are seen as the oldest type of ink and one of the most stable because of its carbon content. Acids, light, alkalis, water or microbials do not have a corrosive impact on it (Crespo & Viñas, 1985: 17).

Sheila Collins, the artist of the elephant dung made paper, used a Heidelberg lithographic printer to print her artworks on the hand-made paper. She used water colour and acrylic for her artwork, and printed it onto the paper with



printer's inks (Collins, S (<u>sheila@magneticsouth.net</u>) 06 June 2022. *Elephant dung paper*. E-mail to Marinda van der Nest (<u>marindavdnest@gmail.com</u>). The lithographic printing system works on the principle that oil and water do not mix. An aluminium plate is treated with a photosensitive substance so that a negative of the artwork can be created using analogue or digital methods. With the analogue method the image areas are exposed to UV light, and the non-image areas are shielded from exposure. The exposed areas polymerise and harden, while the non-image areas stay soft and are removed. With the digital method computer lasers remove the non-image areas. These areas are treated with a gum solution (usually gum Arabic) to prevent the ink attaching to it.

The aluminium plate is then attached to the cylinder of the press and sprayed with oil-based printing pigments. It usually contains water, an acid, a gum, a corrosion protector, an alcohol based solution to increase the viscosity of the ink, an anti-fungal agent, an anti-foaming agent and a drying agent. The pigments are oil-based and dry quickly through polymerisation, oxidation and absorption. Because the pigments are made up of powdered particles added to an oil as binder, it adheres to the surface of the paper and does not dissolve (Lithographic printing, 2019: 2-3).

The pigments contain acid, and other agents for lithographic printing. These agents might transfer to the paper to impact the degradation process. Samples of Sheila Collins' cards made of elephant dung paper from around 1992 with prints of her art work were observed under a Leica S9i optical microscope to see any degradation areas. No degradation was observed, colours did not fade and no ink corrosion were observed (see Figures 7-12). She also confirmed that a painting she did in 1980 did not appear to have changed colour. She has also seen framed prints hanging on walls that were made for a fund-raising project in 1996 that have not faded (Collins, S. (sheila@magneticsouth.net). 6 June 2022. *Elephant dung paper*. E-mail to Marinda van der Nest (marindavdnest@gmail.com).



Two hand painted water colours, one of an elephant and one of zebras, were also observed under the microscope. No fading of colours or any other colour changes was observed and no ink corrosion or any degradation were observed.



Figure 8: Microscope photo of a Bushman's head and hunting gear. Printed on elephant dung paper with a 4-ton Heidelberg Printing Press around 1992. No deterioration was observed (2,5mm).





Figure 9: Bushmen printed on elephant dung made paper with a 4-ton Heidelberg Printing Press around 1992. Photo: Author (2022).



Figure 10: Microscope photo of giraffe head printed on elephant dung made paper with 4-ton Heidelberg Printing Press around 1992 (2,5mm). No degradation was observed. Photo: Leica S9i microscope (2022).





Figure 11: Print of giraffes on elephant dung made paper with a 4-ton Heidelberg Printing Press around 1992. Photo: Author (2022).





Figure 12: Microscope photo of hand painted watercolour of a zebra face on elephant dung made paper by Sheila Cooper around 1992 (2,5mm). No degradation was observed. Photo: Leica S9i microscope (2022).



Figure 13: Hand painted water colour of zebras by Sheila Collins around 1992. Photo: Author (2022).





Figure 14: Microscope photo of an elephant eye painted on elephant dung made paper with water colours by Sheila Collins around 1992 (2,5mm). No degradation was observed. Photo: Leica S9i microscope (2022).



Figure 15: Hand painted water colour of an elephant on elephant dung made paper by Sheila Collins around 1992. No degradation was observed. Photo: Author (2022).



CHAPTER 4: METHODOLOGY

4.1 Introduction

The deterioration of books and documents where the paper became brittle with age, raised the concern of the conservation environment as well as libraries and archives. Research done by the industry concentrated on quality and market related competition and not so much on durability of paper. The conservation environment then began to insist on standards for paper permanence based on specific paper composition (Area & Cheradame, 2011: 5309). Methods for the evaluation of paper permanence were established and divided into studies of chemical properties and of physical properties. The evaluation of chemical properties included the determination of pH, Degree of Polymerization (DP), alkalinity, yellowness, and brightness. Evaluation based on physical properties included the measurement of folding endurance, tensile properties, and tearing resistance (Zervos & Moropoulou, 2006: 2-19).

As Zervos & Moropoulou (2006: 219-220) mention, test methods must be chosen to detect changes that are useful for the specific evaluation of samples. Previous research showed that light and relative humidity are the major contributors to the degradation of paper. The aim of the methodology was the determination of pH, lignin content, the effect of UV light on different paper samples and the hygroscopic property of different paper samples. concentrated on the degradation caused by UV radiation on paper with different pH and lignin content. Optical microscopy was used to evaluate colour changes of paper fibres and the effect of the coloured pigments of the art work on elephant dung made paper. I used samples of paper made with black rhinoceros' dung, black rhinoceros dung sized with corn starch, black rhinoceros' dung and printing paper sized with corn starch, elephant dung paper, and white rhinoceros dung paper, printing paper (Sappi), Chinese artist paper, and newsprint paper. The premise of the University of Pretoria is to choose methods on the basis that any Africa Museum, archive or gallery can copy and use it.



4.2 Paper making

I collected black rhinoceros' dung to make sheets of paper as reference against the original elephant dung made paper and white rhinoceros dung made paper of Sheila Collins the artist. Sappi printing paper, Chinese artist paper and newsprint were also used as reference against the elephant dung made paper. The dung was collected from a farm in Mpumalanga, near the Kruger National Park. The dung was air dried under a shaded roof for about two months, overturning it occasionally to ensure it was thoroughly dried (see Figure 15).

For paper making, the recipe of Sheila Collins was followed where the dung was sterilised by adding 50g of washing soda (sodium hydroxide - NaOH) to 500g of dung in 6l water, boiling it for 2 hours in a stainless steel pot on a gas stove. After cooling, the dung was scooped into a mesh cloth and washed thoroughly until the water was near clear (see Figures 18, 20, 21).

As per Sheila's recipe for internal sizing, 20g Sprayseal was added to the cooked dung and a corn starch solution of 250g on 3,5l water. As Sheila mentioned internal sizing is essential for the printing of the sheets. The paper fibres are smoother and will not catch in the printer. The pH of the Sprayseal was tested before adding it to the dung to confirm that it was an alkaline solution. The pH was 7-8. The pulp was ready for paper making (see Figures 16, 17, 19).

The screen for the sheet making is made from wood with a fine plastic mesh. The pulp was screened and the sheet thickness was checked. The sheet was couched onto a felt sheet and the excess moisture was pressed out with a sponge. The sheet was lifted from the deckle and a plastic sheet was put on top of it. The sheet was left overnight under a stack of 5 heavy books, bonding the fibres into a strong paper sheet (Keller, 2012: 210-212). The next day the sheet was peeled from the plastic and placed in the sun to dry. This sheet was left unsized because it will be one of the reference sheets against the original elephant dung paper (see Figures 22-23).





Figure 16: Black rhinoceros' dung before pulping. Photo: Author (2022).



Figure 17: Alkaline internal sizing. Photo: Author (2022).



Figure 18: pH test of internal sizing (Sprayseal). Photo: Author (2022).



Figure 19: Cooking the black rhinoceros' dung. Photo: Author (2022).







Figure 21: Straining the pulp after cooking. Photo: Author (2022).

Figure 20: Stirring the dung to ensure all ingredients are mixed. Photo: Author (2022).



Figure 22: Washing the pulp until the water is near clear. Photo: Author (2022).



Figure 24: Sheet made with black rhinoceros' dung. Photo: Author (2022).

Figure 23: Screen and deckle. Photo: Author (2022)

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On day three, more sheets were made with the sterilised dung, with some shredded Sappi printing/writing paper added as filler. The same procedure was followed: The black rhinoceros' dung was mixed with some shredded Sappi paper that was submerged in water and left overnight to soak. The mixture was liquidised with a handheld liquidiser to have finer fibres. When the pulp was mixed, more water was added to have a smoother mixture. It was strained with the deckle more than once to get an even sheet and then couched onto felt sheets. The extra water was absorbed with a sponge and then a plastic sheet was placed on top to have a smooth and rough side on the paper sheets. The sheet was not as brittle as the one where only black rhinoceros' dung fibres were used. The Sappi paper filler gave it a smoother and creamier look. To press out the extra water and help with fibre bonding, 2 stacks of 6 thick books were placed on top of the sheets.

On day four the sheets were peeled from the plastic liners and put in the sun to dry completely. When it was dried completely, it was sized with a solution of 50g corn starch in 1l water (cooked until thick), and 280g Sprayseal was added. The extra moisture was rolled out with a rolling pin, also helping to bond the starch to the paper. The sheets were again sundried and when dried, flatten under stacks of books (see Figures 24-27).



Figure 25: Removing excess water on sheet made of dung and shredded paper. Photo: Author (2022).



Figure 26: Sheet couched onto felt and plastic sheet. Photo: Author (2022).





Figure 27: Sheets under stack of books to remove excess water. Photo: Author (2022).



Figure 28: Sheets left in the sun to dry out. Photo: Author (2022).

4.3 Determination of pH

The pH test is according to procedures described in a publication by the American Institute for Conservation (AIC) (Mayer, 2021: 85) and by Brückle (2011: 473). The pH of strips of the sample papers were tested using a pH strip indicator. A drop of distilled water was placed near the edge of the strip and allowed to penetrate the paper. The pH test strip was placed on the wet area of the paper and covered with a piece of Mylar to ensure that the strip makes full contact with the paper surface. After about 30 seconds the test strip was lifted and compared with the colour code on the package. This gave a clear and unambiguous reading. A pH reading of 6 and above is considered acceptable, but 7 and above is preferred. Paper with a pH reading of below 6 is seen as more acidic and not of good durability (see Figures 28-33 and Table 1).





Figure 29: Paper samples ready for pH test. Photo: Author (2022).



Figure 30: Black rhinoceros' dung paper (sized) with droplets of distilled water. Photo: Author (2022).



Figure 31: Black rhinoceros' dung paper (unsized and sized) with pH strip. Photo: Author (2022).



Figure 32: Black rhinoceros' dung with shredded Sappi and Sappi printer paper. Photo: Author (2022).



Figure 33: Elephant dung paper and white rhinoceros' dung paper. Photo: Author (2022).



Figure 34: Chinese art paper and newsprint. Photo: Author (2022).



Analysis of the pH test

Table 1: Determination of pH

Sample	Sample		
number			
1	Black rhinoceros' dung paper (only fibre not sized)	7	
2	Black rhinoceros' dung paper (only fibre, sized)	8	
3	Black rhinoceros' dung paper and Sappi paper	8,5	
4	Sappi paper	8	
5	Elephant dung paper from the Kruger National Park	7	
6	White rhinoceros' dung	6	
7	Chinese art paper	7,5	
8	Newsprint	5	

The distilled water tested at pH 6.

4.4 Test for lignin content

A tiny piece of paper was extracted from the test sheets. From the fibrous rhinoceros and elephant dung made paper, a piece consisting of some fibres were selected. These samples were placed in a glass dish and numbered to keep track of the different samples. A test solution of 0,02g phloroglucinol dissolved in 3,25ml methanol, 3,25ml distilled water and 3,25ml concentrated hydrochloric acid (HCI) was dropped onto each sample. After one minute the reaction was recorded under a USB microscope and a photo was taken (see Figures 34-42).

The test for lignin were used as described in a publication by the American Institute for Conservation (AIC) and by Brückle (2011: 482). The test does not require complicated techniques and all the material and equipment were available in our laboratory to perform the test (Mayer, 2021: 90).





Figure 35: Tiny paper samples for lignin test. Photo: Author (2022).



Figure 36: Lignin test on black rhinoceros' dung (unsized), no reaction. Photo: USB microscope (2022).



Figure 37: Lignin test on black rhinoceros' dung (sized), no reaction. Photo: USB microscope (2022).



Figure 38: Black rhinoceros' dung with shredded Sappi paper (sized), no reaction. Photo: USB microscope (2022).



Figure 39: Sappi printer paper, no reaction. Photo: USB microscope (2022).



Figure 40: Kruger National Park elephant dung paper, no reaction. Photo: USB microscope (2022).







Figure 41: White rhinoceros' dung paper, no reaction. Photo: USB microscope (2022).

Figure 42: Chinese art paper, no reaction. Photo: USB microscope (2022).



Figure 43: Newsprint, paper, magenta coloured stain appeared. Photo: USB microscope (2022).

Analysis of test

A magenta or violet stain would indicate the presence of lignin. Only the newsprint reacted and changed to a magenta stain. No other sample showed any reaction for lignin content and none was observed under the USB microscope (see Figures 34-42).

4.5 Hygroscopic test

A small bowl with 50ml water and test strips of the paper samples that were weighed and numbered were placed in a plastic container with a tight fitting lid (see Figures 43-44). This test is done according to the Lascaux humidification Chamber HC-5 described by Weidner & Zachary (1994: 109-115) The samples were contained for 3 weeks. Each sample was weighed before absorption and



again after absorption (See Table 2). There was 14ml water left in the small bowl after absorption. Each sample were observed under a Leica S9i microscope before absorption and after absorption (see Figures 45-52).

Sample number	Sample	Weight /g	Weight after absorption /g	Weight gained /g	Relative % weight gained
1	Black rhinoceros' dung paper (only fibre not sized)	1.36	1.45	0.09	6.61
2	Black rhinoceros' dung paper (only fibre, sized)	1.39	1.27	0.12	8.48
3	Black rhinoceros' dung paper and Sappi paper	0.57	0.58	0.01	2.46
4	Sappi paper	0.27	0.33	0.06	20.96
5	Elephant dung paper from the Kruger National Park	2.33	2.38	0.05	2.06
6	White rhinoceros' dung	0.80	1.03	0.23	28.55
7	Chinese art paper	0.42	0.78	0.36	87.26
8	Newsprint	0.27	0.31	0.04	12.87

Table 2: Sample weight before absorption.



Table 3: Standard deviation weight using a paper sample of black rhinoceros' dung and Sappi paper.

Paper sample	Total measurements	Average weight calculation /g
Black rhinoceros' dung and Sappi paper	1	0.59
	2	0.59
	3	0.59
	4	0.56
	5	0.59
	6	0.59
	7	0.59
	8	0.59
	9	0.58
	10	0.59
	TOTAL	5.94
	SDEV	0.59

In table 3 the standard deviation of the paper samples was calculated where a paper sample of black rhinoceros' dung and Sappi paper were weighed ten times and then calculated using the standard deviation (SDEV) calculator on the Excel program.



Figure 44: Samples of paper with bowl of water in container. Photo: Author (2022).



Figure 45: Paper samples in container with air tight lid. Photo: Author (2022).





Figure 46: Rhinoceros' dung paper, not sized, before (left) and after absorption (left). No mold or any other growth was observed. Photo: Leica S9i microscope (2022).



Figure 47: Rhinoceros' dung paper sized before (left) and after absorption (right). No mold or any other growth was observed. Photo: Leica S9i microscope (2022).



Figure 48: Rhinoceros' dung and Sappi paper before (left) and after (right) absorption. No mold or any other growth was observed. Photo: Leica S9i microscope (2022).



Figure 49: Sappi paper before (left) and after (right) absorption. No mold or any other growth was observed. Photo: Leica S9i microscope (2022).





Figure 50: Kruger elephant dung paper before (left) and after (right) absorption. No mold or any other growth was observed. Photo: Leica S9i microscope (2022).



Figure 51: White rhinoceros' dung paper before (left) and after (right) absorption. No mold or any other growth was observed. Photo: Leica S9i microscope (2022).



Figure 52: Chinese artist paper before (left) and after (right) absorption. No mold or any other growth was observed. Photo: Leica S9i microscope (2022).



Figure 53: Newsprint paper before (left) and after (right) absorption. No mold or any other growth was observed. Photo: Leica S9i microscope (2022).



Analysis of test

Research done by Malachowska et al (2021: 3) concluded that paper with a neutral pH does not degrade as fast because of low acidity. Cellulose and hemicellulose also show an increase in degradation if the humidity is between 50-75%. In the hygroscopic test done for my research, no degradation was observed in any of the paper samples. The humidity was about 28% which is too low for any significant degradation. Slight degradation with humidity at 10-25% is noted in research studies (Malachowska et al, 2021: 2). No mold or any other growth was observed under the microscope. When the paper samples were weighed after absorption the following was noted: the Chinese artist paper absorbed 87.26% water, followed by the white rhinoceros' dung made paper with 28.55%, the Sappi paper with 20.96%, the newsprint with 12.87%, the black rhinoceros' dung made paper (sized) with 8.48%, the black rhinoceros' dung made paper (unsized) with 6.61%, the black rhinoceros' dung made paper with 2.46% and the Kruger elephant dung made paper with 2.06%.

The newsprint paper had the highest lignin content and an acidic pH count, and absorbed 12.87% water. The handcrafted paper samples (apart from the historic White Rhinoceros' dung), did not absorb as much water and their neutral pH and low lignin content will slow any degradation process (Malachowska et al, 2021: 2).

4.6 Ultra violet light exposure

For this experiment, eight strips of paper were conditioned under near ultra violet (UV) light exposure (320-400 nm) for one month (30 days). The sample paper strips were of black rhinoceros' dung (only fibre and not sized), black rhinoceros' dung (only fibre and sized), black rhinoceros' dung and Sappi paper (sized), Sappi printing paper, paper made of elephant dung from the Kruger National Park, white rhinoceros' dung paper, Chinese art paper, and newsprint paper (see Figures 53-60). The samples were put into the same wooden box used as screen for the paper. The wooden box is 450 mm long, 340 mm wide



and 110 mm high. Two UV lights (510 mm long) were placed on top of the box, one on each longer side of the box, ensuring that the paper strips underneath will receive adequate exposure (see Figures 61-62). The average length and width of the paper strips were between 990 mm (I) and 520 mm (w). Each week a small strip of 550 - 650 mm long and 260 - 300 mm wide was cut from the sample and kept in a manila envelope to be evaluated under the microscope. A Leica S9i microscope were used to analyse the paper strips before UV radiation, after 2 weeks of radiation and after 4 weeks of radiation.



Figure 54: Paper made of rhinoceros' dung, only fibre and not sized. Photo: Author (2022).



Figure 55: Paper samples made of rhinoceros' dung, only fibre and it was sized. Photo: Author (2022).



Figure 56: Paper sample made of rhinoceros' dung and Sappi paper and it was sized. Photo: Author (2022).



Figure 57: Sappi paper. Photo: Author (2022).




Figure 58: Paper made from elephant dung from the Kruger National Park. Photo: Author (2022).



Figure 59: Paper made from white rhinoceros' dung from Itala Reserve. Photo: Author (2022).



Figure 60: Chinese artist paper. Photo: Author Figure 61: Newsprint paper. Photo: Author (2022). (2022)





Figure 63: Paper strips under UV light. Photo: Author (2022).

Figure 62:Paper strips cut and ready for UV light experiment. Photo: Author (2022).







Figure 64: Raw rhinoceros' dung before cooking (5mm). Photo: Leica S9i microscope (2022).



Figure 65: Cooked rhinoceros' dung (5mm). Photo: Leica S9i microscope (2022).





Figure 66: Paper of rhinoceros dung fibre (not sized) before testing (day 0) (x 2) (2,5mm). Photo: Leica S9i microscope (2022).



Figure 67: Paper of rhinoceros dung fibre (not sized after 2 weeks of UV radiation (x 2) (2,5mm). Photo: Leica S9i microscope (2022).



Figure 68: Paper of rhinoceros dung fibre (not sized) after 4 weeks of UV radiation (x 2) (2,5mm). Photo: Leica S9i microscope (2022).





Figure 69: Paper of rhinoceros fibre (sized) before testing at day 0 (x 2) (2,5mm). Photo: Leica S9i microscope (2022).



Figure 70: Paper of rhinoceros dung fibre (sized) after 2 weeks of UV radiation (x 2) (2,5mm). Photo: Leica S9i microscope (2022).



Figure 71: Paper of rhinoceros dung fibre (sized) after 4 weeks of UV radiation (x 2) (2,5mm). Photo: Leica S9i microscope (2022).





Figure 72: Rhinoceros and Sappi paper before UV radiation (x 2) (5mm). Photo: Leica S9i microscope (2022).



Figure 73: Rhinoceros' dung and Sappi paper after 2 weeks of UV radiation (x 2) (2,5mm). Photo: Leica S9i microscope (2022).



Figure 74: Rhinoceros' dung and Sappi paper after 4 weeks of UV radiation (x 2) (2,5mm). Photo: Leica S9i microscope (2022).





Figure 75: Rhinoceros' dung and Sappi paper after 4 weeks of UV radiation with no indication of fibre degradation (x 4) (500 μ m). Photo: Leica S9i microscope (2022).



Figure 76: Sappi paper before testing day 0 (x 2) (2,5mm). Photo: Leica S9i microscope (2022).





Figure 77: Sappi paper after 2 weeks of UV radiation ((x 2) 500 μm). Photo: Leica S9i microscope (2022).



Figure 78: Sappi paper after 4 weeks of UV radiation (x 2) (500 μm). Photo: Leica S9i microscope (2022).





Figure 79: Kruger elephant dung paper before testing (day 0) (x 2) (2,5mm). Photo: Leica S9i microscope (2022).



Figure 80: Kruger elephant dung paper after 2 weeks of UV radiation (x 2) (2,5mm). Photo: Leica S9i microscope (2022).



Figure 81: Kruger elephant dung paper after 4 weeks of UV radiation (x 2) (2,5mm). Photo: Leica S9i microscope (2022).





Figure 82: Kruger elephant dung paper after 4 weeks of radiation with no sign of fibre degradation (x 4) (500 μ m). Photo: Leica S9i microscope (2022).



Figure 83: White rhinoceros' dung before radiation at day 0 (x 2) (1mm). Photo: Leica S9i microscope (2022).



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Figure 84: White rhinoceros' dung paper after 2 weeks of UV radiation (x 2) (2,5mm). Photo: Leica S9i microscope (2022).



Figure 85: White rhinoceros' dung paper after 4 weeks of UV radiation (x 2) (1mm). Photo: Leica S9i microscope (2022).





Figure 86: White rhinoceros' dung paper after 4 weeks of UV radiation with no sign of fibre degradation (x 4) (500 μ m). Photo: Leica S9i microscope (2022).





Figure 87: Chinese art paper before UV testing at day 0 (x 2) (2,5mm). Photo: Leica S9i microscope (2022).



Figure 88: Chinese art paper after 2 weeks of UV radiation (x 2) (1mm). Photo: Leica S9i microscope (2022).



Figure 89: Chinese artist paper after 4 weeks of UV radiation (x 2) (1mm). Photo: Leica S9i microscope (2022).

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Figure 90: Chinese artist paper after 4 weeks of UV radiation with no signs of fibre degradation, but a pink to brownish discolouring (x 4) (500 μ m). Photo: Leica S9i microscope (2022).





Figure 91: Newsprint paper before UV testing at day 0 (x 2) (2,5mm). Photo: Leica S9i microscope (2022).



Figure 92: Newsprint paper after 2 weeks of UV radiation (x 2) (2,5mm). Photo: Leica S9i microscope (2022).



Figure 93: Newsprint paper after 4 weeks of UV radiation (x 2) (2,5mm). Photo: Leica S9i microscope (2022).





Figure 94: Newsprint after 4 weeks of UV radiation with no fibre degradation, but a pink to brownish discolouring (x 4) (500 μ m). Photo: Leica S9i microscope (2022).

<u>Analysis</u>

The microscope photos show the random distribution of fibres in all the paper samples that points to well manufactured paper. In Figure 63 of the uncooked dung random fibres can be seen as opposed to the more flattened and bonded fibres of the cooked dung shown in Figure 64. The microscope photo (see Figure 68) of the sized rhinoceros' dung paper possibly shows the sizing as a slightly shiny effect between the fibres. In Figure 72 the rhinoceros' dung and Sappi paper and the Kruger elephant dung paper of Figure 78 have the same shiny effect as the sized rhinoceros' dung paper. The Chinese artist paper (see Figure 89) and the newsprint paper (see Figure 90) both show spots that might be foxing stains.

The unsized rhinoceros' dung paper and the sized rhinoceros' dung paper both developed darker fibres after the fourth week of UV radiation (see Figures 49-55). The rhinoceros and Sappi paper, the Sappi paper, the Kruger elephant dung made paper and the white rhinoceros' dung made paper had a pinkish discolouring after the fourth week (see Figures 55-68). The Chinese artist paper and the newsprint had a yellow to light brown discolouring after four weeks (see Figures 69-75). The pH test showed that all the paper is alkaline



except the newsprint that has a pH of 5. Studies mentioned by Feller, Lee & Bogaard (1982: 2) confirmed that paper that darkens under UV light is due to having high alkalinity rather than having a high lignin content.

Oxidation causes the darkening or colour change of paper under UV radiation. Carter (1996: 417) mentions in his article that various research on heat treatment and high temperatures showed that cross-linking of aldehyde and ketone groups in cellulose and hemicellulose lead to colour changes in paper. Handmade paper usually has a low percentage of lignin due to the manufacturing process where the lignin is washed out of the pulp. Thus, we can assume that the colour changes of the paper samples are rather due to breaking bonds in the cellulose and hemicellulose than because of the lignin content (Feller, Lee & Bogaard, 1982: 5 and Jiménez-Reyes et al, 2020: 6).

The newsprint had a high lignin count and acidic pH and showed colour changes during UV radiation. Carter (1996: 1068) noted that the chromophores components of lignin absorb light during oxidation, leading to newsprint paper turning yellow or to discolour. This might then be the reason for the discolouring of the newsprint.

No fibre degradation was visible in any of the paper samples after four weeks of UV radiation (see Figures 50, 53, 57, 60, 64, 68, 72, and 76).

4.7 Tearing resistance

Zervos & Moropoulou (2006: 10) see tearing resistance as an important test for paper permanence valuation. It indicates the length and strength of the fibres as well as the bonding strength. Seth & Page (1988: 107) indicates in their research that poorly bonded sheets rely more on the length of the fibres than on the strength, where strongly bonded sheets have better fibre strength. Strongly bonded sheets have a higher tearing resistance than poorly bonded sheets, indicating higher quality paper sheets with a better permanence. Although paper with coarser fibres tend to pull out at the tear while paper with



finer fibres tend to break at the tear, the finer bonded fibres still have a higher permanence.

To test the tearing resistance of the paper samples, five different samples were torn by hand and the tear zone was observed with the Leica S9i microscope (see Figures 94-98).



Figure 95: Unsized rhinoceros' dung made paper with coarser fibres shows the pulling out of fibres rather than the breaking of fibres (2,5 mm). Photo: Leica S9i microscope (2022).



Figure 96: Sized rhinoceros' dung made paper shows the similar effect of fibres that pulled out rather than broke (2.5 mm). Photo: Leica S9i microscope (2022).





Figure 97: Rhinoceros' dung with Sappi paper shows the finer bonded fibres of the Sappi paper that tore while the coarser fibres pulled out (500 μ m). Photo: Leica S9i microscope (2022).



Figure 98: Sappi paper shows how the finer bonded fibres tore (1 mm). Photo: Leica S9i microscope (2022).





Figure 99: Kruger elephant dung made paper shows how the finer bonded fibres tore, while the coarser fibres pulled out at the tear (2,5 mm). Photo: Leica S9i microscope (2022).

<u>Analysis</u>

The microscope photos support the findings of Seth & Page (1988: 107) by indicating how coarser fibres pull out while finer fibres break. The unsized rhinoceros' dung made paper has coarser fibres that pulled out rather than broke. The sized rhinoceros' dung made paper had the similar effect of fibres that pulled out rather than broke. The finer bonded fibres of the rhinoceros' dung with Sappi paper tore while the coarser fibres pulled out. The same was found with the finer bonded fibres of the Sappi paper that tore. The Kruger elephant dung made paper's finer bonded fibres also tore, while the coarser fibres pulled out at the tear.

Seth & Page (1998: 106-107) explain the different tearing resistance for paper can be considered to be because of the stress concentration at the tear zone. As mentioned more fibres break with finer bonded paper while with coarser fibres tend to pull out. This is because more strength is required to pull courser fibre paper sheets apart than to break them. This explains the higher tearing resistance of sheets with coarser fibres.



CHAPTER 5: CONSERVATIONAL GUIDELINES

5.1 Introduction

Worldwide researchers and institutions provide new techniques and understanding on the preservation of paper and paper products. Research on how paper deteriorate and what prescripts to follow to extend the longevity of paper help conservators and restorers to treat these products properly. Conservation guidelines of these worldwide institutions are based on tested methods and are available to provide good conservation practices (Porck & Teygeler, 2000: 2).

Research has shown that the vulnerability of paper lies in deterioration through its inherent volatility, environmental conditions, and storage and handling procedures (Guild, 2018: 1). Storing is seen as the major preventative part of paper where the conservation of paper starts. Good housekeeping procedures with careful handling of paper products, appropriate storage facilities and procedures will lessen damage and extend the life of paper (CCI Notes 11/2, 1995: 2). Some of the housekeeping procedures are to always handle paper items with clean, dry hands. Wash hands regularly and dry hands properly to prevent migrating of oils and dirt. The wearing of cotton gloves can increase damage to objects, because people find it difficult to work with paper items, small fibres can catch on brittle pages, it can pick up dirt more easily and it can absorb unwanted material that can be transferred to the collection (NEDCC, 2007: 9).

Causes of damage that occur regularly that should be guarded against are:

- Handling damage caused by creases, tears, abrasions, folds and stains.
- Acidity because of poor-quality methods and supplies used in the manufacturing of paper.
- Migration of impurities and acidity in adhesives, tapes, and cardboards when in contact with paper.

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• Environmental conditions not properly controlled.

The five practices that should be adhered to as guide for protecting documents and art on paper stated by the American Institute for Conservation (AIC) (2022: 1) are: Proper care and handling, storage, limit light exposure, the control of temperature and relative humidity and limit exposure to air pollution.

The State Library of Queensland (2014: 2-3) concurs with all the previous mentioned causes for damage. In their information guideline for paper-based collection caring, they state the following agents of deterioration: Heat and moisture, light, pests and mold, atmospheric pollutants, storage methods, and handling.

All the existing guidelines agree about the type of damage and preventative methods for works of art on paper and any other archival material. Research has shown that paper and paper products made from good quality materials under controlled manufacturing conditions will most likely have an improved longevity (SL, 2014: 1-2).

The paper made from elephant and rhinoceros' dung are subjected to the same deterioration and damage as the paper products mentioned in the guidelines. I include the conservational guidelines here to affirm the importance thereof.

5.2 Handling

Negligent handling of paper items can result in damage or loss of information. Paper items should always be supported from underneath and laid out on a flat table for best support. Rather use clean hands than gloves that can catch onto items. Use page-turners such as microspatulas, items made out of stiff paper or thin Teflon folders to slip between pages to turn it. It is better to touch only blank areas of the pages when handling the paper items. Brittle or fragile items should not be fed through a photocopying machine or scanner as it may get stuck and tear or fold. It is also best to only copy it once and then when needed



copy the duplicate to reduce handling and light exposure of the original (AIC, 2022: 1, NEDCC, 2007: 8 and SL, 2014: 7).

5.3 Shelving and storage methods

Shelving should be of adequate length and width to ensure the paper collections fit properly. Documents should not extend beyond the edges of the shelves where it can be damaged through friction, leading to frayed edges, or where it can be knocked off the shelf and get mislaid or lost. Shelving units should not have rough edges or contain products that will migrate to the paper collections to cause deterioration. It is best to store the collections in enclosures for protection (NEDCC, 2007: 1).

To prepare paper collections for storage, examine it to assess their condition. Remove dust and dirt with a soft brush. Remove anything that are not part of the document, such as plastic sheeting, acidic wrapping, paper clips, paper fasteners, or any other object that can cause deterioration. Examine paper objects for detection of mold or insects' infestations and store affected objects away from the rest of the collection to prevent migration of the infestation. Poor quality paper should be separated from good quality paper and should be stored separately. The same type of documents can be stored together, but should be free from migrating objects that can damage the collection (CCI Notes 11/2, 1995: 2).

Boards and papers used for storage, should be acid-free, neutral-pH and alkaline-buffered, and should preferably be white or ivory. Non-slip storage material such as lightweight corrugated poly-propylene sheeting (Cor-X, Coroplast or Poly Flute) should be used. Plastic film such as polyester film (Melinex 516) with different thicknesses ranging from 2 mm to 7 mm (thousandth of an inch) can be used to store paper objects. Mylar is another type of plastic and is available as folders, sheets, sleeves, and envelopes. Acid-free tissue paper can be used as inserts and cut to fit into boxes. Individual folders and enclosures can be bought or made from acid-free paper that is strong enough to support the paper. Folders should not be cramped with paper



objects that are pressed together leading to uneven paper sheets. Works of art can be framed to protect it from handling, from fluctuations in temperature and RH, and from dust and damaging air pollutants, but ensure that a sealed micro climate is not created in the process. Mats can be used for flat storage and can have windows to protect image surfaces of paper. It also allows items to be viewed and transported without being damaged. Matted works can also be stored in boxes for better protection. Acid-free boxes are a useful protection against dust, light, air pollutants and accidental damage. Different sizes and types can be made or bought. Boxes with hinged backs that can open flat are popular to lift paper works in and out without damaging it. Boxes should also not be overfilled with paper objects that can damage items when it is removed or replaced (AIC, 2022: 1, CCI notes 11/2, 1995: 3-5, Guild, 2018: 10, and NEDCC, 2007: 7).

Sheila Collins explained that they stored the elephant dung made paper in the cardboard boxes the envelopes for the cards had come in. Both before and after they were packed in cellophane paper with labels and envelopes. These were stored on open shelves. When her business expanded, they bought plastic boxes made for storing paper products (Collins, personal communication 2022, June 26).

5.4 Storage environment

When choosing storage locations, the following should be avoided: Basements and attics, outer walls that can have an influence on the relative humidity and temperature, radiators and heating equipment, water pipes and direct sunlight. The three agents of deterioration that is most harmful for paper items are relative humidity, temperature and light. By controlling these three agents, the inherent instability of paper items can be controlled and the items can be preserved for a much longer period. Air pollution, pests and mold are the other agents of deterioration influenced by humidity and temperature that also play a degrading role in paper items (AIC, 2022: 1-2 and CCI notes 11/2, 1995: 6-7).



Research disclosed that maintaining temperature at 21°C and relative humidity at 50% will preserve paper items for much longer. Mold growth and insects will thrive in warmer and more moist conditions. Paper expands and contracts in temperature variations, causing inherent instability and weaken the printed or painted surface. Paper tends to buckle or distort, becoming more fragile and difficult to handle. Dehumidifiers and fans that circulate the air can help to control temperature and relative humidity. Air conditioning units can also control stable temperatures, but are costly and can cause damage when not working all the time. It is recommended to choose well-insulated rooms to store paper collections. Rooms such as kitchens, bathrooms and basements should be avoided. Rather use storage rooms away from direct heat, light and moisture, water pipes and the sun (AIC, 2022: 1-2 and CCI notes 11/2, 1995: 7).

Light exposure causes deterioration of paper resulting in discolouring where paper turns yellow and darken, while pigments and dyes fade. The exposure of ultraviolet rays in sunlight and fluorescent lights causes irreversible damage to paper items. Light sources should not exceed 75 microwatts/lumen. For items such as watercolours, coloured prints and lesser quality paper, a level of 50 lux of illuminations is recommended. A level of 150 lux is the maximum for good quality paper with stable carbon inks artwork. The wavelength of the light, the extent of exposure and the intensity determine the light damage. It is recommended to reduce the light levels and to restrict exposure time of paper items. Incandescent or tungsten light sources are preferable while UV filters can minimise the UV radiation from fluorescent tubes and sunlight (AIC, 2022: 1-2, CCI notes 11/2, 1995: 7-8 and SL, 2014: 3).

Pollutants from gases, dust, soot and soil are difficult to remove from paper without damaging it. The pollutants can degrade paper by entering the porous surface, bonding to the paper structure and distort its stability. To limit air pollution degradation, paper items should be stored in enclosed protection such as boxes and folders.



Good housekeeping procedures remain an important way to prevent degradation. Pest management programmes help to keep pest and rodents at bay. Paper items should not be stored on the floor where insects, rodents or water leaks can damage it. Regular check-ups on paper items can detect early problems that can be handled in time (SL, 2014: 4-5). Insects that are usually found around paper are cockroaches, silverfish, booklice and bookworms. The cellulose in paper attracts them as well as the glues and sizes (Guild, 2018: 14).

Mold is one of the degradation agents that can completely destroy paper items. Studies done by Michalski (2000: 6-7) shown the lowest humidity of 60% can produce mold and above 75% the growth speeds up significantly. It is important that fluctuation in temperature and RH should be avoided. Rather store paper items in closed containers that will minimise damage should temperature fluctuation occurs.

5.5 Conclusion

By understanding these agents of deterioration paper items in collections will be better cared for. Improved storage methods and handling techniques will lead to better preservation procedures and longevity of paper items. It will not matter what type of paper is in the collection as all types of paper are made from basically the same raw products and follow the same production procedures. Paper made from elephant and rhinoceros' dung must be preserved according to the same guidelines.



CHAPTER 6: CONCLUSION

6.1 Introduction

For the purpose of this study, a literature study was done in which I explained where paper come from, of what components it is made up, how elephant dung is used as a component, and the chemical processes of making a sheet of paper. The study was explored and outlined according to the empirical approach where new and/or existing data were presented and analysed. This conceptual framework was used because of the emphasis that is placed on analysing scientific data to explore the composition of paper and how it might be the cause of deterioration thereof (cf Chapter two).

Eight different types of paper samples were exposed to five different analysing methods: UV light exposure, pH determination, lignin count test, hygroscopic test, and tearing resistance (cf Chapter three). Through the literature study and the scientific data analysis, an attempt was made to analyse and explore the deterioration of elephant dung made paper and to present guidelines to preserve handmade paper (cf Chapter three and four). Conclusions and recommendations are presented in this chapter.

6.2 Research problem, questions and aim of the study

My problem statement of how to preserve elephant dung handmade paper let to the following research questions: What is the composition of elephant dung made paper, how will the composition of the paper impact on its preservation, what causes the deterioration, will paint pigments effect the degradation of the paper, and what conservation guidelines should be followed to preserve this type of paper?

The aim of my study was to provide guidelines to preserve handmade paper made from elephant dung. By using a literature study to understand the composition of paper, how it is made, what the causes of deterioration are and



the preservation guidelines of paper, as well as the scientific analysis of eight different paper samples, the conclusions as discussed below were reached.

6.2.1 The empirical perspective as conceptual framework

The empirical framework is of value to this study because it allows studies in experimental designs in laboratory conditions where specific techniques with small sampling numbers could be analysed against tested measures. In this way connecting associations were inferred and tested. Collins used basically the same recipe for paper making as was used for centuries and what I also used for my control test paper sheets. Through observation and physical measurement, the strength and durability of the paper was tested with findings that will be listed here.

6.2.2 The composition of paper

Research showed that paper consists mainly out of cellulose, hemicellulose, and lignin. Different chemical processes are followed during the pulping process of paper making, but the most general one used for handmade paper is the Kraft process. This was used by Sheila Collins and I also followed this process for paper making. The Kraft process is an alkaline process where sodium hydroxide is used to wash away the lignin in the wood fibre particles left in the elephant and rhinoceros' dung. As seen in par 2.3 about 40% of plant fibre is left in the dung. Sheila also explained that she had to remove or cut bigger wood fibre particles into smaller parts before making her paper. By cooking the dung in the sodium hydroxide mixture nearly all the lignin is removed. In the sample testing of all the paper, the pH test and the lignin test confirmed that paper made using the Kraft process has an alkaline pH and no measurable lignin was detected with the lignin test.

The starch used for the sizing of the paper and for internal sizing of the pulp, also tested an alkaline pH, confirming the paper making process and sheets will not be prone to acid-catalysed degradation.



6.2.3 Major ageing processes of paper

My research showed that it is a normal process for aged paper to lose its strength and flexibility. The major accelerated ageing process is caused by acid-catalysed degradation where the intrinsic strength of fibres and inter-fibre bonding start to break down. This process accelerates through oxidation with the exposure to UV radiation and hydrolysis. The UV light exposure experiment showed that all the paper samples discoloured. This might possibly be because of the breaking of cellulose and hemicellulose bonds, rather than the lignin content, as the manufacturing process should have washed out most of the lignin. The newsprint paper showed a distinctive yellow discolouration. This might be because of its high lignin content and acidic pH. The lignin absorbs light through oxidation showing up as a yellow discolouring of the paper. I could not detect any visible damage to the fibres under the microscope, concluding that the paper is of high quality and durability despite the discolouration.

My research concluded with other studies that the lignin content in paper made under neutral pH conditions does not have an impact on the accelerated ageing conditions of handmade elephant and rhinoceros' dung made paper.

With the hygroscopic experiment no degradation was observed. The humidity was at 28% and previous research showed that it is too low for any significant degradation. The water absorption of the different samples was about 0,119g. Other research mentioned that the neutral pH and the low lignin count of the handmade paper will slow the degradation process. Only the newsprint absorbed 87% of water, the handmade papers absorbed less than 10% which is too low to have an impact. Overall, the experiment demonstrated no mold growth, and no detectable deterioration of any paper fibres.

I could not detect any degradation because of ink pigments on the paper. Research concluded that lithographic inks contain lampblack mixed with organic oils and fats. Lampblack inks are one of the most stable inks and will not have a degrading impact on the paper. I could not detect any deterioration of the paper samples I studied under the microscope.

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The strength test of the handmade paper where its tearing resistance was tested, concluded with previous research. The five paper samples in the experiment differed in fibre length which were noted clearly in the microscope photos. The unsized rhinoceros' dung made paper and the sized rhinoceros' dung made paper have courser fibres that pulled out when torn. The rhinoceros' dung and Sappi handmade paper, the Sappi paper and the Kruger elephant dung paper have finer bonded fibres that broke when the paper was As mentioned in previous research, the experiment concurred that torn. stronger bonded sheets have better fibre strength although it might be shorter. The poorly bonded sheets like the unsized and sized rhinoceros' dung made paper have coarser fibres that pull out when torn, showing a higher tearing resistance although the fibres are longer. Although this is a positive result, care should be taken that fibres can pull out of the handmade sheets resulting in the degrading of paper and paper loss.

6.2.4 Conservational guidelines

Like any other object, paper will age naturally, but there are some preventative measures to implement that will slow the process. Literature showed the five causes of damage that most often occur are handling, storage methods, heat and moisture, pests and mold, light damage, and atmospheric pollutants. My research indicated that by implementing good housekeeping procedures, minimum handling of paper, protection from light by storing it in containers, avoiding temperature fluctuations and keeping the RH around 60%, the longevity of any paper product will be prolonged.

6.3 Recommendations

Recommendations for this study take current developments, the restricted access to financial resources, and the existing limited cultural heritage research into account.



6.3.1 Practice

All the conservational institutions have primary working methods to take proper care of paper products and these should be adhered to. Paper conservationists in museums or archives should always follow these guidelines to ensure the longevity of paper products under their care.

6.3.2 Theory

Scientists and conservators should work together to conduct empirical studies in paper research. Ethnographic research will provide in-depth understanding of different cultures and their way of thinking and practices in paper making and preservation. Comparative studies where different cultures and different nationalities collaborate can focus on similarities and differences. These analytic strategies can compare different viewpoints for better understanding of problems in paper conservation. Laboratory studies can provide controlled experiments and measured outcomes can ensure valid findings.

6.3.3 Training

Training for museum, archival and library personnel is a necessity to ensure that conservational guidelines are followed and to understand the necessity thereof. Training should be given by qualified personnel in an environment where practical experience can be provided to help the student understand and experience how to perform conservational techniques.

6.3.4 Research

My study focussed on the composition of elephant dung made paper and how the composition will impact on the preservation thereof. I studied the pH count, the lignin quantity, and temperature fluctuation of different paper samples. I only compared these effects under microscopic observation. The obtained results showed an alkaline pH of most paper samples and a very low nonmeasurable lignin content. This was helpful in understanding the degradation



mechanisms of paper. It also added to other research that indicated that the lignin presence in paper is not the most degradation factor, but rather the inherent instability of the paper composition itself.

The test of fluctuation in temperature and RH could not be done according to usual prescribed tests due to unavailability of expensive specific equipment. However, the tests performed could provide useful information to compare degradation processes of the paper.

Further research where the different chemical compositions of paper can be identified and compared to obtain a further understanding of the degradation mechanisms of paper products are recommended. Instruments like a Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDS) or Fourier Transform Infrared Spectroscopy (FTIR) can be used to identify chemical elements, organic and inorganic material to better understand paper products and strategies to decrease the degradation thereof.

6.3.5 Policy

As mentioned in Chapter one of my study, there is a definite need for experienced paper conservationists in the conservation environment. Further research and training will provide to the pool of knowledge and expertise. Proper conservational policy will also contribute to the understanding and implementation of strategies to prevent degradation of paper products. Examples are: Regulations to prevent poor manufacturing methods of paper, better controlling of environmental conditions in places like libraries, archives and museums, and protective measure like fire walls in structural housing facilities of paper products. There regulations should be part of policies and should be monitored to ensure the implementation thereof.

6.4 Concluding remarks

The experiments of my study to understand the composition of elephant dung made paper concluded that the paper has an alkaline pH and an unmeasurable



low lignin content. These measurements indicate that the paper is of a good quality and will not degrade at a high rate. The discolouring shown under the UV light exposure indicates the possible breaking of cellulose and hemicellulose bonds rather than because of the presence of lignin. The water absorption experiment indicated no detectable fibre deterioration, nor are the ink pigments contributing to the degradation rate. The strength test indicated the strong bonded fibres of the elephant dung made paper that again point to the good quality of the paper. Overall, the experiments showed that paper made with elephant dung according to the alkaline Kraft process are of good quality and will have a high longevity.



7. APPENDICES

- 7.1 Appendix 1: Semi-structured interview schedule
- 1. Was there a difference in the colour of paper made from white rhinoceros' dung than from black rhinoceros' dung?
 - Was there a difference in the fibre quality of the paper?
- 2. Could you see any difference between paper made with elephant dung and paper made with other big herbivores' dung?
- 3. What advice or help did Sappi offer you in your process of paper making?
 - Did they suggested a certain process to follow?
 - Did they suggested certain chemicals to use?
- 4. Is the same process of paper making still used?
- 5. Did you paint on the handmade paper, or did you only print your designs on it?
 - Do you think there is a difference in ink absorption between the two techniques? If yes, why?
- 6. What painting technique did you follow?
 - Oil or water colour?
- Did you find a difference in colour when you inspected your art work from 30 years ago?
 - Did the paper change colour?
 - Did the paint change colour?
- 8. How did you store your handmade paper?
 - How did you separate blank paper from paper with designs on?
 - Where did you store it?



7.2 Appendix 2: Letter requesting research access and permission



School of the Arts Tangible Heritage Conservation

20 May 2022

Letter requesting research access and permission

Dear Sheila

You are herewith invited to participate in a Masters mini dissertation by Marinda van der Nest for the requirements of the MSocSci Tangible Heritage Conservation at the University of Pretoria. The study is provisionally titled: *An analysis of paper made from the dung of elephant, rhinoceros and other wild herbivores to develop a conservation plan.*

The research aims to give guidelines to preserve handmade paper made from the dung of herbivores.

Permission is requested to interview the artist through telephone conversations and electronic mail correspondence. The interviews will be one-on-one.

Any questions you may have about this study can be directed to Marinda van der Nest at 0724412624 or marindavdnest@gmail.com, or the dissertation supervisor Maggi Loubser at 0829228184 or maggi.loubser@up.ac.za

Regards

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Indirest

Marinda van der Nest

Maggi Loubser



Page 1 of 2



7.3 Appendix 3: Informed consent form



Faculty of Humanities School of the Arts

Research Consent Form

Statement of voluntary consent:

When signing this form, I am agreeing to voluntarily participate in the research entitle: An analysis of paper made from the dung of elephant, rhinoceros and other wild herbivores to develop conservation guidelines. I have had a chance to read this consent form, and it was explained to me in a language which I understand. I have had the opportunity to ask guestions and have received satisfactory answers. I understand that participation is voluntary, unremunerated and that I can choose to opt out, or withdraw as a later stage even if I initially opted in. By signing this form, I also agree that data generated during the research process will be kept at the School of Arts, at the University of Pretoria for 15 years and can be accessed by requesting permission from the researcher or the dissertation supervisor.

Opting in (Circle which is appropriate: YES/NO

Alus Signature of participant:

Print name: Capacity: Date: Place:

Sheila Collins Artist 24 February 2022 Sedgefield

By signing below, I indicate that the participant has read and, to the best of my knowledge, understands the details contained in this document and has been given a copy.

Signature of researcher:

Print name: Date: Place: Marinda van der Nest 24 February 2022 Pretoria

Midnest

Van Wouw House 299 Clark Street, Brooklyn University of Pretoria Private Bag X20 Hatfield 0028 South Africa Tel +27 (0)829228184





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