International Journal of Life Sciences
International Peer Reviewed Open Access Journal

Special Issue A18, May 2022
ISSN:2320-7817(p) 2320-964X(0)

Original Article Open Access

Paper is where history is written, & chemistry is required for its conservation

Aher Sanchita Santosh* and Sanap Shrihari [1]

*Student at Institute of Forensic Science, Mumbai University
[1]Asst. Professor, Head of the Dept., Forensic Chemistry and Toxicology, Institute of Forensic Science, Mumbai University.
Email id: sanchitaaher2000@gmail.com

Manuscript details:

Available online on http://www.ijlsci.in
ISSN: 2320-964X (Online)
ISSN: 2320-7817 (Print)

Cite this article as:
Aher Sanchita Santosh and Sanap Shrihari (2022) Paper is where history is written, & chemistry is required for its conservation, Int. J. of. Life Sciences, Special Issue, A18: 59-65.

Article published in Special issue of 1st National Conference on Forensic Science & Digital Forensics 2022 organised by Applied Forensic Research Science From 18th to 20th March 2022.

ABSTRACT

Paper is such evidence through which we can collect more objects than any other material like prints, drawings, watercolours, stamps, banknotes, labels; where owners of such objects want them to remain in good circumstances. Although, one third of paper in copyright libraries is too brittle to handle & another third will need attention over the next 100 years. As the paper is composed of several materials; the deterioration of paper depends upon these factors, if not conserved properly. The deterioration of paper is caused by many factors such as pH level, metal ions, lignin, heat, humidity, light, air pollution, or even presence of microorganisms. The main cause of degradation is decomposition of cellulose by acid hydrolysis, oxidative agents, alkaline degradation, thermal, radiation exposure. Yet cellulose with supramolecular structure impedes this degradation. The pure cellulose gets embrittled and loses paper strength due to acid – hydrolysis caused by low initial pH and degree of polymerisation. Although, deacidifying agent provide an alkaline reserve to avoid acid hydrolysis; the cellulose chain ends can react and undergo the depolymerisation reaction. Also, free radicals generated by the light can cut the cellulose chain causing the oxidative degradation. This review focuses on the deterioration and the steps taken to avoid it in detail as it is essential to know the accurate prevention of destruction of paper, as this damage can lead to the loss of a handy evidence.

Keywords: Paper evidence, Paper Chemistry, Paper Degradation, Conservation.

INTRODUCTION

Paper is nothing but a network of plant fibers laid down as a flat sheet. Pulp i.e. suspension of plant tissues in water is used to make papers. Most pulp is made from wood, but recycled paper and other plant sources including hemp, cotton, esparto grass, sugarcane bagasse and bamboo is also used. Now-a-days, we all know that paper is used for every type of printed material right from books to encyclopedias.

Also, the type of paper getting manufactured varies according to its final use and life time of the paper. E.g., Banknotes, which must be strong and durable are made from high-quality pulp which is derived from cotton rag and flax. Also, the packaging industry depends upon a continued supply of paper. Paperboard is another example where, a high proportion of paper is made in this form, which is used in many different types of packaging. Not just limited to this, but other specialist products made from paper consists of insulation for electrical boards, disposable clothing for medical uses, bandages, car filters, shot-gun cartridges, etc. To make paper, flame resistant or capable of holding security information that is only visible under UV light; special treatments can be applied over the same (Michael Seery, 2013). There are also handmade papers preferred for high-quality book publishing as well as for conservation purposes, as the fibres in handmade paper tend to be considerably longer than those in mechanically produced paper where it is much stronger and can be used after oiling to make it waterproof. However, paper can get damaged or destructed by several ways whether it is through mechanical reason or natural ways and there is a necessity to conserve paper from such deterioration by the factors affecting it. As it is a resource of prints, drawings, watercolours, stamps, labels, etc. owners of such objects will definitely want them to be in good condition despite the fact that many of them were only intended to have a lifetime of as little as a few hours, e.g., tickets. Yet some papers and information over the same is inherently unstable and others deteriorate quickly when stored under wrong conditions.

LITERATURE REVIEW

History related to Paper:

Paper which is used for writing material sheets which were made by pressing strips together of the stem of sedge, *Cyperus papyrus* is derived from Egyptian term *"Papyrus"*. Paper is nothing but made up of a mesh of randomly arranged plant fibres, was invented by the Chinese in the second century AD.

In 105 AD a Chinese court official, Ts'ai Lun, produced a paper web from a slurry of paper mulberry fibres in water. In a rectangular sieve consisting of a sheet of silk was used to lift up a small amount of the slurry by a frame. To spread the fibres evenly and to drain off the water, the sieve used to be shaken gently thus settling into a form of sheet which was then dried in the sun (Daniels, 1996). This process produced a long-lasting, high-quality paper. There could be more variety of characteristics of the paper produced by using different plants as the source of fibres was found by the Chinese paper-makers.

In Samarkand a Chinese paper-making factory was captured by an Arab army for over 600 years. The expertise of the Chinese paper-makers was used by the Arab conquerors to set up factories throughout the Moslem world and Europe was then the continent where the paper-making techniques first arrived when the Moors conquered Spain. Including some from the wrappings of mummies, hemp and linen rags were used as the raw materials for paper-making. In Hertfordshire of Britain, the first paper-mill was built in 1488 which was referred to a book printed by Caxton in 1490.

Over 24 million tonnes of rags per year was used by paper-making factories hence supplies of the raw material fell short of requirements, therefore a cheap, readily available and easily renewable substitute search was began. The Wasps nests were made of a form of paper by macerating wood, which was observed by a French biologist where he suggested that wood can be used as a material to make papers. It was in 1769, the wood was first used for paper-making in Europe, but it was not until 1840 when entirely wood pulp paper appeared. The New York Times was the first newspaper made from an all-wood pulp in 1870. Two slowly spinning stones were used to grind logs to make the early wood pulps. Until 1851, the pulp made by dissolving the woody substances in cell walls did not appear.

Fourdrinier paper making machine was invented for cheaper and fasten the paper-making process, which used a continuous wire-mesh belt instead of individual paper moulds for forming a sheet of paper and it was first used in England in 1803.

The composition of Paper:

Paper is essentially composed of cellulose fibres into a sheet by draining a suspension of fibres in water through a mesh. Hydrogen bonds play a large part in bonding the fibres together after drying. Cellulose is not just the component paper is composed of, but many other

materials can be added to prepare the sheets of paper. Cotton and linen are today used for preparing high grade paper for example, wedding invitation paper, paper for drawing whereas a bleach is added to get precise shade of white that manufacturer wants as the natural colour of paper is not white. Also, industrial manufacturers of paper have to add special sizing agents to make the structure firm and stronger like resin, gum and starch; and to increase the mass of the paper and give it the stronger structure fillers like clay, chalk or titanium oxide are added too. Not only bleach, but also various dyes and inks are added to the mixture if the manufacturer aims to create paper of specific colour.

Though paper is composed of several materials the main interest of a paper object is writing or surface decoration in the form of pencil, chalk, pastel or watercolours, printing and writing inks. With huge variety of materials involved the study of the conservation of paper artefacts becomes wide ranging (Maria and Herve, 2011). Cellulose occurs as a component of many plants cell walls. Its amount varies from plants to plant like for e.g., wood has 40-70% of cellulose, while cotton seed has 96% of cellulose, the purest source. These sources of cellulose are firstly processed with purification before they are used to make papers so as to increase the amount of cellulose present in the fibrous components. The cellulose molecule is a linear polymer of β-D-glucose. To indicate the average number of glucose molecules in the cellulose chain, it's degree of polymerisation (DP) is considered, which varies with the plant source and the severity of the any purification method used.

When two glucose molecules condense to form part of a cellulose chain one of them has to rotate by 180° forming cellobiose, as the real unit of cellulose:

This molecule possesses a very high concentration of hydroxy groups and thus interacts strongly with water. The cellulose used for paper making is present as fibres which retain some of the shape of the cells from which they were derived and thus occur in a variety of shapes and sizes depending on the plant source. Most Europeans used recycled cellulose to make papers from cotton and linen rags, but as the demand for the paper increased, the new source was needed and wood having the correct properties, thus from 1870 until today wood and cotton is used for making most of papers whereas linen is used for the making of banknotes, filter and artists papers. Wood as it contains cellulose and other two main components like hemicellulose and lignin. The most permanent papers are usually those with a high proportion of cellulose but for economic reasons the amount of purification used on wood pulps is often less.

Deterioration of Paper:

We often notice it sometimes, that the papers 500-years old are in better condition than the one's from 50 years ago; i.e., some papers deteriorate rapidly and other papers deteriorate slowly because, the rate and severity of deterioration is due to the internal and external factors mostly due to the composition of paper and the conditions under which the paper is stored and this is where one needs to know the chemistry of paper composition. As we discussed above that the paper with long-fibred are stronger and more flexible and durable than short-fibred paper. Degradation of the cellulose macromolecules can be brought about with various kinds of energy inputs i.e., chemical, thermal, mechanical or radiation energy which can cause many reactions. The mode of cellulose degradation within paper includes chemical (acid hydrolysis, enzymatic hydrolysis, alkaline degradation and oxidative degradation), thermal (different levels of temperature), radiation (exposure to UV/visible radiation, exposure to high-energy radiation). In nearly all modes of cellulose degradation, cellulose supramolecular structure plays a decisive role to determine the rate and also the course of a degradation process.

Due to presence of moisture, acids from the environment e.g., polluted air, enclosures of poor-quality, or from within the paper like the raw materials used, while manufacturing process, repeatedly cut the glucose chains into shorter lengths and this acid hydrolysis reaction produces more acid causing more degradation. Paper becomes yellow and loses strength due to its aging, in which most prominent reaction is the hydrolytic degradation of the cellulose macromolecules. The rate of this acid hydrolytic process is determined by the temperature where it is stored, the acidity and the water content present in the paper (paper's equilibrium moisture content). The accelerated aging of papers of pure cellulose with low initial to strong bases, cellulose chain ends can react and undergo the well-known

depolymerisation reaction. The oxidised groups of cellulose are potential sites of degradation, since oxidation cellulose chains are not actually broken, but in both acidic and alkaline medium they can be easily degraded then even at room temperature under mild condition. Primarily, the presence of oxygen from the environmental air, the oxidative degradation of cellulose can occur. Oxidation of cellulose polymer introduces side groups, aldehydes and ketones which make the molecule more easily hydrolysed. Oxidation produces free radicals which results in the cutting of cellulose chain. The concentration of the acid in paper is even raised due to the oxidation of the cellulose, as the primary alcohol groups in the cellulose can get oxidized to aldehydes converting further into carboxylic acid species.

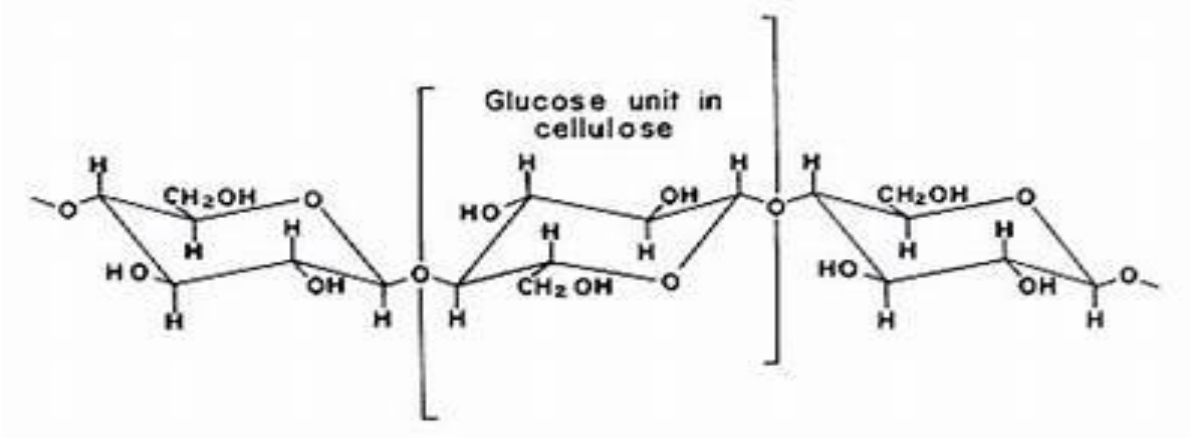

Fig no. 1. Structure of Glucose monomer and Cellulose Polymer

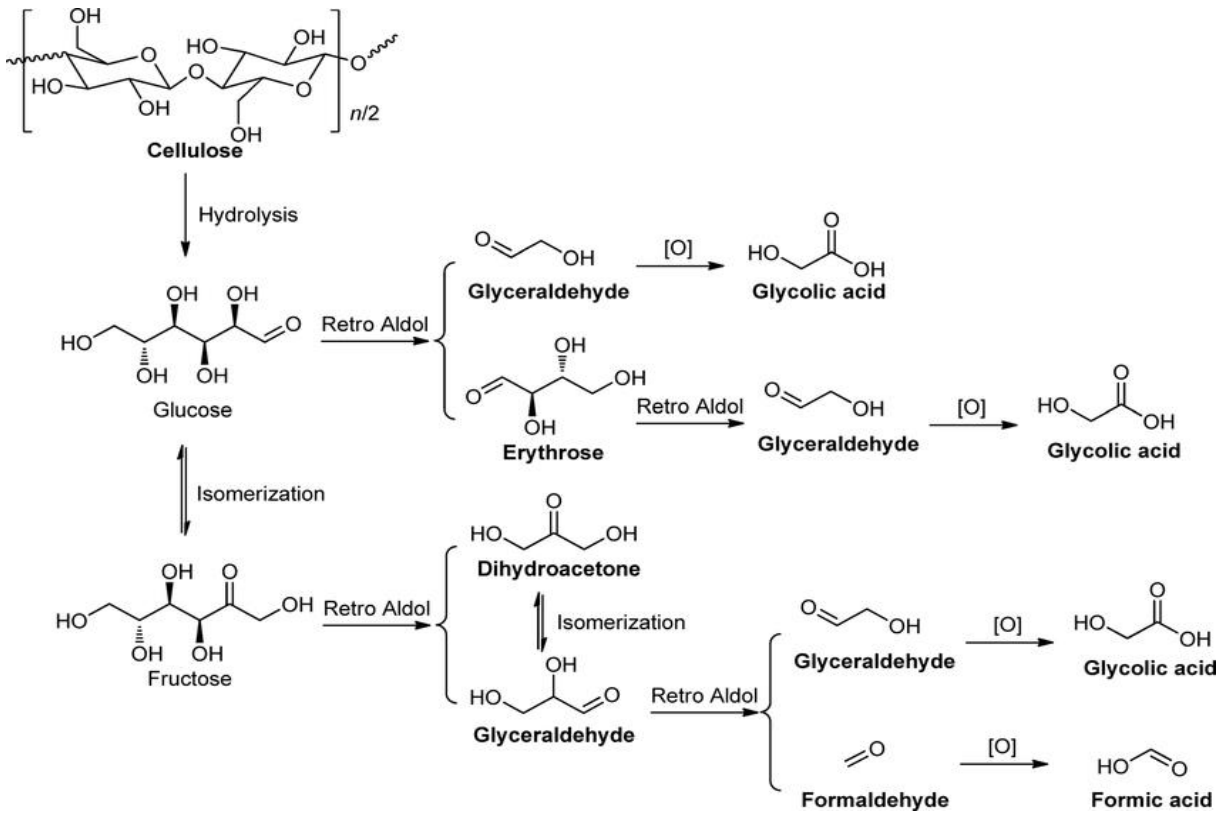

Fig.2. Acid Hydrolysis of Cellulose, cutting the glucose chain and producing more acid

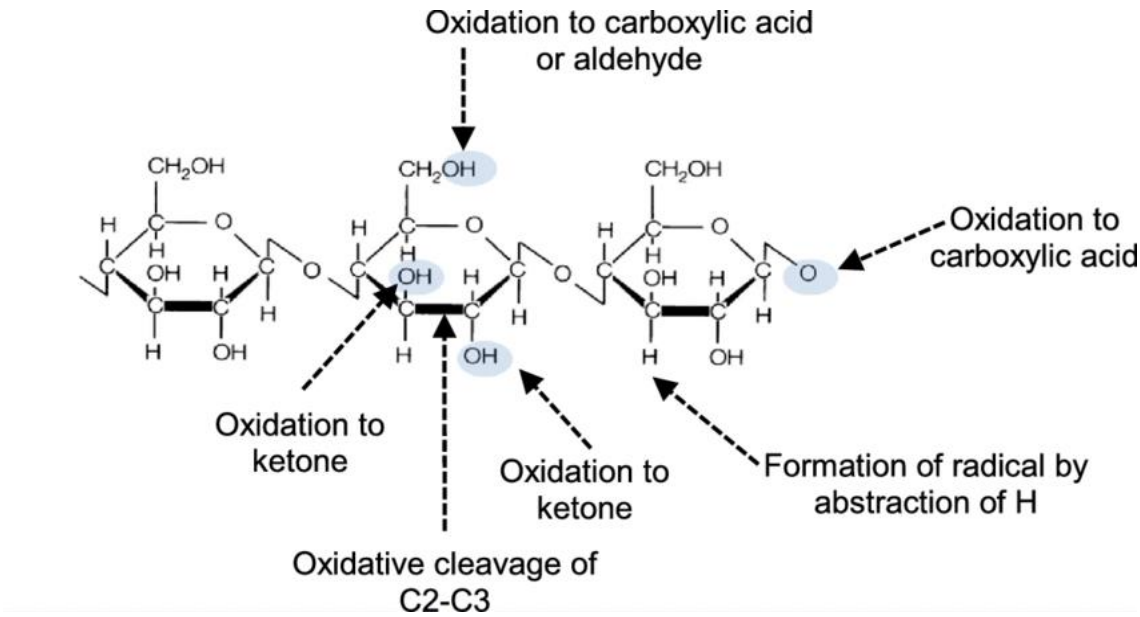

Fig no. 3. Possible positions of the cellulose chain to participate in oxidation.

Biological contaminants are possible, even in libraries and archives, and their effect can vary as a function of environmental situations and composition of the substrate. Insects and moulds are the most frequent cause of biological problems. This can be more frequently detected source of degradation in the countries located in tropical and subtropical areas. More than 200 moulds are detected when biological degradation is concerned, where from a single cell itself they proliferate and produce mycelium, a substratum over the most solid surfaces. For more growth and development, these moulds prefer organic substrates like cellulose. In order to grow up, moulds produce enzymes that will chemically attack paper fibres and cleave cellulose macromolecules.

DISCUSSION

Forensic Significance of Paper Preservation:

As we all know, in forensics there is a special field of questioned documents which deals with any type of document whose authentication is in doubt to determine whether a document is genuine, where an examiner examines to confirm who created the document, the timeframe when it was created and also identify the materials used for its preparations then, it can either be banknotes, contract papers, currency notes, suicide notes, question papers, newspapers, etc. In this then the documents can be examined for evidence of alterations, obliterations, erasures and page substitutions or the examiner can study the methods, materials or machines that created the documents, providing key information that can identify or narrow the possible sources of the document. The composition of paper, ink, writing tools, ribbons, stamps and seals, etc, used in production of the document may all reveal important clues to solve cases related to questioned documents. So, it is an essential part to preserve the document and content related to document and conserve it. A key element of document examination focuses on handwriting which occurs due to the ink by handwritten or printed format. A document under question is needed to be taken proper care and preservation of to avoid the loss of handy evidence. For this not marking anything upon the document, not to mutilate by creasing, repeated refolding, cutting or tearing, not to carry in pocket a prolonged period of time or handle excessively, to preserve them in proper envelope or protective folders, do not allow anyone except a qualified expert to make chemical or other types of tests, to handover the document at the earliest to the laboratory for the examination; not only these preservations but these documents should kept at dry place and away from

excessive heat and strong light to avoid its degradation by environmental pollutants.

Paper conservation:

As even degradation of paper occurs due to the iron gall inks in the documents been used for several last years. Therefore, while treating any document, the conservators need to consider that inks and pigments over the papers. Iron gall inks was popular for several centuries until the mid-nineteenth century, so while conserving a paper having ink over the same should not avoid its effect on paper structure because, this ink was formed by reacting gallic acid (derived from tannins extracted from gall-nuts) with iron (II) sulphate where, the presence of excess Fe (II) ions can catalyse the oxidation of cellulose through the production of hydrogen peroxide:

$Fe^{2+} + O_2 + H^+ \rightarrow Fe^{3+} + HOO^{\cdot}$

$Fe^{2+} + HOO^{\cdot} + H^+ \rightarrow Fe^{3+} + H_2O_2$

This can lead to significant destruction of the paper along the lines of the ink, so much that the paper can leave a lace-like pattern disturbing its structure. This decomposition can be stopped by introducing chelating agents – preferably phytate (inositol hexakiphosphate) to complex the Fe (II) in the ink.

To conserve the paper from degradation, it is essential to understand the degradation pathways. The acid decomposition can be deacidified by this solution. This involves washing paper in a bath of mild alkali such as calcium hydroxide, calcium hydrogen carbonate, as the benefit is two-fold. Firstly, soaking up water into the cellulose and then drying it reforms the hydrogen bonds between the fibres, which can restore some of the paper's strength. Secondly, the reserves of the alkali remain after the acid in the paper is neutralised which is used against future acidification. Of course, this is a process with which conservators need to take great care of, as paper may simply disintegrate or its contents may be removed when added to water. For the alkaline wash, the fragile materials are mounted on the mesh. Though this process bears the risk, it is still the main method used for the conservation of the paper that is degrading due to acid.

The simplest way to slow down the acidification of the paper is storing them in proper temperature and humidity, as majorly a document is damaged by acids and very fewer options are there for its recovery. Although, not all paper products can be conserved by an alkaline reserve like for example, architectural blueprints will react negatively to alkaline due to ferro-gallic prints are unstable and should be stored in unbuffered, pH neutral storage containers. So, conservators need to check how the paper type will react to an alkaline reserve.

CONCLUSION

In the digital age of the 21st century, our reliance on paper is rapidly declining. Smartphones or tablet screens and electronic paper displays like those of Amazon's Kindle are becoming essential for everything from cinema tickets to best-selling books. But what about the papers which have turned to be the part of history and can be of need in future anytime, so we face an ever-growing urgency to preserve paper-based artefacts before they are lost. To preserve the paper from getting degraded, one needs to understand the chemistry behind it. As of such, the entire paper is based on chemical science, chemistry is the heart of paper conservation, as we saw to decrease the percentage of paper degradation, it is essential to understand the pathways directed towards the paper degradation, and today this is yet a challenging field we need to look after, to understand paper chemistry and its conservation. But by then an alternative method to be used to preserve the documents from past or the ones in current use, can be digitized where they can be viewed and studied without handling the original physical document. This may allow fragile or already damaged documents to remain in safely in storage. It will also make possible safe sharing of documents from person to person. Digitization will also improve the ability to search a collection.

Yet this too has some limitations, like if one has to examine the original document physically will make it difficult and also if digitization is considered, the documents authenticity will have to kept secured. So, looking this as an emerging field which has an upgrowing scope to study and research about the types of documents in use and the specific actions that can be used to protect them

Conflicts of interest: The authors stated that no conflicts of interest.

REFERENCES

Daniels VD (1996) The chemistry of paper conservation – Chemical Society Reviews (RSC Publishing) https://pubs.rsc.org/en/content/articlelanding/1996/cs/cs9962500179

How Can Physical Preservation Prevent Document Degradation? https://andersonarchival.com/learn/how-can-physical-preservation-prevent-document-degradation/

Maria Cristina Area and Herve Cheradame (2011) PAPER AGING AND DEGRADATION: RECENT FINDINGS AND RESEARCH METHODS | Area | BioResources https://bioresources.cnr.ncsu.edu/BioRes_06/BioRes_06_4_5307_Area_Cheradame_Paper_Aging_Degrad_Review_2177.pdf

Michael Seery (2013) Paper conservation | Feature | RSC Education https://edu.rsc.org/feature/paperconservation/2020204.article

Paper Raw Materials – The main Ingredients of Paper http://www.historyofpaper.net/making-paper/ingredients-of-paper/

The Deterioration and Preservation of Paper: Some Essential Facts – Collections Care – Resources (Preservation, Library of Congress) https://www.loc.gov/preservation/care/deterioratebrochure.html

What is paper? History of paper – making https://www.uibk.ac.at/