A COMPARATIVE STUDY ON CHEMICAL CHARACTERIZATION OF DIFFERENT INK INGREDIENTS USED IN ANCIENT ORNAMENTED MANUSCRIPTS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ESRA MERT

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
ARCHAEOMETRY

SEPTEMBER 2008

Approval of the thesis:

A COMPARATIVE STUDY ON CHEMICAL CHARACTERIZATION OF DIFFERENT INK INGREDIENTS USED IN ANCIENT ORNAMENTED MANUSCRIPTS

submitted by **ESRA MERT** in partial fulfillment of the requirements for the degree of **Master of Science in Archaeometry Department, Middle East Technical University** by,

Prof. Dr. Canan Ozgen ____________________________
Director, Gradute School of
Natural and Applied Sciences

Prof. Dr. Asuman Türkmenoğlu ____________________________
Head of Department, **Archaeometry**

Prof. Dr. Lemi Türker ____________________________
Supervisor, **Chemistry Department, METU**

Prof. Dr. Şahinde Demirci ____________________________
Co-Supervisor, **Chemistry Department, METU**

Examining Committee Members:

Prof. Dr. Asuman G. Türkmenoğlu ____________________________
Geology Eng. Department, METU

Prof. Dr. Lemi Türker ____________________________
Chemistry Department, METU

Prof. Dr. Şahinde Demirci ____________________________
Chemistry Department, METU

Prof. Dr. Ay Melek Özer ____________________________
Physics Department, METU

Niyazi Ünver (M.S.) ____________________________
Ministry of Culture and Tourism
of Rebuplic of Turkey

Date: **05.09.2008**

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Esra Mert

Signature :

ABSTRACT

A COMPARATIVE STUDY ON CHEMICAL CHARACTERIZATION OF DIFFERENT INK INGREDIENTS USED IN ANCIENT ORNAMENTED MANUSCRIPTS

MERT, Esra
M.Sc., Department of Archaeometry
Supervisor: Prof. Dr. Lemi Türker
Co-supervisor: Prof. Dr. Şahinde Demirci

September 2008, 106 pages

Manuscripts have an essential importance as being irreplaceable parts of our cultural heritage. It has long been known that these works have been suffered from serious damages due to the corrosive effects of the inks. In this study, the influence of inks prepared according to historical recipes on the degradation of model paper has been investigated. Totally, sixteen ink solutions were prepared and applied on Whatman No. 41 filter papers. The mostly examined ink is the iron-gall-ink which is known as very corrosive. Changing the ratios of the ingredients in the ink, it is aimed to understand the degradation mechanism of the cellulose caused by the iron-gall-ink. Influence of iron to gallic acid ratio, copper to iron ratio and the effect of saffron on ink corrosion were examined. Also the influence of colored inks (red and green); prepared according to the historical recipes on cellulose degradation was studied. In order to determine the changes in the cellulose in time, dry heat accelerated ageing was performed on the paper samples. UV-Vis spectroscopy, FTIR-ATR and Color spectrophotometry were used to investigate the changes in the chemical composition of the cellulose after accelerated ageing.

Key Words: Iron-gall-ink, cellulose degradation, saffron, colorimetry.

ÖZ

ESKİ TEZHİPLİ YAZMA ESERLERDE KULLANILAN FARKLI MÜREKKEP BİLEŞENLERİNİN KİMYASAL KARAKTERİZASYONU ÜZERİNE KARŞILAŞTIRMALI BİR ÇALIŞMA

MERT, Esra
Yüksek Lisans, Arkeometri Bölümü
Tez Danışmanı: Prof. Dr. Lemi Türker
Ortak Tez Danışmanı: Prof. Dr. Şahinde Demirci

Eylül 2008, 106 sayfa

Yazma eserler, kültürümüzün vazgeçilmez önemli parçalarıdır. Bu eserlerde mürekkeplerin zararlı etkilerinden dolayı hasar meydana gelmektedir. Bu çalışmada değişik kompozisyonlardaki tarihi reçetelere göre hazırlanan mürekkeplerin model kağıtların bozulması üzerine etkileri araştırılmıştır. Bu amaçla, toplam onaltı mürekkep Whatman No.41 filtre kağıtlarına uygulanmıştır. Çalışmada en çok üzerinde durulan mürekkep zararlı olduğu bilinen demir- mazı mürekkebidir. Demir- mazı mürekkebinde kullanılan bileşenlerin oranları değiştirilerek, demir-mazı mürekkebinin selülozda neden olduğu bozulmaların anlaşılması amaçlanmıştır. Bu kapsamda, demir /gallik asit oranının, bakır/ demir oranının ve safran varlığının mürekkep korozyonuna etkisi incelenmiştir. Ayrıca, tarihi reçetelere göre hazırlanan diğer renkli mürekkeplerin (kırmızı, yeşil) selüloz bozulmasına etkisi çalışılmıştır. Selülozda zamanla oluşan değişimi inceleyebilmek amacıyla kağıt örneklere kuru ısı yöntemiyle hızlandırılmış yaşlandırma uygulanmıştır. Hızlı yaşlandırma uygulaması sonrasında selülozun kimyasal bileşimindeki değişimleri incelemek amacıyla UV-Vis spektroskopisi, FTIR-ATR spektroskopisi ve renk spektroskopisi yöntemleri kullanılmıştır.

Anahtar Kelimeler: Demir Mazı Mürekkebi, selüloz bozulması, safran, kolorimetri

To the memory of my father
and
to my mother and my husband

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to Prof. Dr. Lemi Türker for his supervision and care.

Special thanks are to Prof. Dr. Şahinde Demirci for her invaluable contributions in the progress of the thesis and especially for her constant encouragement during the study.

The technical assistance of Metu Central Laboratory is gratefully acknowledged.

Deepest thanks to my mother and my husband for their invaluable support and unwavering patience during the study.

This study was also supported by LTP (MS Thesis Project, METU Graduate School of Natural and Applied Sciences)

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INTRODUCTION

Throughout the history, man had needed to store his emotions, thoughts and information. For this purpose various materials such as clay tokens, tablets, cuneiforms, bones, silk, papyrus, etc.had been used as writing materials until the invention of paper.

In our country, throughout the history many manuscripts had been produced on culture, art, philosophy, medicine, mathematics, astronomy, etc.. Manuscripts have an essential importance both in reflecting the properties of our identity in art, culture, and science and being the authentic historical resources that have never been renewed.

There are about 600 000 manuscripts in Turkey that most of them were written in Turkish, Arabic and Persian. Most of these works in our country include many unique and beautiful bindings, gold gilded and miniature illustrations relating to the Ottoman history i.e. Ottoman laws, foreign policy, sciences, medicine, literature and culture. They also display a number of calligraphic styles and they form an invaluable archive demonstrating the multilingual and multicultural properties of that period (Atılgan, 2000).

Preservation and conservation as well as archaeometrical investigations of these works of art have a vital importance both for the Turkish and World Cultural Heritage.

1.1 Turkish Inks

The use of inks by Turks was as old as the Middle Asia Civilization. Ibn-i Mukle and Ibn-i Bevvab who are the famous calligraphers of Xth and XIth centuries were known to manufacture ink by burning the hair of black goat and mixing its ash with a gum and green vitriol (Yaman, 1995).

Ottomans have been known to be very successful in ink- manufacturing with respect to color and quality. Ink manufacturing had become an art in Ottoman Empire.

In XVIIth century, it has been said that there were forty ink- manufacturing shops and sixty-five people in İstanbul dealing with ink manufacturing. In that period, ink-manufacturing shops were in Bayezid district. Moreover, Ottomans founded a trust to meet the demands of calligraphers (Yaman, 1995).

Inks were produced according to the type of calligraphy. Obtaining soot and making ink were different jobs. Different methods and materials were used in manufacturing ink. There were two types of black ink; one is ink prepared with soot called lampblack ink while the other ink is composed of green vitriol and galls (Yaman, 1995). The samples of lampblack ink writing and iron-gall-ink writing can be seen in Figure 1.1 and Figure 1.2, respectively.

Soot, the main ingredient of lampblack ink is obtained by burning such substances as linseed oil, beeswax, naphtha, or kerosene. The lampblack is produced by collecting the soot deposited on an inverted earthenware bowl from a lamp burning hemp oil. Baking the collected soot in the center of a dough ball extracted oil residues and resulted in a pigment consisting largely of amorphous carbon, a deep black powder. The chemical name of lampblack ink is carbon black. It is very stable being unaffected by light, air, hot concentrated acids and alkalis. It can only be destroyed by burning which converts it to carbondioxide. It is fairly stable in terms of solubility and it also has a good permenance. The optical micrograph of carbon black is given in Appendix Fig. A.1.

Gum Arabic was used to bind the carbon particles to the paper that is a natural composite polysaccharide desired from exudates of Acacia Senegal trees (Minorsky, 1959; http://turkishculture.com).

The lampblack ink is known to be very stable but sensitive to water. It can easily be smeared by water as can be seen in Figure 1.3. In Ottoman times, the calligraphers had used their tongues to correct their mistakes. The Turkish idiom of “licking ink” that is used for educated people has been originated from this process.

The other type of black ink that is produced from green vitriol and galls is the iron-gall-ink that was widely used in European countries. It is given in detail in Section 1.2. There are also some recipes containing both iron (II) sulphate and soot together (Nefeszade, 1938).

Ottomans have also used many different colored pigments in illustrations besides black pigments. In Ottoman calligraphy, the most commonly used colored inks were red, yellow, white, gold, (Derman, 1998) blue and green (Nefeszade, 1938).

Red ink was mostly used in manuscripts for titles and punctuation. The red ink had been kept making lastly in the beginning of the XXth century by a specialist from Eyüp. By the death of him the composition ofhis red ink has been left as a mystery (Yaman, 1995). The sample of red orange pigment used in a historical manuscript can be seen in Figure 1.4.

There were many resources to be used as a pigment in red inks. These are artificial pigments such as red lead, vermillion, animal originated organic pigments such as lac, kermes and cochineal, plant originated organic pigments such as Madder roots (*Rubia tinctorium* L.), *Brazil wood*, Caesalpinia *brasiliensis* L.

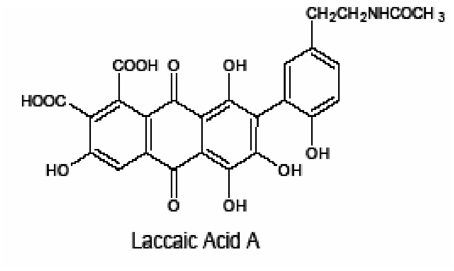
Red pigments mentioned in Ottoman recipes are artificial pigments such as cinnabar, used with white lead to make rose-colored red; animal originated red pigments such as lac, kermes and cochineal (Nefeszade, 1938).

Cinnabar, a dense mineral, is the principal ore of the metal mercury or quicksilver; it is found widely but not abundantly, distributed on the world. The appearance of native cinnabar is given in Figure 1.5. Vermilion is the standard name given in England and the United States to the red artists' pigment based on artificially made mercuric sulfide (HgS). There are three kinds of mercuric sulfide pigments; the natural, which is simply fine-grained cinnabar; synthetic one made by the dry process, commonly called vermillion and third is the synthetic one made by wet process (Rutherford *et al.*, 1972).

The only defect of the vermillion is that it is slightly toxic and also can darken to a black substance. Since Roman times it has been known that specimens of vermilion darken when exposed to light. Some tests have shown that impurities in the alkali polysulfides used to "digest" the pigment lead to this instability. They catalyze the transition of red to black. It has also been found that the darkening of vermilion occurs mainly in paintings used egg tempera binder. The optical micrograph of vermillion can be seen in Appendix Figure A.2.

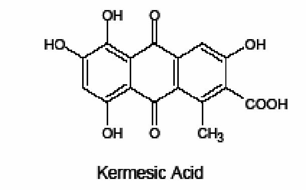
The animal originated organic pigments, lac (*lök),* kermes (*kırmız)* and *cochineal* are animal dyestuffs extracted from insects. They were also used as red pigments.

The lac insect, *Laccifer lacca,* is native to India and Southeast Asia (Wheat and Hedlund, 2003). There are four chemical species within the lac beetle that produce the red dye: laccaic acid A (Structure 1.1), B, C and D, with A being most abundant (Duffy, 2007).



Structure 1.1

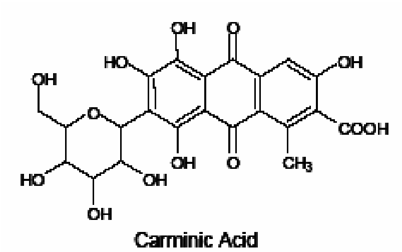
Kermes, *Kermes vermilio*, is a parasite that feeds on Mediterranean oak (Cardon, 1990), found in the Mediterranean region of southern Europe and Turkey. Kermesic acid, kermes (Structure 1.2) is the aglycone of carminic acid (cochineal), and both acids are responsible for producing red color of the dyes (Bingham and Tyman, 2000).



Structure 1.2

The cochineal pigment is native to the New World and used for centuries by the Aztecs and Mayan people as a dye in textiles and pigments in paints. It was brought to Europe in 16th Century. Its earliest recorded use was a textile dye in the Peruvian Paracus culture of 700 B.C. It was brought to Europe shortly after the discovery of the America and the conquest of Mexico in 1523 and was first described by Mathioli in 1549 http://www.library.cornell.edu/preservation/paper/4PigAtlasWestern1.pdf). It is obtained from the dried bodies of the female insect “Dactylopius coccus”. The female beetles are collected 2-4 times a year and are killed with hot water. The resultant color is dependent upon the amount of soaking, the quantity of pigment used and the chemicals added to the mordanting process. Dried and powdered samples of cochineal insects can be seen in Figure 1.6 and 1.7.

The organic pigment obtained from cochineal is carmine. Its main dye constituent is carminic acid (7-α-D-Glucopyranosyl-9, 10-dihydro-3, 5, 6, 8-tetrahydroxy-1-methyl-9, 10-dioxoanthracenecarboxylic acid, ($C_{22}H_{20}0_{13}$). (Structure 1.3) It is soluble in water and alcohol but not in ether. It has a tendency to change to a more orange hue on exposure to acids and a more purple hue on exposure to alkalis. The optical micrograph of cochineal carmine can be seen in Appendix Figure A.3.



Structure 1.3

According to Ottoman tradition, in making yellow inks, the natural pigment called orpiment was ground with gum Arabic and mixed with water (Derman, 1998). Apperance of yellow pigment used in an illustration is given in Figure 1.8.

Orpiment, As_2S_3, may be found in natural and artificial form. It is difficult to differentiate between natural and artificial orpiment, except that the artificial form is more finely grained. Orpiment has been identified in objects of the 31st century B.C. in Egypt, some scientists suggesting that the pigment was used in Egyptian cosmetics despite its toxicity.

The Chinese used the toxic properties of Orpiment to repel insects from book rolls, as described in 5th century treatises. The pigment decomposes slowly in water, and is soluble in hydrochloric acid and sodium hydroxide. It is incompatible with lead and copper pigments and will darken them when in close proximity. It also has a corrosive action on binding materials, often decaying and coming away from the parchment (Baker, 2004). The samples of mineral orpiment and the optical micrograph of the orpiment pigment can be seen in Figure 1.9 and Figure A.4, respectively.

In making white ink that was primarily used for writing *sure* or chapter or headings in ornamented Qur'ans, lead white had been used as a pigment. The sample of white ink used in an illustration is given in Figure 1.10. Lead white is a manufactured pigment and it has been prepared artificially since the earliest historical times and used until the nineteenth century. It was prepared by suspending strips of lead above vinegar or urine in a vase, sealing it and burying it in a dung heap for several days. After a few days the artist scraped off the crust formation on the lead and ground it for use. The pigment is poisonous when ingested or inhaled. Lead white tends to darken when exposed to air and is incompatible with verdigris and orpiment. Bone white was often an alternative choice when working in proximity with these two pigments (Ross, 1971).

Lead white is a basic lead carbonate, soluble in dilute nitric and acetic acid and its chemical formula is, ($2.Pb(CO_3)_2\ .Pb(OH)_2$); the purity of the color depends on the purity of the lead. Lead white shows remarkable permanence and is unaffected by light. Hydrogen sulfide in the air can cause the pigment to turn black perhaps because of the formation of PbS due to the reaction 1.1 and can be seen in Figure 1.11. The black color formation can be converted to a more stable state using hydrogen peroxide, as shown in the treatment of certain wall paintings (Feller, 1993). Optical characteristics include high opacity and high density (Baker, 2004).

In twentieth century zinc oxide had been begun to be used as a white pigment then titanium oxide being superior to lead in many ways and became the competitor of lead white. The microscopic appearance of lead white is given in App. A Figure A.5.

$$PbCO_3(s) + H_2S(g) \rightarrow PbS(s) + H_2O(g) + CO_2(g) \qquad (R.1.1)$$

In making blue inks, indigo and copper compounds had been used. In Ottoman calligraphy, indigo was used with lead white to obtain azure color (Nefeszade, 1938).

Blue pigments were generally used in illustrations in historical manuscripts. The sample of the blue pigment used in an illustration is given in Figure 1.10.

Indigo is a vegetable extraction from *Indigofera tinctoria*. The first mention of the trading of indigo is seen in 12th century accounting book of a European merchant. Synthetic indigo was not produced until 1870. The difference between natural and synthetic indigo is determined by the amount of the isomer indirubin present in the pigment. Indigo is insoluble in water, dilute alkali solutions and acids. Under the microscope indigo particles are very fine and opaque (Baker, 2004). The optical micrograph of the indigo pigment can be seen in Appendix A Figure A.6.

There were three types of green inks in Ottomans as mentioned in resources about the Ottoman calligraphy; mixture of orpiment and copper (II) sulphate, mixture of gall juice and copper (II) sulphate and mixture of saffron and copper (II) sulphate (Nefeszade, 1938). Mixing orpiment and indigo to produce shades of green was not only seen in the Islamic world of the 14th century but also due to Cenini this is a popular practice in 15th century Florence (Baker, 2004).

Verdigris, cupric acetate, was produced by the corrosion of strips of copper with vinegar fumes. After the pigment was scraped from the plate, it was mixed with wine and allowed to thicken. It is not compatible with white lead and orpiment as well as many media and surfaces. The color ranges from green, green-blue to blue and it exists in two forms: basic and neutral verdigris. Verdigris reacts destructively with its binding medium and binding surface. It is commonly known that the reflectance of verdigris pigment changes as it dries. Verdigris mixed with sulfur containing pigments in an aqueous media may darken due to the formation of copper sulfide (Baker, 2004).

In Ottoman resources, verdigris so-called "*jengar or zangar*" was said to be used generally for ruling the text. But it is destructive and degrades the cellulosic materials and parchment, however due to a research of Barkeshli and Ataie (2002); in some Persian miniature paintings the presence of saffron appears to mitigate the harmful effect of the verdigris. Research of them shows that verdigris mixed with saffron did not char the paper support, and charring occurred only where the pure verdigris existed. The optical micrograph of it is given in Appendix A Figure A.7.

Gold was often used in gilding manuscripts with decorative borders or laid in gold leaf form. First, a base adherent or bole was put on the desired areas. Next, the gold lead was carefully positioned on the page. Then it was allowed to dry and the excess was removed with a tool like a soft brush.

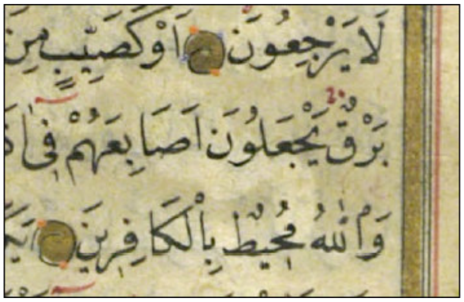


Figure 1.1 Sample of carbon black pigment

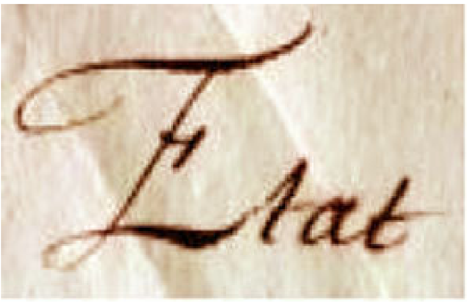


Figure 1.2 Sample of iron-gall-ink

Figure 1.3 Sample of smeared soot ink

Figure 1.4 Sample of red orange pigment

Figure 1.5 Native cinnabar associated with calcite[1]

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[1] http://webmineral.com

Figure 1.6 Dried cochineal

Figure 1.7 Powdered cochineals

Figure 1.8 Sample of yellow pigment

Figure 1.9 Mineral orpiment[2]

Figure 1.10 Blue and white pigments

Figure 1.11 Corroded white lead pigment**,** black colored regions show occurence of PbS

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[2] http://webmineral.com

1.2 Iron-gall-ink

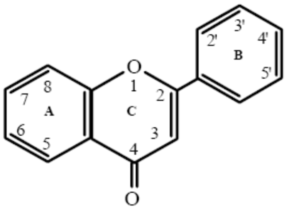
Iron-gall-ink which was the most important ink in the Western history was also a popular ink for drawing favour by many artists from the fifteenth century onward (Kanngieber *et al.*, 2004). It was attractive due to simplicity in its preparation, good quality of writing and the fact that it was practically irremovable when applied.

There have been many recipes for iron-gall-ink preparation. It is produced from four main ingredients; tannin, vitriol, Gum Arabic and a fluid medium (Kanngieber *et al.*, 2004).

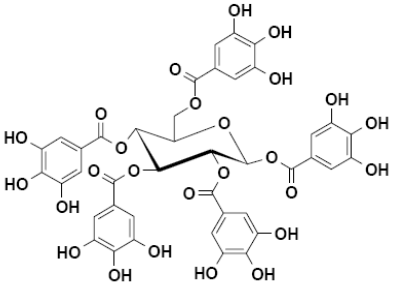
Tannins may be found in the leaves and bark of many plant species. Plants contain a large variety of compounds including alkaloids, terpenes and phenolics. These compounds do not have a role in “primary” metabolism such as biosynthesis, biodegradation and other energy conversions of intermediary metabolism but they are efficient in biological activities such as toxicity and hormonal mimicry. They also have a role in protecting plants from herbivory and disease. The group of phenolics known as *tannins* is different from other plant secondary phenolics in terms of chemical reactivities and biological activities (Hagermann, 2002).

Tannins are defined as water-soluble phenolic compounds having molecular weights between 500 and 3000. They give usually phenolic reactions and have special properties such as precipitating alkaloids, gelatin and other proteins. They are usually divided into hydrolysable tannins and condensed tannins. Condensed tannins, proanthocyanidins, are polymeric flavonoids (Structure 1.4), which are a diverse group of metabolites based on a heterocyclic ring system derived from phenylalanine and polyketidebiosynthesis. They are polymers of 2 to 50 (or more) flavonoid units that are joined by carbon-carbon bonds, which are not susceptible to cleavage by hydrolysis (Hagermann, 2002).

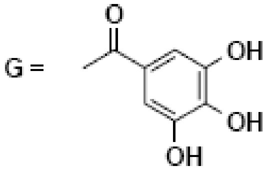
Hydrolysable tannins are derivatives of gallic acid, 3, 4, 5 tri-hydroxy benzoic acid. The simplest hydrolyzable tannins are gallotannins. They are polygalloyl esters of glucose. The prototypical gallotannin is pentagalloyl glucose (β-1, 2, 3, 4, 5, 6-Pentagalloyl-O-D-Glucopyranose) (Structure 1.5). It has five identical galloyl esters; the galloyl moiety is given in structure 1.6 which involves linkages with aliphatic hydroxyl groups of the core sugar (Hagermann, 2002).



Structure 1.4 Flavonoid Unit



Structure 1.5 β-1, 2, 3, 4, 5, 6-Pentagalloyl-O-D-Glucopyranose



Structure 1.6 Galloyl Moiety

The function of tannins in iron-gall-inks depends on their metal ion chelating property. Phenolics can affect the activity of metal ions by chelating the metal (Mc Donald, 1996). Chelation depends upon the pH of the medium. It should be above the pKa of the phenolic group (10.0). Phenolic-metal ion complexes are often colored and it has been said that characteristic colors can be used to identify specific arrangements of phenolic groups (Waterman, 1987; Hagermann, 2002).

Galls are the most important resources of hydrolyzable tannin. As early as the 5th century BC, oak galls (also called gallnuts or oak apples) were collected and used commercially as a source of tannic acid. There are many different types of galls, all with varying tannin content such as Aleppo galls, acorn galls, oak-marble galls, Chinese galls and Japanese galls. Tannin could also be extracted from other sources such as chestnut wood, bark, the Sumac plant and pomegranate peels.

Simple gallotannins with up to twelve esterified galloyl groups and core glucose are generally found in tannins from oak galls and sumac (Hagermann, 2002; http://www.knaw.nl/ECPA/ink/ink_ingredients.html).

Oak galls (*Quercus infectoria*) (Figure1.12) have the highest amount of tannin that is about 60-70 w% whose 28-35 w% is gallic acid (Kavak, 2006).

Figure 1.12 Oak Galls

Glucose esters of tannin (gallotannic acid) hydrolyze into gallic acid and glucose during the preparation of ink (Reaction 1.2). Hydrolysis of gallotannic acid occurs in three ways; one is leaving the galls in distilled water, other is boiling the galls in distilled water for hours, third one is by using acids or by letting the galls to ferment after boiling (http://www.knaw.nl/ecpa/ink/make_ink.html).

$$\underset{\text{Gallotannic acid}}{C_{76}H_{52}O_{46}} + 5\ H2O \rightarrow 5\ \underset{\text{Gallic acid}}{C_7H_6O_5} + \underset{\text{Glucose}}{C_6H_{12}O_6} \qquad \text{(R.1.2)}$$

Vitriol, the main inorganic component of the ink, is also referred to in recipes as *copperas, sal martis, vitriolum commune, vitriolum romanorum* and *vitriolum cyprinum*. It has several varieties. The iron and copper varieties of vitriol were widely utilized in antiquity, and were commonly referred to as green and blue vitriol, respectively. In modern mineralogical terminology, the green and blue vitriol correspond to melanterite ($FeSO_4.7H_2O$) and chalcanthite ($CuSO_4.5H_2O$), respectively (Karpenko and Norris, 2000).

Melanterite is one of the water-soluble sulphate minerals. It forms in the near-surface secondary oxidation zone of ore deposits. Appereance of melanterite can be seen in Figure 1.13.

Figure 1.13 Appearance of Melanterite

Chalcanthite like melanterite is soluble in water and it thus makes a solution of copper sulphate. The appearance of it can be seen in Figure 1.14.

Figure 1.14 Appearance of Chalcanthite

Another component of ink is Gum Arabic, a natural polysaccharide derived from exudates of Acacia Senegal trees. An Acacia Senegal tree is shown in Figure 1.15. Acacia Senegal is one variety of 1100 acacia tree. It is most commonly found in the African grassland savannas along the southern edge of the Sahara Desert also as far East as Oman and India.

Figure 1.15 Acacia Senegal

Though some gum will flow naturally from cracks in the bark of the *Acacia senegal* tree, commercial tappers stimulate the flow by removing thin strips of bark, an operation that requires some skill if the tree is not to be injured (Figure 1.16,1.17) (Botti *et al.*, 2005).

Figure 1.16 Gum accumulated on the bark

Figure 1.17 Collecting the Gum (Botti etal, 2005)

Gum Arabic (GA) consists of mainly three fractions: (1) The major one is a highly branched polysaccarides (M_w=3x10^5) consisting of β- (1-3) galactose backbone with linked branches of arabinose and rhamnose, which terminate in glucuronic acid (found in nature as magnesium, potassium and calcium salt) (2) A smaller fraction (~10 wt% of the total) is a higher molecular weight (~1x10^6 g/mol) arabinogalactan-protein complex in which arabinogalactan chains are covalently linked to a protein chain through serine and hydroxypyroline groups. The attached arabinogalactan in the complex contains ~13 %(by mole) glucuronic acid. (3) The smallest fraction (~ 1% of the total) having the highest protein content (~ 50 wt %) is a glycoprotein which differs in its aminoacids composition from the second fraction. Studies showed extensive variation in the molecular weight distributions of the various components between individual samples, even those supplied from a common vender. Variations are traced to the origin, type and age of tree, and even to possible effects of processing conditions such as spray dying (Dror *et al.*, 2006).

The macromolecules of gum Arabic have a molecular weight between 250 000 and 300 000. The molecules are almost spherical; being about 100 A° long and with a diameter of 110 A°. The gum dissolves in water slowly, but completely, in water in twice of its volume. It appears that the macromolecules readily change their shape and dimensions in solution, and this indicates that the forces of attraction between the constituent sugars are weak. This confirms the hypothesis of a highly branched structure inducing a relative compact shape (Dror *et al.*, 2006).

The maximum viscosity is reached at the neutral pH (7.0), at ordinary room temperature. There is a decrease in viscosity when the solution is heated, and the macromolecules start to break down, as seen by the liberation of sugars. This molecular degradation can also be brought about by a number of other factors, such as the presence of acids, salts, ultraviolet light or even by simple mechanical grinding. The ageing of gum Arabic has been well studied (Daniels and Sashoua, 1993). It is understood that ageing does not change solubility of gum Arabic. Only a heating to 100 °C makes it brown and insoluble.

Gum Arabic is an excellent protective colloid, and for this reason it is often used to stabilize emulsions or dispersions and a thickening agent. So it is important in ink recipes (Masschelein and Kleiner, 1995).

An aqueous solution of the gum is used as a binding medium in water-colors, inks and gouaches and serves as an adhesive for paper and cardboard. Gum Arabic was also the binding medium of miniatures on ivory (Chizzola, 1985).

The analysis of the mural paintings in the tomb of Nefertari, the wife of Rameses II, indicates the presence of a gum Arabic without rhamnose, which could have come from a local acacia species still growing in the Luxor region (Masschelein and Kleiner, 1995).

Gum Arabic used as a binding material decreases the possibility of the precipitation of ferric gallate pigment through adsorption of gum Arabic particles on the surface of ferric gallate particles. It also adjusts the viscosity of the ink (Kolar *et al.*, 2006).

In a recent study, it has been found that gum Arabic delays the degradation of paper, due to physical factors, as the gum coats the paper fibers and limits the diffusion of oxygen or free iron (Rouchon-Quillet *et al.*, 2004).

Other main ingredient of the iron-gall-ink is the fluid medium such as distilled water, wine, beer, vinegar, etc. Beside the main ingredients mentioned above the other ingredients of iron-gall-inks are indigo, logwoods, saffron, henna, pomegranates, crystalline sugar, alum, rose-water, etc.

Saffron was present in many ink recipes both of European and Ottoman. It consists of stigmas of flowers of *Crocus Sativus* that is a bulbous perennial plant of the family *Iridaceous*. (Figure 1.18, 1.19) The stigmas of flowers are dried and used to act as flavor and coloring agent for foods as well as a dye for inks and textiles. (Fig. 1.20) Saffron is a spice known only in cultivation and principally grown in Spain and Iran, but also cultivated on a lower scale in Greece, Turkey, India, Azerbaijan, France, Italy, India, China, Morocco, Israel, Egypt, United Arab Emirates, Mexico, Switzerland, Algeria, Australia, and New Zealand.

Figure 1.18 Saffron flower

Figure 1.19 Saffron flower

Figure 1.20 Stigmas of Saffron

In Turkey cultivation of saffron is limited. It is cultivated only in Davutobası, Yörük, and Aşağıgüney villages of Safranbolu and in Harran, Şanlıurfa.

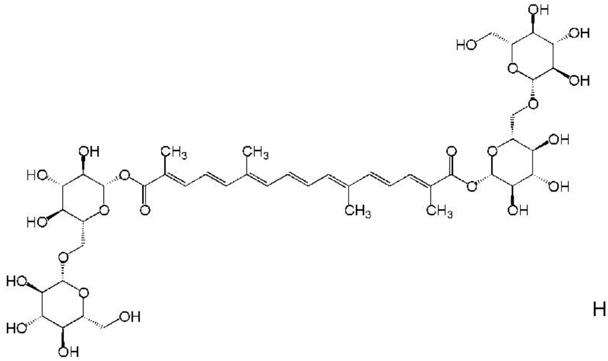
The name saffron comes from the Arabic *za'faran*, which means yellow. The use of saffron also goes back to ancient Egypt and Rome, where it was used as a dye, in perfumes, and as a drug as well as for culinary purposes (Abdullaev and Espinosa-Aguirre, 2004).

The stigmas of the saffron flower contain many chemical substances. Carbohydrates, minerals, musilage, vitamins, especially riboflavin, thiamine and pigments including crocin, anthocianin, carotene, lycopene, zigzantin, flavonoids, amino acids, proteins, starch, gums, and other chemical compounds have also been identified in saffron.

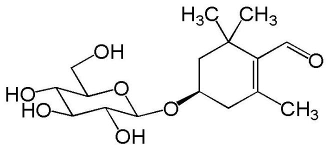
The saffron stigma, which is commercial form of saffron, has a distinct and unique color, flavor and aroma. One of the coloring pigments in saffron is crocin (Structure 1.7), which is easily soluble in water. In addition to crocin, saffron contains crocetin and small amounts of the pigment anthocianin, a-carotene, b-carotene, and zegxantin (Abdullaev and Espinosa-Aguirre, 2004).

Saffron has a bitter taste. The bitter-taste of it comes from the picrocrocin ($C_{16}H_{26}O_7$) (Structure 1.8), a monoterpene glycoside precursor of safranal ($C_{10}H_{14}O$) (Structure 1.9), and the main volatile oil responsible for the aroma. β-Glucosidase action on picrocrocin liberates the aglycone, 4-hydroxy-2, 6, 6-trimethyl-1-cyclohexene-1-carboxaldehyde ($C_{10}H_{16}O_2$), which is then transformed to safranal by dehydration during the drying process of the plant material. The colour of saffron comes from the water-soluble glycosidic cis- and transcarotenoids crocins, glucosyl esters of crocetin (8, 8'-diapocarotene-8, 8'-dioic acid; $C_{20}H_{24}O_4$) (Ortega *et al.*, 2007).

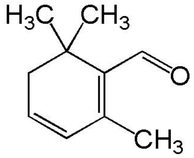
Saffron has found nearly in all of Ottoman recipes especially in green ink and black ink with gall, iron and copper. In recipes, it was advised saffron to be used in ink in order to make the ink better and brighter.



Structure 1.7 Structure of Crocin



Structure 1.8 Picrocrocin



Structure 1.9 Safranal

1.3 Paper Degradation

Historical manuscripts have been unique parts of our cultural heritage. Thus, their preservation and conservation are important cultural tasks.

The main carrier material used in historical manuscripts is paper and millions of books worldwide now are menaced by paper disintegration through malignant and inevitably progressive degradation of cellulose chains (Lojewska *et al.*, 2005).

Paper consists of mostly bonded cellulose fibres that are linear polymers of glucose (β-D glucopyronose) monomers linked by β -1, 4-glycosidic bonds. All chemical reactions occur at glycosidic bond and/or at hydroxyl groups (Proniewicz *et al.*, 2001). (Figure 1.21).

Polymerization of cellulose gives a linear molecule with cyclic glucose units which have three hydroxyl groups in carbons C_2, C_3 and C_6 as shown in Figure 1.22 (Sistach *et al.*, 1998).

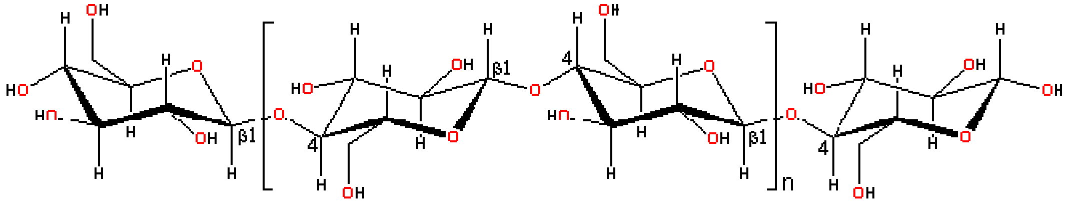


Figure.1.21 Molecule of cellulose (Sequeira *et al.*, 2006)

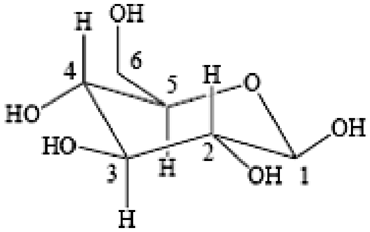


Figure 1.22 C1 to C6 positions in glucose (Carlsson, 2005)

According to recent findings, cellulose degradation should be regarded in terms of mixed oxidative and hydrolytic mechanisms where the two reactions are autocatalytically accelerated by active oxygen species and by protons, respectively (Lojewska *et al.*, 2005).

The molecular mechanism of acid-catalyzed hydrolysis of cellulose (cleavage of β -1, 4-glycosidic bond) occurs in three steps. (Fig. 1.23) First, a proton from acid interacts rapidly with the glycosidic oxygen linking two sugar units, forming a conjugate acid. Then the cleavage of the C-O bond occurs and the conjugate acid breakdowns to the cyclic carbonium ion, which adopts a half-chair conformation. After a rapid addition of water, free sugar and a proton are liberated. The formation of the intermediate carbonium ion takes place more rapidly at the end than in the middle of the polysaccharide chain (Nutt, 2006).

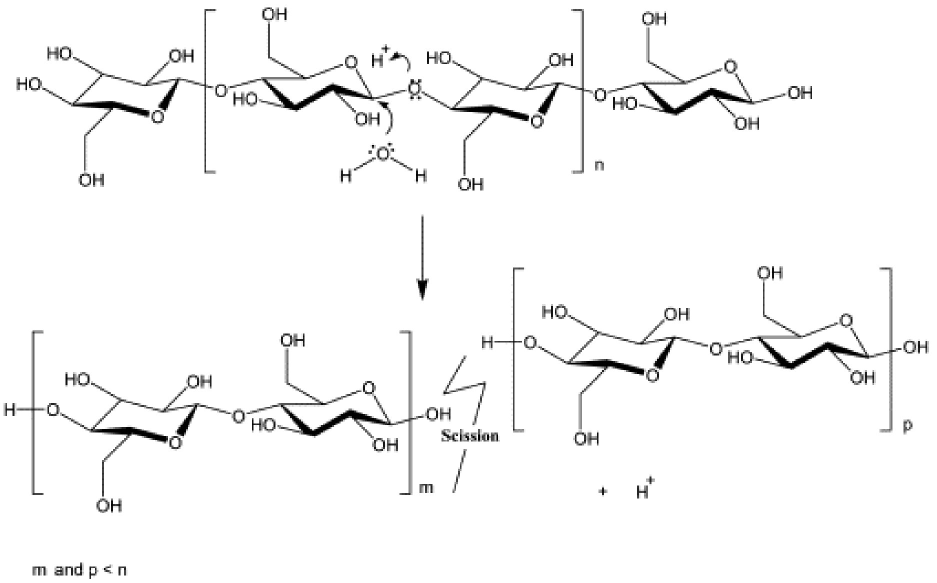


Figure 1.23 Acid catalyzed hydrolysis of the β -1, 4-glycosidic bond in cellulose (Hydrolysis can occur at any glycosidic bond in the chain) (Sequeira *et al.*, 2006).

Depolymerization of cellulose is a continuous and consecutive process. This process essentially results in the progressive loss of tensile strength and color change of the paper (Banik, 1996).

The acidity problem is specific to the paper produced over around 150 years between the mid-19th century and the late 20th century (modern paper). The bad situation of modern paper has always been attributed to the unavailable storage conditions such as overheated, humid libraries and acid polluted atmospheres however, documents of the Middle Ages have been able to survive under the same conditions. Since the modern paper is acidic due to the alum ($KAl(SO_4)_2.12H_2O$) added during the paper manufacture while old papers were made at neutral pH(Williams, 1971).

Paper made before the 19th century was often made by hand from linen and cotton rag materials which are excellent sources of high cellulose, long fibers. Gelatin, from animal hides, was used to size such papers and because the resulting papers were neutral to only slightly alkaline they had very good storage properties (Zicherman, 2007).

At the beginning of the 19th century, wood fiber took the place of cotton and linen. However, wood has shorter fibers and lower cellulose content along with lignin. Lignin contains phenolic entities sensitive to light which develop chromophores or conjugated double bonds in the chemical structure which can absorb light in the visible range. This makes paper containing high amounts of lignin very prone to discoloration or yellowing (Zicherman, 2007).

Besides lignin, alum $(Kal(SO_4)_2.12H_2O)$ was another degradation factor in old papers. Alum was used to precipitate the rosin onto paper forming an alum/rosin sizing. Aluminum sulfate reacts with water and produces sulfuric acid and production of paper on the paper machine demanded additional alum, so papermakers often used the salt in excess (Zicherman, 2007).

Besides acid catalyzed hydrolysis, alkaline medium also causes hydrolysis of cellulose polymer as seen in Figure 1.24. It has not been taken into consideration as much as acidic hydrolysis since the depolymerization level of alkaline samples is much lower than the acidic ones. This is due to the fact that alkaline hydrolysis of cellulose can only take place in the reduction end of the polymer or in oxidized groups while the acid scission can happen in any of the glycosidic bonds between the monomers and this raises the occurrence probability of acidic scission (Sequeira *et al.*, 2006).

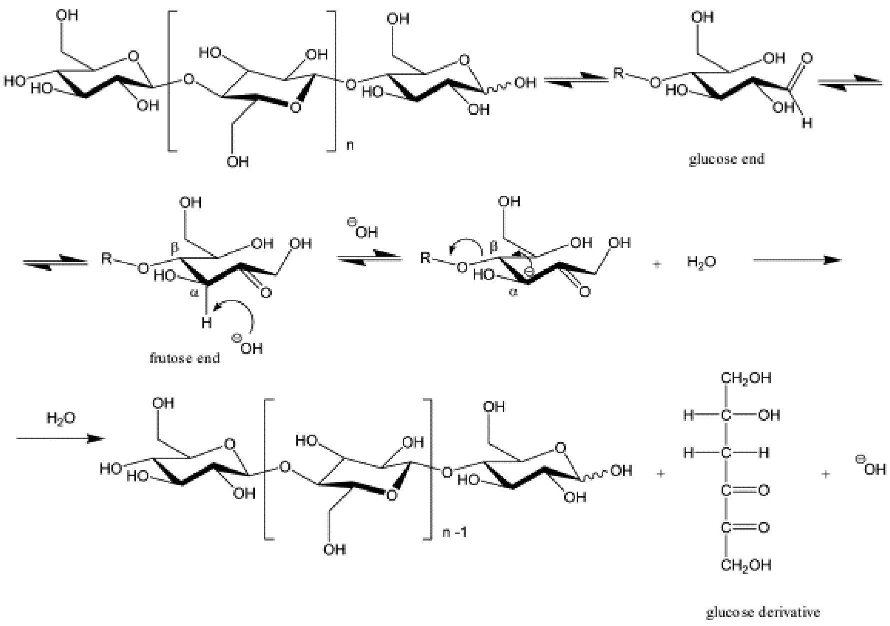
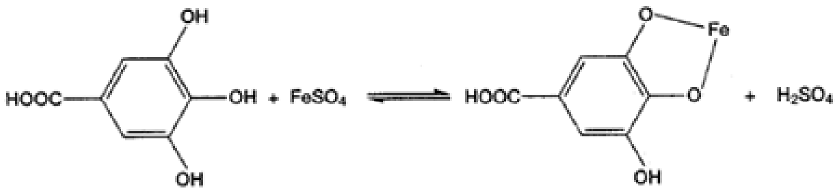


Figure 1.24 Alkaline hydrolysis mechanism in cellulose (Sequeira et al, 2006).

Another reason for the degradation of cellulose is the iron-gall-ink used in many historical manuscripts. The large variety of different recipes and the compositional diversity of the natural raw materials result in a diversity of distinguishable degradation mechanisms leading to changes in color in time and, occasionally, resulting in iron-gall-ink corrosion.

Two principal causes are usually considered to be responsible for the paper degradation. The first one is the high acidity of some inks that leads to hydrolytic splitting of the cellulose (formation of sulphuric acid). The second one is the presence of soluble and mobile iron ions that may act as catalysts for oxidative decomposition of the cellulose (Kanngieber *et al.*, 2004).

The acidity of iron-gall-ink comes from the reaction of gallic acid with ferrous sulphate; iron-gall-ink contains sulphuric acid that is a by-product of the ink. This acid can go through the paper and penetrates into the fibers when this ink is used in writing. The reaction is given below (Reaction 1.3) (Sistach *et al.*, 1998).



(R.1.3)

Gallic Acid Ferrous gallate complex

Other major process that causes degradation of paper is the metal-catalyzed oxidation of cellulose. Most old iron-gall-ink recipes, however, contained an excess of iron(II) sulphate compared to the tannin content (Neevel, 1995) so after many years or even centuries the ink may still contain substantial amounts of iron ions and sulfuric acid. According to Neevel (1995), iron bound to gallic acid does not participate in the degradation of paper whereas iron ions are likely to be responsible for the metal-catalyzed oxidation of cellulose (Wagner *et al.*, 2004).

Iron (II) ions are suspected to cause the oxidative degradation of cellulose by catalyzing the formation of hydroxyl radicals (·OH) from hydrogen peroxide in the so-called “Fenton reaction”. The reaction sequence can be given as follows (Neevel, 1995):

Iron (II) ions reduce atmospheric oxygen in acidic medium to give hydrogen peroxide in two steps. (Reaction 1.4 and 1.5)

$$Fe^{2+} + O_2 + H^+ \rightarrow Fe^{3+} + HOO\bullet \qquad \text{(R. 1.4)}$$

$$Fe^{2+} + HOO\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2 \qquad \text{(R. 1.5)}$$

Then in the third step hydrogen peroxide reacts with Fe^{+2} present in the medium to give hydroxyl radicals and Fe (III) ion. (Reaction 1.6)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \qquad \text{(R.1.6)}$$

Hydroxyl radicals are very reactive and take out hydrogen from cellulose and oxidize hydroxyl groups of cellulose into carbonyl groups (Figure 1.25).

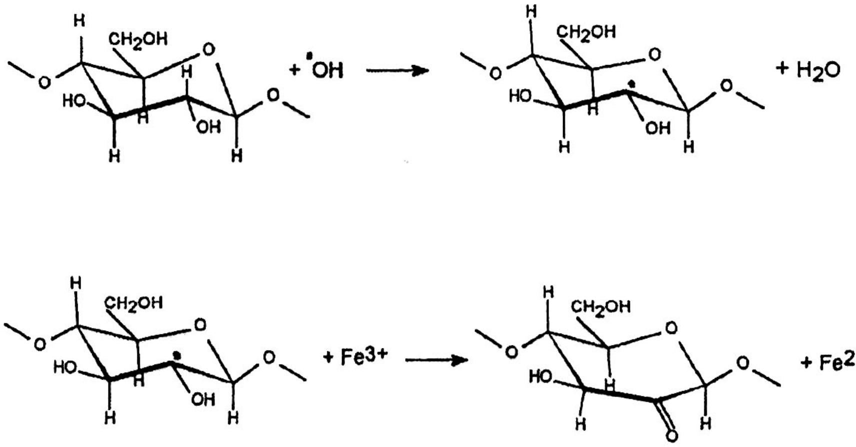
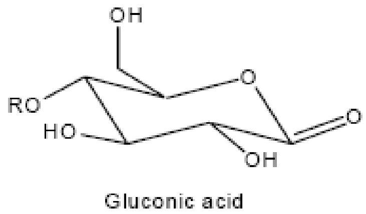


Figure 1.25 Formation of carbonyl groups in cellulose oxidation by OH radicals in the presence of Fe (II) ions (Gibert *et al.*, 1999).

In reaction between cellulose and •OH radicals, following processes are possible (Gibert *et al.*, 1999):

- Hydrolytic cleavage of C_1 and oxidation of the remaining aldehyde group to carboxyl which gives gluconic acids (structure 1.10)



Structure 1.10 Gluconic Acid lactone form (Carlsson, 2005)

- Hydrolytic cleavage in C_4 giving glucoside fragments
- Oxidation of carbon C_2, C_3 to give keto groups. Oxidized groups in C_2, C_3 are shown below (Fig. 1.26 and 1.27).

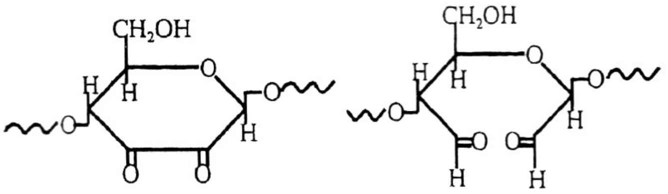


Figure 1.26 Oxidized Groups in C_2 and C_3 (Sistach *et al.*, 1998).

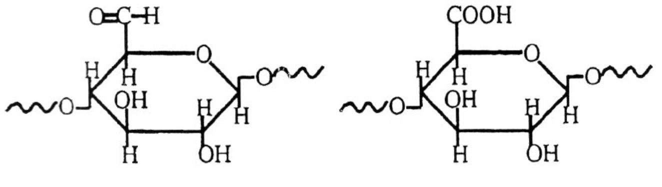
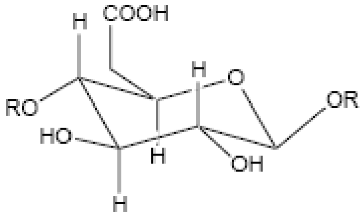


Figure 1.27 Oxidized Groups in C_6 (Sistach *et al.*, 1998).

- Oxidation of C_6 to give aldehyde groups and then to glucuronic acids (structure 1.11). the residual oxidized cellulose and other fragments from hydrolysis tend to degrade more readily by heat and acids than the initial cellulose (Gibert *et al.*, 1999).



Structure 1.11 Glucuronic acid (Carlsson, 2005)

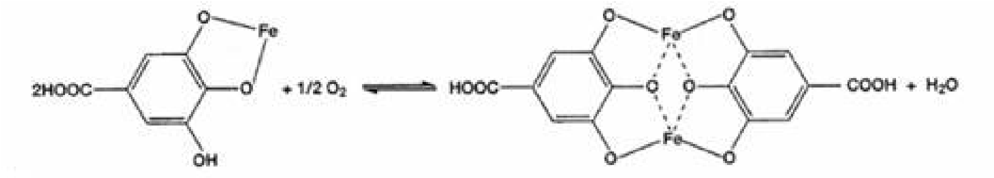
Although iron has known to be the main metal in the iron-gall-ink catalyzing the oxidation of cellulose by Fenton- like reactions, there are many metals affecting the permanence of paper which interferes with the paper during the manufacture of it. Various metals such as manganese, copper, aluminum, calcium, magnesium, zinc, cobalt and barium may be found in the wood used for paper. Also metals can be found as contaminants in the additives. Moreover, metals can also be found in the inks used in the manuscripts beside iron especially copper. Studies performed on historical manuscripts demonstrated that substantial amount of copper were used in inks (Strlic *et al.*, 2003).

It is important to note that copper is known to catalyze free radical production much more efficiently than iron (Pihlar *et al.*, 1999). In a low acidic medium, copper ions catalyze the oxidation on the anhydroglucose ring while in low alkaline medium, copper ions seem to be active on the cleavage of the glycosidic bond (Bicchiere, 1996). Especially in alkaline conditions ($pH \geq 8$) copper ions are much better catalysts for peroxide decompositions than iron ions (Budnar *et al.*, 2004). Therefore, copper ions should also be considered in studying the degradation of cellulose.

In another hypothesis for cellulose degradation, iron-gallic acid complex (structure II) is considered as a hydroxyl radical conveyor in the cellulose oxidation (Gibert *et al.*, 1999).

Iron-gallic acid complex (Structure II) shown below constitutes a redox system together with hydrogen peroxide. Gallic acid initially reacts with ferrous sulphate to form ferrous gallate and H^+ ions that combine with the excess sulphate ions to form sulphuric acid. (Reaction 1.3)

Ferrous gallate (Structure I) shown below is a colorless and water-soluble substance, oxidized by atmospheric oxygen to form ferric pyrogallate, blackish purple complex that is insoluble in water. (Reaction 1.7) In the complex there are totally four molecules of water bound to the iron (III) ions above and below the plane of the molecule, occupying the remaining sites of coordination of the octahedral iron (III) ions (Gibert *et al.*, 1999).

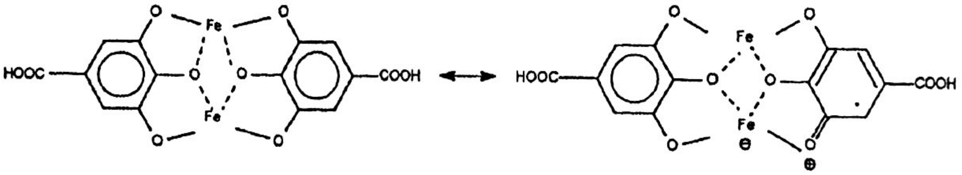


Ferrous gallate Ferric pyrogallate complex

(I) **(II)** (R.1.7)

When first prepared the color of an iron-gall-ink solution is pale. The oxygen present in water reacts to produce a light gray color in the initial ink. When iron-gall-ink is applied to paper, it remains as gray for a while then it turns to dark blue.

Due to Gibert *et al.*(1999), this dark blue color of iron-gallic complex is explained by the charge transfer from an aromatic nucleus in gallic molecule to the Fe (III) central ion generating a conjugated double bond system responsible for energy absorption in the visible region. (Reaction 1.8) Also cellulose molecule may have a role in the color formation.



(II) **(III)** (R.1.8)

In this redox system iron-gallic complex (Structure III) is activated with peroxide to give intermediate product (Structure IV) and transformed into quinone like structure (Structure V) by loosing water. (Quinone is a class of cyclic organic compounds containing two carbonyl groups). This quinone like structure (Structure V) is capable of abstracting hydrogens from cellulose to give structure VI and yielding radicals as seen in structure VII.

These radicals finally become oxidized cellulose containing chromophoric carbonyl groups (Structure VIII). In this redox system active radicals are continuously generated by interaction between iron, gallic acid, cellulose and peroxides.

This hypothesis is called *Fenton-Hamilton mechanism.* (Gibert *et al.*, 1999) (Figure 1.28)

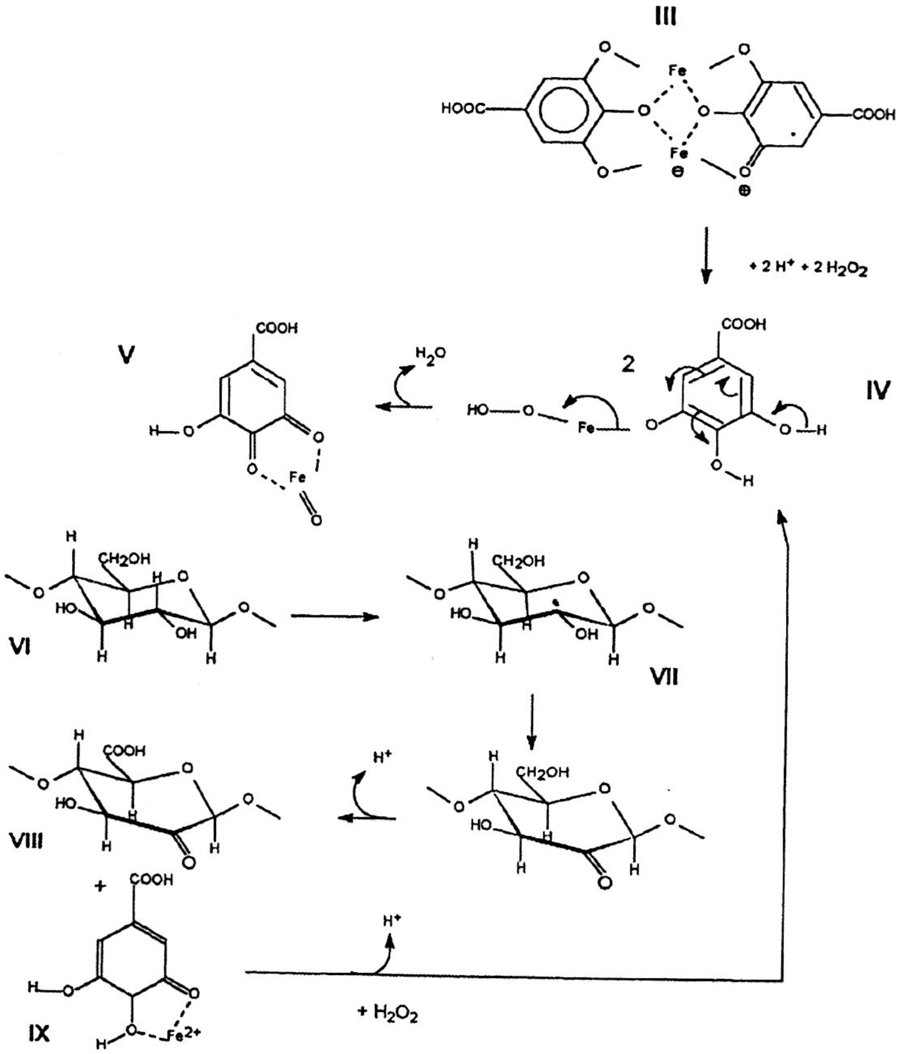


Figure 1.28 Suggested mechanism for the reaction between iron-gallic complex and cellulose (Gibert *et al.*, 1999).

In order to illustrate the progress of the ink corrosion process, a model that has been developed by the researchers in Netherlands Institute for Cultural Heritage. According to their model the cross-section shows the cross-section of an iron-gall-inked paper during ageing (Reißland and Hofenk De Graaff, 2001). (Figure 1.29)

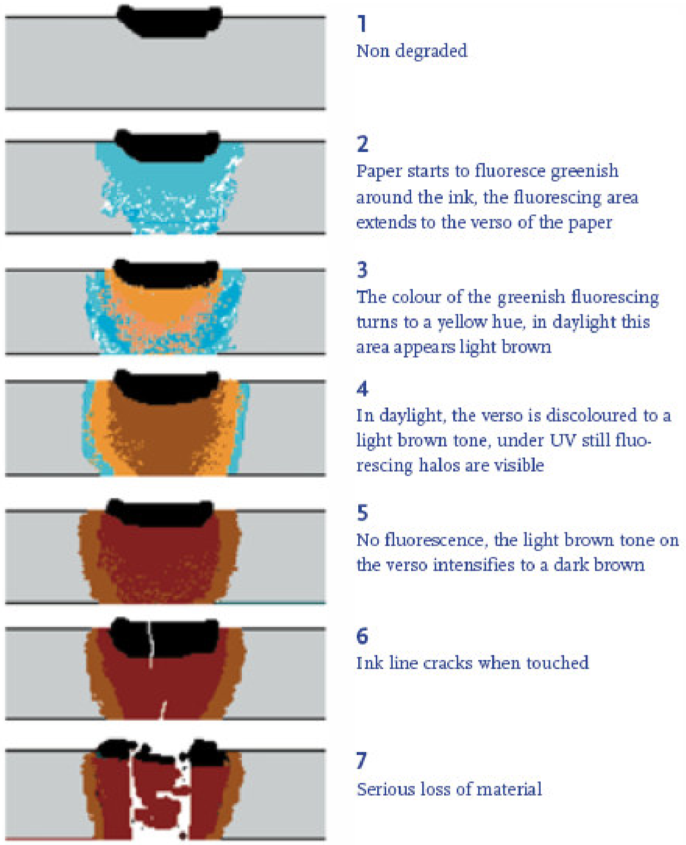


Figure 1.29 Progress of corrosion during ageing of iron-gall inked paper

All these degradation mechanisms of cellulose break out the depolymerization of cellulose and this affects the stability of fibers and causes breakages in the fibers of cellulose. A manuscript that belongs to the collection of National Library of Turkey and degraded due to iron-gall-ink corrosion can be seen in Figure 1.30 as an example.

Figure 1.30 Degraded manuscript from the collection of National Library of Turkey

1.4 Previous Archaeometric Studies on Historical Inks

Libraries, museums and archives have great number of manuscripts, historical documents and precious art works that suffer serious damage due to the corrosive effects of different kinds of historical inks.

In order to prevent these valuable works from further deterioration, the degradation mechanisms should be understood clearly. For this purpose, several researches have been carried out on historical inks and their effects on paper degradation.

Although there are some studies on original works, most of the studies have been performed by using model inks that were prepared in laboratories and applied on filter papers without any additive. Here some important studies have been summarized.

Neevel (1995) carried out a study on preventing the corrosive effect of iron-gall-inks on paper degradation. He suggested that acidity can not be the only reason for the ink corrosion. He focused on the effect of Fe (II) ions on the cellulose degradation and reports that the free Fe (II) ions have a dominant role in the degradation by catalyzing the oxidation of cellulose.

Several studies were performed on the chemical characterization of historical inks prepared in laboratory by using various analytical methods. Senvaitiene *et al.*,(2005) studied on series of different inks prepared according to historical recipes and analyzed them by means of FTIR spectroscopy and reported that IR spectroscopy may provide important information on the chemical composition of historical inks. Also Senvaitiene *et al.*(2006) carried out another study on historical inks using FTIR, UV and visible spectroscopies and capillary electrophoresis in order to develop a new methodological approach for the qualitative determination of nature of unknown historical inks.

UV-Vis spectrophotometry was used in another study to determine the hydroxyl radicals during ageing of cellulose by Kolar *et al.* (2001).

Another study of historical inks using FTIR spectroscopy was performed by Remazeilles *et al.* (2000). In the study, original and laboratory probes of one kind of iron-gall-ink were analyzed by FTIR using different techniques; reflectance microscopy, diffuse reflectometry with KBr and transmission electron microscopy.

The same group carried out another study on iron-gall-ink impregnated papers in order to determine the evolution of the organic materials present in iron-gall-ink manuscripts by using GC-MS. They suggested that gum Arabic degrades during the ageing especially in the presence of ferrous sulphate (Bleton *et al.*, 2003).

Keheyan and Giulianelli (2006) performed a study in identification of historical ink ingredients. In this study historical ink ingredients such as Gum Arabic, saffron, and henna were analyzed by pyrolysis GC-MS technique for their chemical characterization.

In 2007, Csefalvayova *et al.*, performed a study on iron-gall-ink treated papers using FTIR spectroscopy and mechanical tests in order to determine the effect of iron-gall-ink and ferrous sulphate alone on paper degradation during ageing.

Another forthcoming study for the effect of ink ingredients on cellulose degradation was carried out by Rouchon-Quillet *et al.* (2004) in order to detect the impact of Gum Arabic on iron-gall-ink corrosion using FTIR, GC-MS and Size Exclusion Chromotography. In this study, gum Arabic is suggested to reduce the rate of degradation of cellulose.

In 2004, same group again studied on iron-gallic-ink impregnated papers using FTIR spectroscopy to determine the effect of gallic acid on iron-gall-ink corrosion and they suggested that gallic acid enhances the cellulose oxidation by effecting on Fe (III) / Fe (II) ratio, probably because of its reducing property.

Gibert *et al.* (1999) studied on paper samples treated with laboratory prepared iron-gall-inks using color spectrophotometry in order to determine the changes in the lightness and the chromatic values of the samples depending on the iron-gall-ink corrosion. In this study it is understood that color spectrophotometry is a useful tool in analyzing the changes occur in the paper due to the impact of different inks. Especially, measured changes in the chromatic values (Δa^* and Δb^*) show the degree of the oxidation of cellulose.

In another study performed in 2005 by Lojewska *et al.* FTIR spectroscopy was used to study the oxidative and hydrolytic degradation of cellulose during accelerated ageing under controlled conditions.

In 2002, Calvini and Gorassini performed a study on $FeCl_3$ and $CuCl_2$ doped cellulose papers in order to determine the effect of these transition metals on cellulose degradation using FTIR Deconvolution analysis.

Sivakova *et al.* (2008) carried out a research work related to effects of historical inks on the degradation of cellulose. Eight different ink recipes were applied on paper samples and analyzed with FTIR before and after artificial ageing. In this study it was seen that absorption variation in the region of 1500-1900 cm^{-1} is informative for the cellulose degradation and changes due to ink composition.

1.5 Aim of the Study

Preservation, conservation and archaeometrical investigations of historical manuscripts are important cultural tasks since they have been unique parts of our cultural heritage. However, most of them are in deteriorated condition due to the external factors such as temperature, humidity, light, usage, storage conditions and internal factors such as acidity, corrosive inks, etc.

In this study, the degradation of cellulose due to historical inks especially iron-gall-ink were evaluated. The corrosive character of iron-gall-ink had been known since the end of 19th century. It causes degradation of cellulose by various mechanisms, as suggested by the previous researchers.

There have been many studies for developing methods to diminish or even stop the corrosiveness of ink. In order to find effective solutions for the cellulose degradation, the ink corrosion mechanism under various conditions should be understood clearly.

The object of this study is to investigate the influence of different ink compositions on the degradation of cellulose and contribute the restoration studies on manuscripts.

CHAPTER 2

MATERIALS AND METHODS

2.1 Sample Preparation

Sample preparation consists of preparation of various inks application of them to the special filter papers of highest purity.

2.1.1 Ink Preparation

Sixteen ink solutions were prepared in which one was red, two were green and others were black. Analytical grade reagents (if possible) were used for the preparation of inks.

The main ingredients used in the black inks are gallic acid monohydrate (Ga) ($C_7H_6O_5.H_2O$, M_W: 188.14g/mol, Aldrich) and ferrous sulphate hepta hydrate ($FeSO_4.7H_2O$, M_W: 278.02g/mol, Merck). The other ingredients are copper sulphate penta hydrate ($CuSO_4.5\ H_2O$ Aklar Kimya., M_W: 249.68g/mol), gum Arabic (commercial), saffron (commercial), alum; $KAl\ (SO_4)_2.12.H_2O$ (commercial), cochineal (commercial), oak galls (commercial). The ratio of ferrous sulphate heptahydrate to gallic acid monohydrate was decided according to historical Turkish resources and recent studies (Nefeszade, 1938; Yaman, 1995). In most of the historical recipes, tannin was used instead of gallic acid. Considering that the tannin content of oak galls is between 60-70% by weight whose 28-35% by weight of this is gallic acid (Kavak, 2006) mole ratios of iron (II) sulphate (Fe) to gallic acid (GA) were calculated and given in Table 2.1.

Table 2.1 Fe: Ga mole ratios due to historical Turkish recipes

Oak galls (g)	**$FeSO_4$. $7H_2O$ (g)**	**Mole of Gallic acid[*] $C_7H_6O_5.H_2O$**	**Mole of $FeSO_4$. $7H_2O$**	**Mole ratio Fe:Ga**	**Reference**
10	3	0.001	0.0108	1.09	Yaman,1995
50	20	0.049	0.072	1.47	Yaman,1995
20	10	0.020	0.036	1.8	Yaman,1995
2	2	0.002	0.0072	4	Yaman,1995
3	3	0.003	0.0108	3.6	Yaman,1995
50	25	0.050	0.09	1.8	Yaman,1995
20	12	0.020	0.043	2.15	Yaman,1995
100	50	0.098	0.18	1.84	Yaman,1995

[*] Calculations;

Weight of gallic acid content in tannin: $W_{\text{oak galls}}$x 60/100x 28/100.

Mole of gallic acid: $W_{\text{oak galls}}$x 60/100x 28/100/$Mw_{\text{gallic acid}}$

As it can be seen in the Table 2.1, the mole ratio of iron (II) sulphate to gallic acid changes between 1 and 4 in Ottoman recipes (Yaman, 1995). Considering the ratios used in the historical recipes and recent studies (Remazeilles *et al.*, 2000), the mole ratio of iron(II) sulphate to gallic acid was taken as 3.6 in most of the iron-gall-inks prepared in this study.

The ideal complex formation ratio of ferrous sulphate to gallic acid has been said to be 1.49 which corresponds to the ratio of molecular weight of ferrous sulphate to molecular weight of gallic acid (Gibert *et al.*, 1999). However in a research, it was suggested that iron-gall-ink which has the mole ratio of iron to tannin of 3.6:1 (so-called balanced ink) will theoretically form a non-corrosive writing media (Neevel, 1995). This was also examined in this study.

Laboratory prepared inks were grouped into seven in order to determine the effect of different ink compositions on cellulose degradation.

First Group Experiments

Three iron-gall-inks with iron to gallic acid mole ratios; 0.17 (ink 3), 1.5(ink 2) and 3.6 (ink1) were prepared and analyzed in order to evaluate the effect of Fe/Ga ratio on the degradation of cellulose.

In the preparation of the inks; 100 ml distilled water was mixed with three different amounts of gallic acid (Table 2.2), 1.0 g $FeSO_4$. $7H_2O$ and 1.0 g gum Arabic. The mixture was stored in dark colored bottle at room temperature.

The compositions of inks in Group 1 are presented in Table 2.2.

Table 2.2 Composition of inks in Group 1

Inks	**Distilled Water (mL)**	**Gallic acid $C_7H_6O_5.H_2O$ (g)**	**$FeSO_4$. $7H_2O$ (g)**	**Gum Arabic (g)**	**Mole ratio Fe/Ga**
Ink 1	100	0.19	1.0	1.0	**3.6**
Ink 2	100	0.45	1.0	1.0	**1.5**
Ink 3	100	4.0	1.0	1.0	**0.17**

Second Group Experiments

Three iron-gall-inks with copper to iron mole ratios 0.01 (ink 6), 0.4 (ink 4) and 0.8 (ink 5) were prepared and analyzed. Ink 1 was used as a reference since there is no any copper in it. The compositions of the inks are given in Table 2.3.

Same procedure as in Group 1 inks were performed in this group but with different amounts of $CuSO_4.5\ H_2O$ and same amounts of gallic acid monohydrate. (Table 2.3)

Table 2.3 Compositions of inks in Group 2

Inks	**Distilled Water (mL)**	**Gallic acid $C_7H_6O_5.H_2O$ (g)**	**Gum Arabic (g)**	**$FeSO_4$. 7 H_2O (g)**	**$CuSO_4$. 5 H_2O (g)**	**Mole Ratio Cu:Fe**
4	100	0.19	1.0	1.0	0.36	**0.4**
5	100	0.19	1.0	1.0	0.72	**0.8**
6	100	0.19	1.0	1.0	0.009	**0.01**
1 (Reference)	100	0.19	1.0	1.0	-	-

Third Group Experiments

Three iron-gall-inks with saffron to iron weight ratios 0.03 (ink 11), 0.17 (ink 9) and 1.0 (ink 10) were analyzed. Ink 1 is again used as a reference since there is no any saffron in it.

The amounts of saffron added to ink solutions was decided according to the old ink recipes. (Table 2.4) Since it is hard to determine the molecular weight of saffron, in this study the weight ratios were used in the calculations to get the ratio of ferrous sulphate to saffron. The amounts of saffron in old references were given in Table 2.4.

Table 2.4 The saffron amounts in old ink recipes

$FeSO_4$.7 H_2O (g)	**Saffron (g)**	**Weight Ratio Fe:Sa**	**Reference**
9	2	4.5	Yaman,1995
3	3	1	Yaman,1995
12	1	12	Yaman,1995
56	8.4	6.6	Nefeszade,1938

The weight ratio of $FeSO_4.7\ H_2O$ to saffron is 5.82 as average. Therefore in this study the ideal weight ratio of iron to saffron was considered as 6.

The preparation of saffron solution

5 g saffron stigmas were ground with a clean china pestle until it becomes a powder. 100 ml cold water was added to this powder. It was then heated and stirred on a magnetic heater until a homogeneous dye solution was obtained. The color of the solution is deep bright orange (Barkeshli, Ataie, 2002). The saffron solution was kept in a dark colored bottle.

After the ink solutions were prepared according to the same procedure used in Group 1 and 2, saffron solution was added in the amounts given in Table 2.5.

Table 2.5 Compositions of inks in Group 3

Inks	**Distilled Water (mL)**	**Gallic acid $C_7H_6O_5.H_2O$ (g)**	**Gum Arabic (g)**	**$FeSO_4.$ $7\ H_2O$ (g)**	**Saffron (g)**	**Weight Ratio W_{Sa}/W_{Fe}**	**5% saffron solution (ml)**
9	100	0.19	1.0	1.0	0.166	0.17	3.32
10	100	0.19	1.0	1.0	1.0	1	20
11	100	0.19	1.0	1.0	0.03	0.03	0.6
1 (Reference)	100	0.19	1.0	1.0	-	-	-

Fourth Group Experiments

Two iron-gall-inks (ink 7 and ink 8) containing different amounts of copper to iron mole ratio and the same amount of saffron were prepared. Ink 4 and ink 5 were used as references for ink 7 and ink 8, respectively.

Ink preparation procedure was same as those of the previous groups. The compositions of the inks are presented in Table 2.6.

Table 2.6 Compositions of inks in Group 4

Inks	**Distilled Water (mL)**	**Gallic Acid $C_7H_6O_5.H_2O$ (g)**	**Gum Arabic (g)**	**$FeSO_4$. 7 H_2O (g)**	**$CuSO_4$. 5 H_2O (g)**	**Saffron (g)**	**5% saffron solution (mL)**
7	100	0.19	1.0	1.0	0.36	0.166	3.7
8	100	0.19	1.0	1.0	0.72	0.166	3.7
4 (Reference)	100	0.19	1.0	1.0	0.36	-	-
5 (Reference)	100	0.19	1.0	1.0	0.72	-	-

Fifth Group Experiments

Two different iron-gall-inks were prepared according to different historical recipes (ink 12, ink 13) (Senvaitiene *et al.*, 2005).

Preparation of ink 12: 16 mL of distilled water and 1 mL of 10% acetic acid were added to 1.0 g of powdered oak galls 0.53 g of $FeSO_4.7H_2O$ and 0.53 g of gum Arabic. After careful grinding the mixture was stored for 8 weeks with occasionally mixing in a closed bottle and then filtered (Senvaitiene *et al.*, 2005). The pH of the final ink solutions was 2.21.

Preparation of ink 13: 66.8 mL of distilled water was mixed with 7.688 g of powdered oak galls and mixture was left for 3 days. To this solution, 2.528 g $FeSO_4.7H_2O$, 0.2 g of NaCl, 2 mL of 10% acetic acid and 0.318 g alum were added. The obtained mixture was stored for 2 weeks with intermediate mixing and filtered. The pH of the final ink solution was 2.03.

Sixth Group Experiments

Two different green inks prepared according to historical recipes were analyzed. (ink 14 and ink 15) (Yaman, 1995)

Preparation of ink 14: 10.0 g oak galls were boiled in 150 ml distilled water then 10.0 g $CuSO_4.5\ H_2O$ was added and heated for 10 minutes and 2.0 g of gum Arabic was added to this mixture. After cooling the solution was filtered. The pH of the filtrate was 2.25.

Preparation of ink 15: 5.0 g of $CuSO_4.5\ H_2O$ was added to 50 mL of 8% acetic acid solution(instead of vinegar) , 15 mL 5% saffron solution was added and mixed vigorously for 10 minutes and lastly 2.0 g of gum Arabic was added and the solution was filtered. The pH of the filtrate was 2.58.

Seventh Group Experiments

One red ink (ink 16) was prepared according to the historical recipe (Nefeszade, 1938) composed of cochineal, alum and *soapwort* (which is a kind of plant) was analyzed.

Preparation of ink 16: 0.4 g soapwort[3] were ground and lapped with a cloth then boiled in 50 mL distilled water and 6.0 g cochineal that was ground with clean china pestle until becoming a powder added to the boiling water and 0.25 g alum was added lastly (Nefeszade, 1938).The amount of the each ingredient in the original recipe was decreased in the ratio of 1/8. The pH of the final solution is 3.91.

All ink solutions were kept in dark bottles for about a week to get stabilization.

2.1.2 Paper Substrate

In the study, purified cotton linters cellulose sheets, (Whatman filter papers No.1; 86.0 g m^{-2}, degree of polymerisation (DP): 2630, RSD 0.74%) were used for applying inks.

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[3] Soapwort: a kind of plant which belongs to Caryophyllaceae plant family.

The above mentioned filter papers have been used as a model papers in these kinds of studies since they have no additives.

Paper samples were immersed into the ink solutions for a few seconds and dried in ambient conditions for 24 hours for normalization. Preliminary studies showed that ink spreads out homogenously on the paper without any accumulation.

Paper samples were named with the inks applied on them, eg. Filter paper treated with ink 1 was called as Sample 1.

2.1.3 Ink content of the samples

Laboratory samples were weighed before and after the ink application process to determine their ink contents. The ink contents of the samples were given in the Table 2.7.

Table 2.7 Ink contents of the samples

Samples	Color	Ink Content (g)
1	Black	0.0379
2	Black	0.0246
3	Black	0.0091
4	Black	0.0431
5	Black	0.0486
6	Black	0.0401
7	Black	0.0373
8	Black	0.0437
9	Black	0.0385
10	Black	0.0422
11	Black	0.0387
12	Black	0.0367
13	Black	0.0542
14	Green	0.0722
15	Green	0.0535
16	Red	0.0327

2.2 Accelerated Ageing

In order to observe long-term effects of inks on paper, accelerated ageing was performed. By the use of elevated temperatures, changes which might require years or decades to occur under normal service conditions can be achieved with much shorter time periods.

In this study, the ink-treated paper samples were submitted to accelerated ageing procedure according to TS 4839 ISO 5630-1. They were artificially aged by exposing them to 105±2°C in the hot-drying unit for 24 days.

2.3 Visual Examination

The photographs of samples were taken by using Panasonic DMC- FX8 digital machine in order to record the visual changes in the samples after accelerated ageing in 24 days.

2.4 pH Measurements

The initial and stabilized acidity levels of ink solutions were measured by using digital pH meter 890, Nel Elektronik (Figure 2.1)

The initial pH measurements were done after the preparation of the ink solutions, the pH electrode was immersed into the ink solution and when the pH values were stabilized the measurement was taken. The stabilized pH measurements were also taken after a week.

The surface pH measurements of ink-treated filter papers were measured using flat surface electrode before and after accelerated ageing in order to understand the effect of ageing on papers.

While taking the surface pH measurements of ink- treated paper samples, a piece of Mylar, a kind of folio, was placed underneath the sample to be tested, a drop of distilled water was placed on the sample and the flat electrode is then placed on the droplet and it was allowed to marinate for about one minute. When the display has stabilized the proper reading was taken (Verheyen, 1989). (Fig. 2.2)

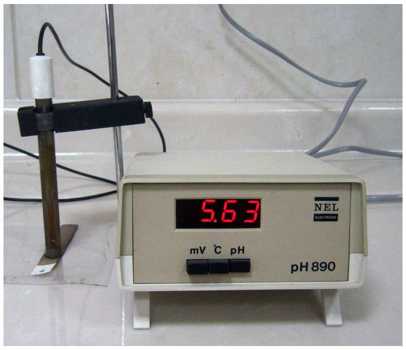


Figure 2.1 Surface pH Measurements

Figure 2.2 Flat surface electrode

2.5 Color Spectrophotometry

Molecular modifications formed by the degradation reactions in the cellulose polymer causes chromatic changes. These chromatic changes can be measured by the CIE Lab system- the standard color model established by the Commission Internationale d’Eclairage (Sequeira et al, 2006).

The CIE L*a*b* space is a standard commonly used in the paint, plastic, and textile industries. Lightness, L*, is a quantity that measures the percentage of total solar spectral reflectance in relation to a pure white surface; a* is a measure of the degree red - green; and b* characterizes the quantity of yellow – blue (Figure 2.3) (Havlinova *et al.*,2002) the corresponding polar coordinates are chroma; $C: (a^2+b^2)^{1/2}$ and hue angle ; $H: atan(b/a)$.

The total color difference, ΔE*, was calculated according to equation 2.1(Csefalvayova *et al.*, 2007) given below where $\Delta L^* = L_2 - L_1$; $\Delta a^* = a_2 - a_1$; $\Delta b^* = b_2 - b_1$ are the differences calculated for aged samples (2) and not aged samples (1)

$$\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2} \qquad (2.1)$$

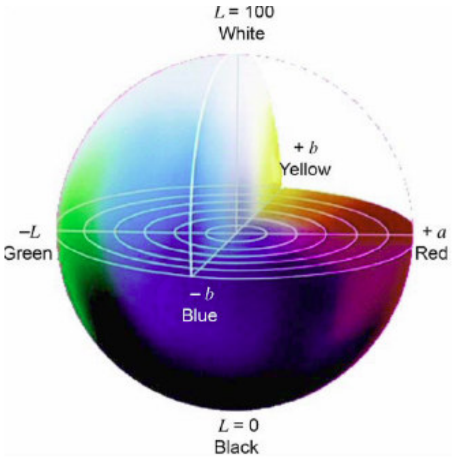


Figure 2.3 Color Model for L*a*b* values (Bicchierini *et al.*, 2005)

In order to examine the effect of the ink composition on the paper, the colorimetric measurements of the ink-treated paper samples were obtained by the use of a Datacolor Mercury 2000 Color spectrophotometer in D65/10° mode before and after ageing procedures. A background measurement was taken under identical conditions, using a non-treated paper sample. For each colorimetric value an average of five measurements was calculated.

Colorimetric measurements were realized in the METU Central Laboratory.

2.6 UV-Visible Spectroscopy

The ink solutions were analyzed using Spekol UV-Vis spectrophotometer, Carl Zeiss Technology in order to examine the effect of ink ingredients on inks. The ink solutions were scanned in the visible region between 400-800 nm at a spectral bandwidth of 2 nm.

First, baseline was recorded using distilled water as a blank solution then the spectrum of each solution was recorded against this baseline.

In order to obtain clear spectra, the ink solutions were filtered through Whatman No. 41 filter paper and diluted to get convenient absorbance value (~0.8) by distilled water before analysis.

2.7 FTIR Spectroscopy

FTIR spectroscopy has been widely used in characterization of ink components on paper based materials. It provides information on the actual paper-ink interactions. The spectra display certain bands that are typical for particular groups of atoms and which are defined by definite ranges of frequencies and intensities in the IR spectra.

In this study, reflection technique, attenuated total reflectance (ATR) is used since transmission techniques require the removal of some particles from the ink-treated surface (Ferrer and Sistach, 2005). ATR method is especially useful when the sample is either too thick or can not be destroyed, separated or manipulated.

In ATR technique; it is important to provide a perfect contact between the ZnSe crystal and sample. The ZnSe crystal of the objective is pressed against the sample and a single reflection penetrates the sample slightly (Ferrer and Sistach, 2005).

The FTIR spectra of ink-treated paper samples were obtained with Hyperion 2000 IR microscope attached to a Bruker FTIR spectrometer, model IFS 66/S with ATR objective in the spectral range of 4.000 to 600 cm^{-1} with a resolution of 8 cm^{-1}. 200 scans were taken in order to obtain an appropriate signal-to-noise ratio. Air was taken as a background in order to determine the influence of ink and ageing on paper.

The measurements were obtained before and after accelerated ageing. FTIR measurements were realized in the METU Central Laboratory.

Figure 2.4 FTIR Spectrometer with ATR objective

CHAPTER 3

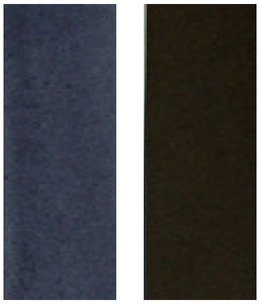
RESULTS AND DISCUSSION

Results of the experiments were discussed with the headings given below.

3.1 Visual Examination

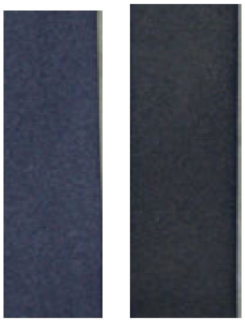
The color of the samples was changed after accelerated ageing at 105°C and dry condition during 24 days. The visual change since the color of the samples can be seen in the Figures 3.1-3.16.

GROUP I



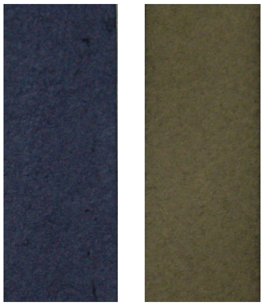
Before Age. After Age.

Figure 3.1 Sample 1



Before Age. After Age.

Figure 3.2 Sample 2

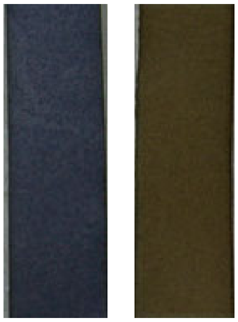


Before Age. After Age.

Figure 3.3 Sample 3

GROUP II


Before Age. After Age.
Figure 3.4 Sample 4

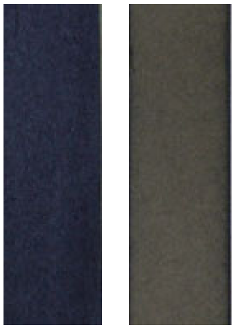

Before Age. After Age.
Figure 3.5 Sample 5


Before Ag. After Age.
Figure 3.6 Sample 6

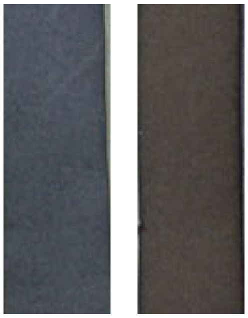
GROUP III

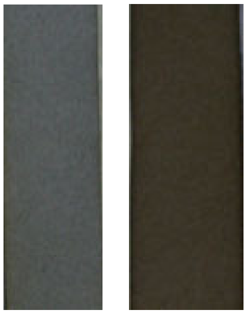

Before Age. After Age.
Figure 3.7 Sample 9


Before Age. After Age.
Figure 3.8 Sample 10


Before Age. After Age.
Figure 3.9 Sample 11

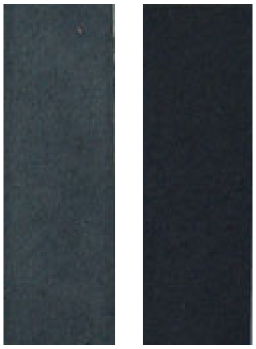
GROUP IV


Before Age. After Age.
Figure 3.10 Sample 7


Before Age. After Age.
Figure 3.11 Sample 8

GROUP V

Before Age. After Age.
Figure 3.12 Sample 12



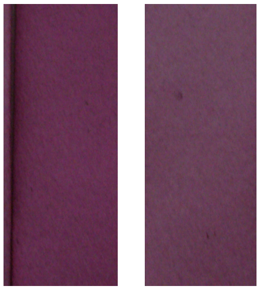
Before Age. After Age.
Figure 3.13 Sample 13

GROUP VI

Before Age. After Age.
Figure 3.14 Sample 14

Before Age. After Age.
Figure 3.15 Sample 15

GROUP VI



Before Age. After Age.
Figure 3.16 Sample 16

In groups 1, 2, 5 and 6 considerable color changes were observed after ageing. This change may be attributed to the increase in the oxygen containing groups such as carbonyls and carboxylic acid formed in the cellulose due to degradation. These groups are the chromophores that cause changes in the polymer color from colorless to yellow and even brown.

When compared to the group 1, 2 and 5, the color change in group 3, 4 and 6 was slighter. In group 3 and 4, there is saffron in the inks that applied on filter paper and by adjusting the pH, saffron prevents the cellulose from degradation. In group 6, the stable pigment carmen was used so less color change was observed in that sample.

In group 7 (sample 16) color change was almost negligible.

3.2 pH Measurements

The initial pH measurements of the inks solutions were carried out at 5 min after the preparation of the inks and stabilized pH values were measured 4 hours after the preparation. The results of the pH measurements are presented in the Table 3.1.

Table 3.1 pH values of initial and stabilized ink solutions

Ink Number	pH after 5 min.	pH after 4 hours
1	2.65	2.24
2	2.78	2.34
3	2.82	2.38
4	2.85	2.41
5	2.88	2.49
6	2.83	2.35
7	3.19	3.05
8	3.42	3.27
9	3.21	3.09
10	3.51	3.38
11	2.31	2.06
12	2.51	2.21
13	2.40	2.03
14	2.45	2.25
15	2.72	2.58
16	4.23	3.91

Decrease in the pH of the solutions after 4 hours may be due to the production of sulfuric acid (a by-product of the complex formation) in iron-gall-inks, or oxidation of the excess ferrous sulphate by oxygen from air as can be presented in Reaction 1.2.

The surface pH values were measured before and after ageing in order to determine the change in the acidity of the samples after ageing.

The surface pH measurements of the samples before and after ageing were presented in Table 3.2.

Table 3.2 pH values of the samples before and after ageing

Sample Number	pH_1	pH_2	ΔpH
1	4.12	2.96	1.16
2	4.20	3.12	1.08
3	4.26	3.15	1.11
4	4.22	3.26	0.96
5	4.28	3.33	0.95
6	4.15	3.20	0.95
7	4.82	4.68	0.14
8	5.10	4.89	0.21
9	4.85	4.63	0.22
10	5.14	4.92	0.22
11	3.93	3.59	0.34
12	4.08	2.89	1.19
13	3.93	2.31	1.62
14	3.85	2.23	1.62
15	3.95	2.85	1.10
16	5.68	5.22	0.46

The pH values of the ink-treated paper samples were higher than the pH values of ink solutions (Table 3.2) since the pH value of filter paper is around 7.

In group 1, the pH values of the paper samples treated with three iron-gall-inks (having iron to gallic acid mole ratios of 0.17 (Sample 3), 1.5 (Sample 2) and 3.6 (Sample 1)) were measured before and after ageing. The ΔpH was the least in sample 2 while the most decrease in pH values was observed in sample 1 which was the most degraded sample in this group. The ΔpH was almost constant with the value of 1.12 as average for this group.

In group 2, the pH values of the paper samples treated with three iron-gall-inks having copper to iron mole ratios of 0.01(Sample 6), 0.4 (Sample 4) and 0.8 (Sample 5) were measured. Sample 1 was used as a reference since there is no any copper in the ink applied on it. The decrease in the pH values of the samples was nearly same. The different copper amounts of the inks can not be said to cause any effect on the pH values of the samples on ageing. The ΔpH was almost constant with the value of 0.95 as average for this group.

In group 3, the pH values of the paper samples treated with three iron-gall-inks having saffron to iron weight ratios of 0.03 (Sample 11), 0.17 (Sample 9) and 1 (Sample 10) were measured. Sample 1 was again used as a reference since there was no any saffron in the ink applied on it. The effect of saffron on the pH change after ageing was significant especially for the samples 9 and 10 which contain considerable amounts of saffron. ΔpH was almost constant with the value of 0.26 as average for this group. Among the groups studied the smallest value of ΔpH was observed in the samples of this group.

In group 4, the pH values of the paper samples treated with two iron-gall-inks containing different amounts of copper to iron mole ratio and the same amount of saffron; Cu/Fe: 0.4 and 0.17 g saffron (Sample 7), Cu/Fe: 0.8 and 0.17 g saffron (Sample 8) were measured. Sample 4 (Cu/Fe: 0.4) and sample 5 (Cu/Fe: 0.8) were used as references for sample 7 and sample 8, respectively.

In group 5, the pH values of the samples treated with two different iron-gall-inks prepared according to different historical recipes (Sample 12, sample 13) were measured. The pH decrease was more significant in sample 13 than sample 12 due to the presence of gum Arabic in the ink 12. Gum Arabic helps to keep the pH of the ink solution constant. Moreover the presence of alum may also be effective in the smaller pH that was present in ink 13.

In group 6, paper samples treated with two different green inks prepared regarding historical recipes were measured (sample 14 and sample 15). The pH change was smaller in sample 15 due to the presence of saffron in ink 15 while there was no any saffron in ink 14.

In group 7, the pH value of paper sample treated with red ink; sample 16 was measured. The ΔpH of sample 16 was one of the smallest regarding all samples.

In all samples, as expected the pH decreased after ageing. Although the samples treated with saffron contained inks (sample 9, 10, 11, 7 and 8) and the sample 16 (treated with red ink) showed smaller decrease after ageing when compared to other samples. ΔpH varied between 0.14-0.34 with the average value of 0.23 whereas the ΔpH of others varyied between 0.46-1.62 with the average value of 0.93.

3.3 UV-Vis Spectroscopy

UV-Visible spectroscopy is an effective tool for characterization and qualitative analysis of the compounds.

In this study, laboratory prepared ink solutions have been analyzed in order to determine the specific features of different inks depending on their chemical composition using UV-Vis spectroscopy. In the analysis, the absorbance of the aqueous solutions of inks has been examined in the region of 400-800 nm.

As it is mentioned before, the experiments done are classified into seven groups. In the first group, the effect of iron to gallic acid ratio on iron-gall-inks has been investigated, in the second group the effect of copper to iron ratio on iron-gall-inks, in the third group the effect of saffron on iron-gall-ink, in the fourth group the effect of saffron on copper containing iron-gall-inks, in the fifth, sixth and seventh groups black, green and red inks prepared according to the to original recipes were analyzed.

First Group Experiments

Three iron-gall-inks with iron to gallic acid mole ratios; 0.17 (ink 3), 1.5 (ink 2) and 3.6 (ink 1) were analyzed in order to evaluate the effect of Fe/Ga ratio on complex formation.

Gallic acid does not absorb energy in the visible region. After addition of gallic acid monohydrate to ferrous sulphate, new absorbance band appeared. Spectra exhibited wide spectra having maxima between 560 and 600 nm. This absorbance band is the result of colored complex formed by gallic acid with iron (II) (See Reaction 1.3). The complex formation depends on metal ligand ratio and pH of the medium.

It was seen that the complex formation is slow. It took about 4 hours to increase absorbance maximum from 0.38 to 0.62 (Fig.3.17, 3.18 and Fig.3.19). This increment was seen for the inks 2 and 1.

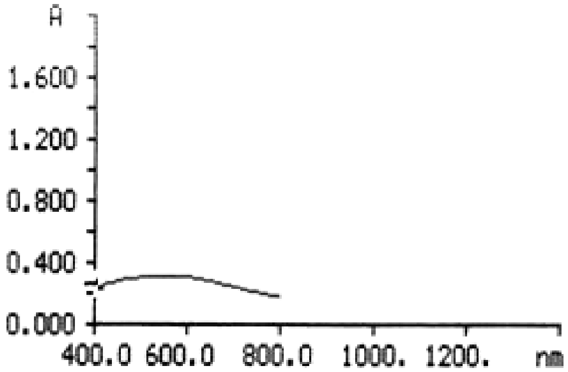


Figure 3.17 Absorption spectrum of ink 3 (Fe/Ga: 0.17) after 5 minutes (λ_{max}= 560 nm; A_{max}= 0.3824)

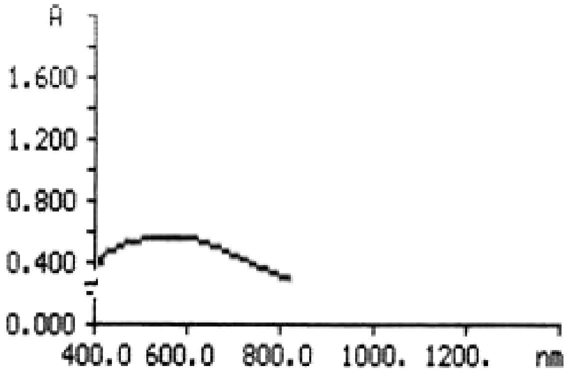


Figure 3.18 Absorption spectrum of ink 3 (Fe/Ga: 0.17) after 30 minutes (λ_{max}= 560 nm; A_{max}= 0.5781)

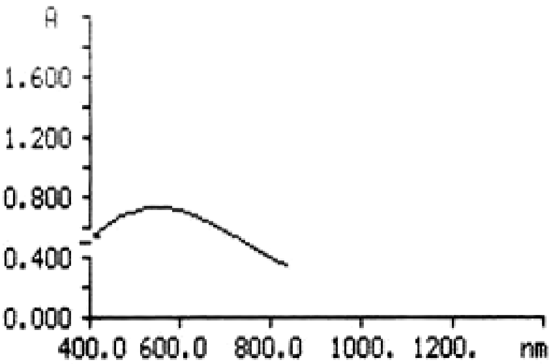


Figure 3.19 Absorption spectrum of ink 3 (Fe/Ga: 0.17) after 4 hours (λ_{max}= 560 nm; A_{max}= 0.6234)

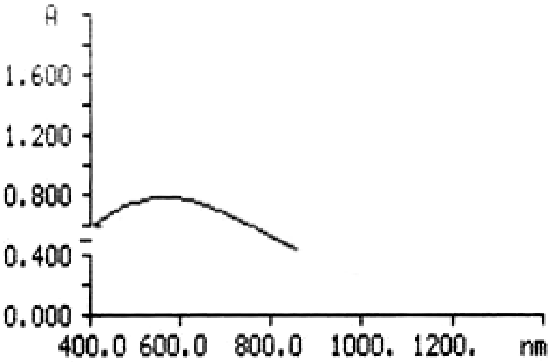


Figure 3.20 Absorption spectrum of ink 2 (Fe/Ga: 1.5) (λ_{max}= 590 nm; A_{max}= 0.7874)

In ink 1 the iron to gallic acid ratio was maximized that was 3.6 and it gave an absorption band with maximum at 600 nm and maximum absorbance as can be seen in Figure 3.21.

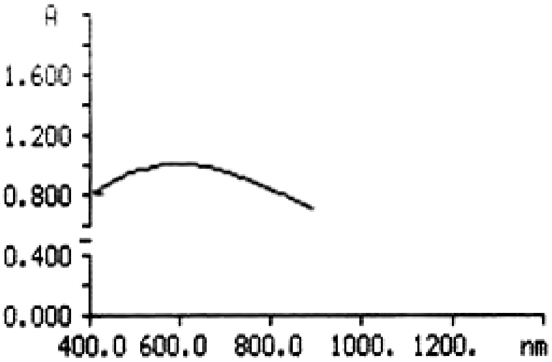


Figure 3.21 Absorption spectrum of ink 1(Fe/Ga: 3.6) (λ_{max}= 600 nm; A_{max}= 1.0983)

The values of λ_{max} and A_{max} are presented in the Table 3.3.

Table 3.3 λ_{max} and A_{max} values of the inks in Group 1

Ink	**pH**	**Fe/Ga**	**λ_{max} (nm)**	**A_{max}**
1	2.24	3.6	600	1.10
2	2.34	1.5	590	0.78
3	2.38	0.17	560	0.62

With increasing iron to gallic acid ratio from 0.17 to 1.5 λ_{max} of the spectrum shifted to longer wavelength. In other words, λ_{max} of 560 nm became 590nm. Besides, value of maximum absorbance also increased namely from 0.62 to 0.78. (Table 3.3) Shifting the wavelength to higher value and increasing the absorbance may be due to the formation of two or more different complexes between iron and gallic acid.

Still increasing the iron to gallic acid ratio to 3.6 resulted in shifting λ_{max} toward longer wavelength (600nm) and increasing maximum absorbance of 1.10.

Consequently, it can be said that maximum absorbance wavelength and absorbance values increase as the ratio of iron to gallic acid increases.

Second Group Experiments

Three iron-gall-inks with copper to iron mole ratios of 0.01(ink 6), 0.4 (ink 4), 0.8 (ink 5) were analyzed. Ink 1 was used as a reference since there is no any copper in it.

The visible spectra of the ink samples; ink 6, ink 5 and ink 4 are given in Figures 3.22, 3.23 and 3.24, respectively.

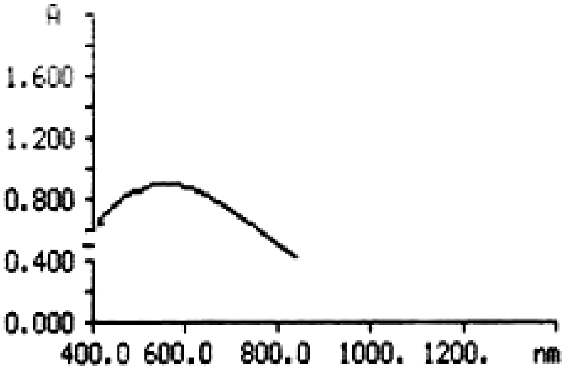


Figure 3.22 Absorption spectrum of ink 6 (Cu/Fe: 0.01) (λ_{max}= 590 nm; A_{max}= 0.9756)

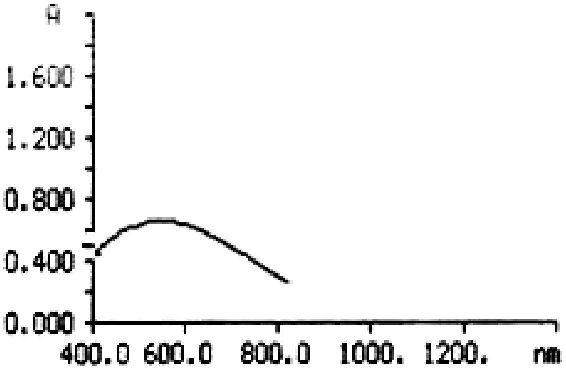


Figure 3.23 Absorption spectrum of ink 4 (Cu/Fe: 0.4) (λ_{max}=575 nm; A_{max}= 0.7894)

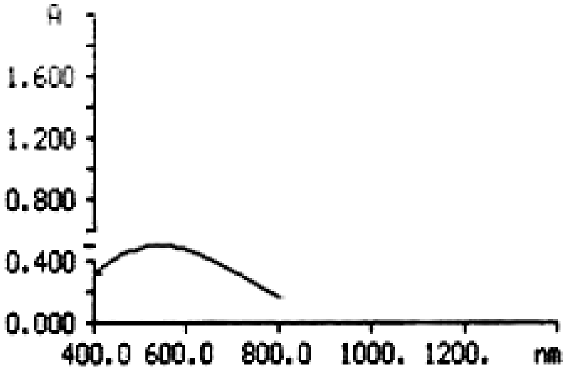


Figure 3.24 Absorption spectrum of ink 5 (Cu/Fe: 0.8) (λ_{max}=560 nm; A_{max}= 0.5873)

The values of λ_{max} and A_{max} are presented in the Table 3.4.

Table 3.4 λ_{max} and A_{max} values of the inks in Group 2

Ink	**pH**	**Cu/Fe**	**λ_{max} (nm)**	**A_{max}**
4	2.41	0.4	575	0.79
5	2.49	0.8	560	0.59
6	2.35	0.01	590	0.97

With increasing copper to iron ratio from 0.01 to 0.8, λ_{max} shifted toward shorter wavelength from 590 to 560 nm, and maximum absorbance also decreased from 0.97 to 0.59. Cu^{2+} ions can oxidize the gallic acid and prevent the chelating property of it by decomposing its phenolic structure so it prevents the complex formation. Also, Cu^{2+} ions may oxidize Fe (II) to Fe (III) due to following Reaction 3.1 (Matocha *et al.*, 2005). The lower the complex formation the lower is the absorbance. (Fig. 3.22-3.24) (Table 3.4)

$$Cu^{2+} + Fe^{2+} \rightarrow Cu^{+} + Fe^{3+} \qquad \text{(R. 3.1)}$$

Third Group Experiments

Three iron-gall-inks having saffron to iron weight ratios of 0.03 (ink 11), 0.17 (ink 9), 1(ink 10) were analyzed. Ink 1 was again used as a reference since there is no any saffron in it.

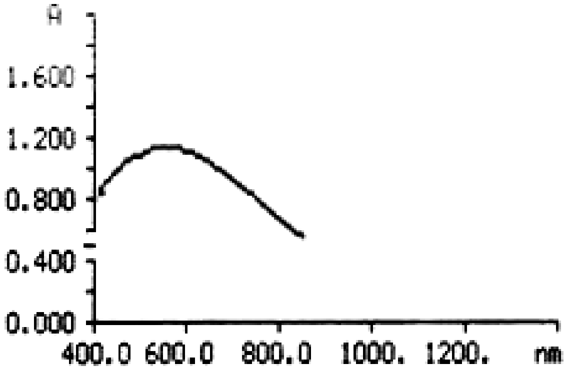


Figure 3.25 Absorbance spectra of ink 11(Sa/Fe: 0.03) (λ_{max}= 590 nm; A_{max}= 1.1230)

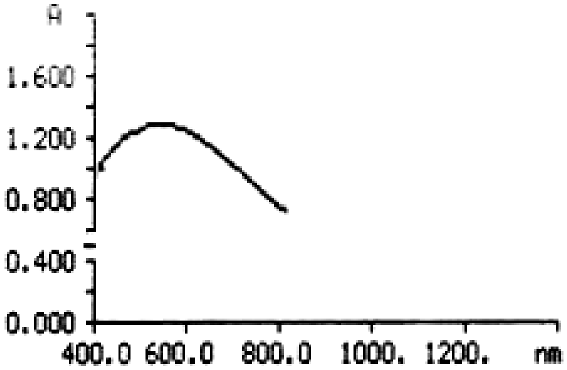


Figure 3.26 Absorption spectrum of ink 9 (Sa/Fe: 0.17) (λ_{max}=575 nm; A_{max}= 1.2864)

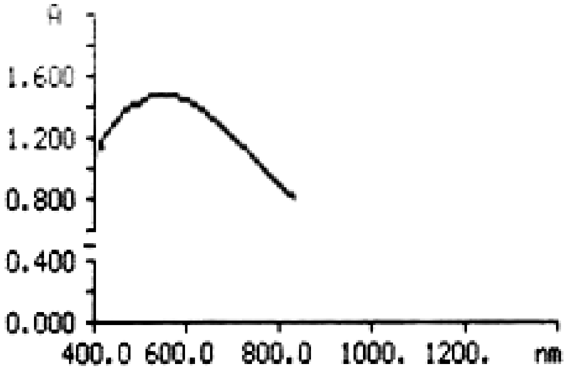


Figure 3.27 Absorption spectrum of ink 10 (Sa/Fe: 1) (λ_{max}= 560nm; A_{max}= 1.5073)

The values of λ_{max} and A_{max} are presented in the Table 3.5.

Table 3.5 λ_{max} and A_{max} values of the inks in Group 3

Ink	pH	Sa/Fe weight ratio	λ_{max} (nm)	A_{max}
9	3.09	0.17	575	1.30
10	3.38	1	560	1.51
11	2.06	0.03	590	1.12

With increasing saffron to iron weight ratio from 0.03 to 1.0, λ_{max} shifted toward shorter wavelength from 590 to 560 nm and maximum absorbance increased from 1.12 to 1.51. (Fig.3.25-3.27) (Table 3.5)

The change in λ_{max} and absorbance maximum can be due to buffer effect of saffron and this may increase the degree of complex formation between iron and gallic acid.

As pH increases the degree of complexation increases since at very low pH (≤3), most of the ligands remain protonated and only a few binding sites may be available for a metal ion (Maqsood, 1991). Also the aldehydes in the chemical composition of saffron such as safranal can reduce the Fe^{3+} ions to Fe^{2+} ions and decompose the complex forming new complexes.

Fourth Group Experiments

Two iron-gall-inks containing different amounts of copper to iron mole ratio and same amount of saffron; Cu/Fe: 0.4 and 0.17 g saffron (ink 7), Cu/Fe: 0.8 and 0.17 g saffron (ink 8) were analyzed. Ink 4 and ink 5 were used as references for ink 7 and ink 8, respectively.

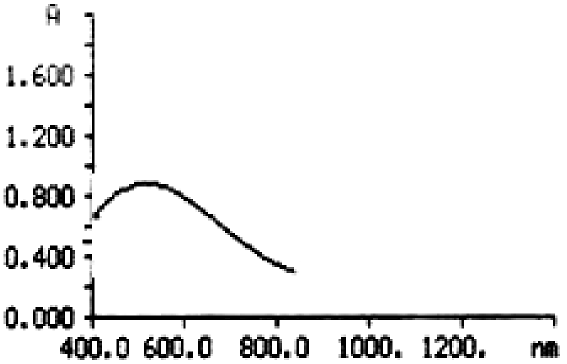


Figure 3.28 Absorption spectrum of ink 7 (λ_{max}=565 nm; A_{max}= 0.9854)

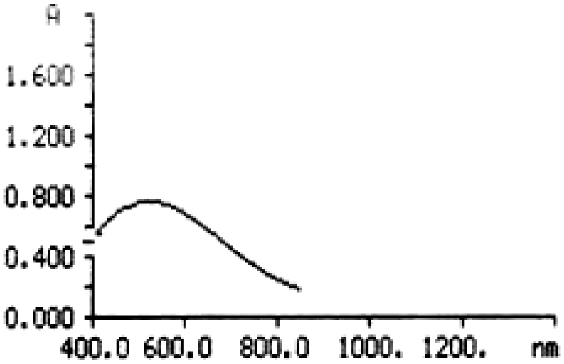


Figure 3.29 Absorption spectrum of ink 8 (λ_{max}=550 nm; A_{max}= 0.7764)

The values of λ_{max} and A_{max} are presented in the Table 3.6.

Table 3.6 λ_{max} and A_{max} values of the inks in Group 4

Ink	**pH**	**λ_{max} (nm)**	**A_{max}**
7	3.05	565	0.98
8	3.27	550	0.78

Similar to its effect on iron-gall-inks, saffron, when added to copper containing iron-gall-inks, increased the pH of the medium and caused an increase in maximum absorbance value and decrease the wavelength of the maximum absorbance (Fig.2.6.11 and 2.6.12) when compared to the inks without saffron. (Fig.3.28 and 3.29) (Table 3.6) This may be due to the buffer effect of saffron and pH effect on λ_{max} and A_{max} as explained before.

Fifth Group Experiments

Two different iron-gall-inks prepared according to different historical recipes (ink 12, ink 13) were analyzed (See Table 2.7).

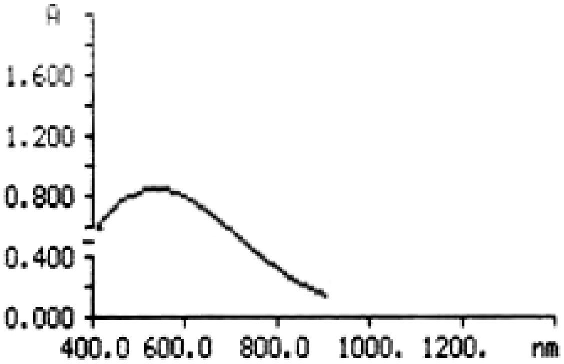


Figure 3.30 Absorbance spectra of ink12 (λ_{max}= 585nm; A_{max}= 0.9018)

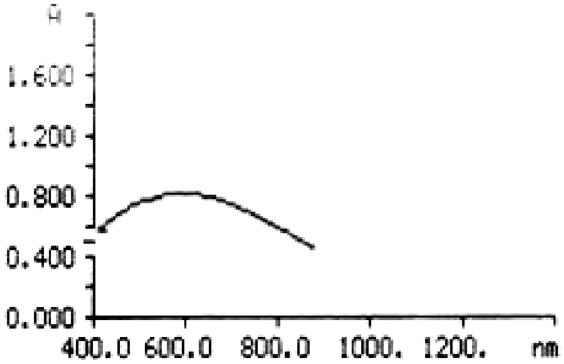


Figure 3.31 Absorption spectrum of ink 13 (λ_{max}= 590 nm; A_{max}= 0.8863)

The values of λ_{max} and A_{max} are presented in the Table 3.7.

Table 3.7 λ_{max} and A_{max} values of the inks in Group 5

Ink	**pH**	λ_{max}	A_{max}
12	2.21	585	0.90
13	2.03	590	0.89

Absorption maximum and wavelength maximum gave similar results for these two inks in other words λ_{max} for ink 12 and ink 13 corresponded to 585 nm and 590 nm, respectively. This value is the absorbance value of the colored complex between iron and gallic acid. The ingredients of ink 13 such as $KAl(SO_4)_2.12H_2O$ and NaCl and oak galls used instead of gallic acid which was also used in ink 12 did not make a considerable difference in the absorbance wavelength of the complex (ferric pyrogallate) as expected.

On the other hand, absorbance maxima were somewhat different, ink 12 has greater absorbance (0.90) than ink 13 (0.89), these slight differences may come from the difference of pH of the ink solutions. (Table 3.7) The difference in pH of the inks may be due to the fact that ink 13 has alum in its content and alum may act as acidifying agent and the presence of gum Arabic in ink 12 which is said to adjust the pH of the inks.

Sixth Group Experiments

In this group, two different green inks (ink 14 and ink 15) which were prepared regarding historical recipes were analyzed. (See Table 2.8)

Ink 14 contained copper (II) sulphate pentahydrate and oak gall sap whereas ink 15 contains copper (II) sulphate pentahydrate, saffron and vinegar.

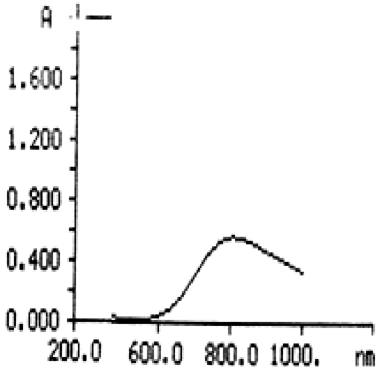


Figure 3.32 Absorption spectrum of ink 14 (λ_{max}=800 nm; A_{max}=0.5796)

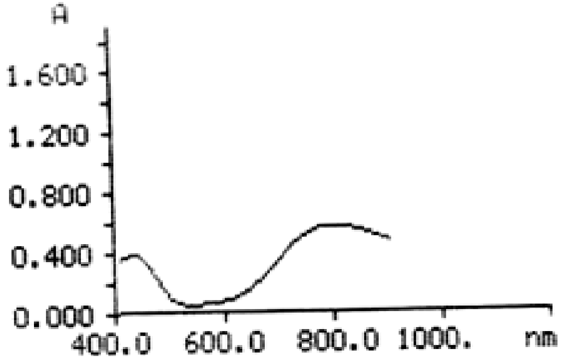


Figure 3.33 Absorption spectrum of ink 15 (λ_{max}=800 nm; A_{max}= 0.6247; A_{405}=0.4357)

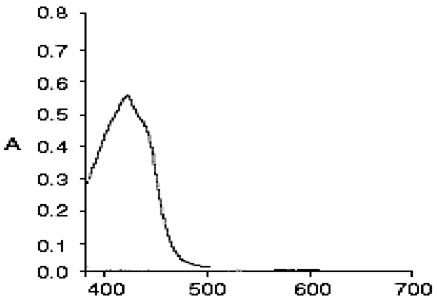


Figure 3.34 Absorption spectrum of saffron exract (λ_{max}=410 nm)

The values of λ_{max} and A_{max} are presented in the Table 3.8.

Table 3.8 λ_{max} and A_{max} values of the inks in Group 6

Ink	**λ_{max} (nm)**	**A_{max}**
14	800	0.58
15	800	0.62

Ink 14 gave the absorbance maximum at 800 nm which was due to the copper (II) sulphate penta hydrate. It shows that copper does not form a new complex with gallic acid. (Figure 3.32)

Ink 15 was composed of saffron, copper (II) sulphate penta hydrate and vinegar. The visible spectrum of the ink gave two peaks in the visible region; one is at 405 nm which was thought to belong to saffron (due to the literature and spectrum of pure saffron shown in Figure 3.34) and the second one was at 800 nm that belongs to copper (II) sulphate penta hydrate. (Figure 3.33)

Seventh Group Experiments

One red ink (ink 16) prepared according to the historical recipe (Nefeszade, 1938) composed of cochineal, alum and soapwort which belongs to Caryophyllaceae plant family was analyzed.

The ink gave an absorption maximum at 500 nm and it belongs to the carminic acid found in cochineal due to the literature (Whitney *et al.*, 2007). (Figure 3.34)

The presence of alum and soapwort in the ink did not have any effect on the absorption peaks for visible region. (Figure 3.35)

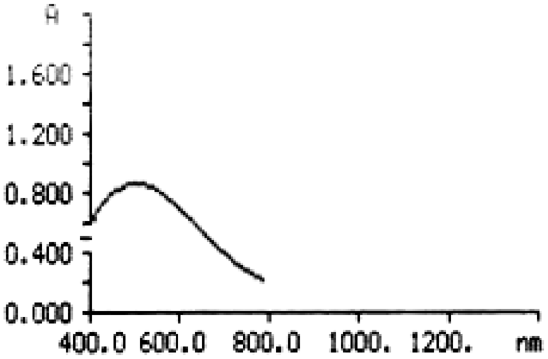


Figure 3.35 Absorption spectrum of red ink (λ_{max}=500 nm; A_{max}= 0.8759)

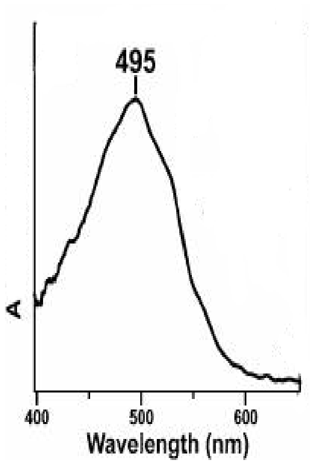


Figure 3.36 Absorption spectrum of carminic acid (Whitney *et al.*, 2007)

The values of λ_{max} and A_{max} are presented in the Table 3.9.

Table 3.9 λ_{max} and A_{max} values of the red ink

Ink	**λ_{max} (nm)**	**A_{max}**
16	500	0.88

3.3 Colorimetric Analysis

Ink-treated paper samples were scanned by the colorimeter in the wavelength region of 400-800 nm before and after accelerated ageing.

Results have been given in the Table 3.10, for ink-treated paper samples before ageing as X_1 and after ageing as X_2.

Colorimetric results have been presented in three colorimetric parameters; Lightness (L*), value for red-green axis (a*) and value for yellow-blue axis (b*) and total color change (ΔE*).

Presently, totally 16 ink samples have been studied. For each sample, colorimetric measurements have been done on five different points of the sample. The results were given as the average of these five measurements. These results have been summarized in Table 3.10.

Table 3.10 Results of the L* a* b* values of the samples before and after ageing

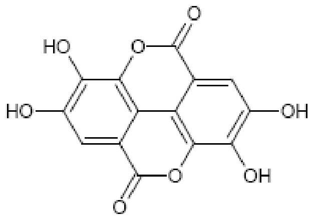
Samples	L^*_1	A^*_1	b^*_1	L^*_2	a^*_2	b^*_2	ΔE*
1	53	1.94	-12	46.43	2.21	1.64	**15.14**
2	42.35	1.69	-2.08	38.94	1.76	8.72	**11.33**
3	42.36	1.41	-9.22	39.08	1.56	3.36	**13.00**
4	52.67	1.41	-8.34	44.77	1.88	7.31	**17.54**
5	55.85	1.53	-8.49	47.55	2.03	10.71	**20.92**
6	52.41	2.05	-12.21	45.11	2.36	1.8	**15.80**
7	56.39	1.05	-6.89	53.43	1.08	3.95	**11.24**
8	59.14	0.58	-2.13	55.43	0.6	10.32	**12.99**
9	44.82	2.08	-10.42	43.55	2.19	-3.71	**6.83**
10	46.51	0.26	-2.97	45.47	0.28	3.56	**6.61**
11	42.11	2.02	-11.46	39.25	2.17	-0.91	**10.93**
12	52.64	1.68	-9.47	47.1	1.83	0.27	**11.21**
13	40.51	1.09	-5.66	37.94	1.17	8.85	**14.74**
14	81.98	-22.7	7.06	38.54	4.81	19.72	**52.95**
15	81.75	-24.3	10.07	47.49	1.66	20.45	**44.22**
16	62.92	25.58	-17.75	61.71	21.12	-9.58	**9.39**

L^*_1: Lightness value before ageing**;** **a^*_1:** value for red-green axis before ageing;
b^*_1: value for yellow-blue axis before ageing; **L^*_2:** Lightness value after ageing
a^*_2: : value for red-green axis after ageing; **b^*_2:** value for yellow-blue axis after ageing
ΔE*:Total color change after ageing

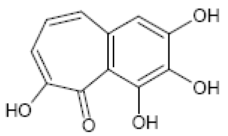
Changes in color coordinates; L*, a*, b* Values

On ageing changes can be observed in the lightness of the paper samples, paper becomes darker due to degradation. The darkening may be due to the formation of ink degradation products such as purpurogallin (structure 3.1) and ellagic acid (structure 3.2) which formed when the sulphuric acid and other acids in inks break down the cellulose and the colorants of the ink (Sequira *et al.*, 2006). The browning in the ink can also be caused by the gallic acid oxidation reaction (R.3.2).

L-axis extends from 0 (black) to 100 (white). As the sample darkens, L* value of it decreases so the negative value of ΔL^* (L^*_2-L^*_1) corresponds to the darkening.



Structure 3.1 Purpurogallin



Structure 3.2 Ellagic acid

$$Fe^{3+}\ \tfrac{1}{2}\ \text{phenol} \rightarrow Fe^{2+} + \tfrac{1}{2}\ \text{quinone} + H^{+} \qquad \text{(R.3.2)}$$

By investigating the changes in the lightness of the ink-treated samples after ageing changes in a* and b* values were evaluated. Increase in a component in the chromatic coordinates can be due to the gallic acid oxidation reaction (Reaction 3.2) and the oxidation of cellulose catalyzed by the metal ions (Fe^{2+}, Cu^{2+}) present in ink.

In the oxidation of cellulose, oxygen is absorbed at certain sites on the cellulose molecule and causes an increase in oxygen containing groups such as carbonyls and carboxylic acids. Carbonyl groups formed in the cellulose oxidation reactions are chromophores that cause changes in the polymer color from colorless to yellow and even brown when they are present as part of a conjugated system (Sequeira *et al.*, 2006).

At low pH, rate of Fe^{3+} reduction to Fe^{2+} increases and the increase in the concentration of this powerful cellulose oxidation catalyst contributes the oxidative degradation of cellulose (Sequeira *et al.*, 2006).

There were significant changes especially in b* values; an increase was observed in the b* values after ageing that corresponds to increase in yellowness. The change in this coordinate is due to the decomposition of the grayish-blue iron-gall complex to yellow-brown products.

First Group Experiments

In this group, paper samples treated with three iron-gall-inks with iron to gallic acid mole ratios; 0.17 (Sample 3), 1.5 (Sample 2) and 3.6 (Sample 1) were analyzed before and after ageing in order to investigate the effect of Fe/Ga ratio on darkening of the cellulose. Colorimetric analysis results of those samples are given in Table 3.11.

Table 3.11 Changes in L*a*b* values of the samples in Group 1

Sample	Fe/Ga mole ratio	ΔL*	Δa*	Δb*
1	3.6	-6.57	0.27	13.64
2	1.5	-3.41	0.07	5.83
3	0.17	-3.28	5.83	12.58

With increasing ratio of Fe to Ga from 0.17 to 3.6, ΔL* became rather more minus, from -3.28 to -6.57. This can be attributed to the fact that the darkening is the result of the excess free Fe^{2+} ions in the ink. Ink 2 had much more iron than ink 3, however there was no so much difference between the ΔL* values of the two samples. Sample with highest iron to gallic acid ratio had the largest ΔL* value about -6.57 due to the highest amount of excess Fe^{2+}ions.

The results of the change in lightness showed that Fe/Ga ratio have some effect in the darkening of the paper, it is considerable when the amount of the iron increases.

The increment in Δa* and Δb* values as the Fe/Ga mole ratio increased was an expected result since the excess of Fe^{2+} ions act as catalyst in the oxidation reaction of cellulose and this reaction results in chromatic changes in the cellulose. But, sample 3 although having less iron content had greater Δa* and Δb* values than sample 2.

The increase in the chromatic values of sample 1 can be explained by the oxidation reaction of cellulose catalyzed by the excess free Fe^{2+} ions. The increase in the chromatic values of sample 3 that had lowest Fe/Ga ratio might be attributed to the reducing agent property of gallic acid as many polyphenols.

The reduction potential of gallic acid/quinonic acid (0.799V) is so close to that of Fe^{2+}/Fe^{3+}(0.771V) that it may undergo redox processes with Fe^{3+} and forms Fe^{2+} and quinonic acid (Reaction 3.2). So it might be suggested that high gallic acid content causes high oxidation of cellulose (Rouchon-Quillet *et al.*, 2004). Also the color changes may be due to the color difference between Fe^{2+} and Fe^{3+}.

As it can be seen from the plot, sample 2 had the least Δb* value that was treated with the ink which had the mole ratio of Fe/Ga of 1.5. Therefore, it can be said that this mole ratio is the ideal ratio for a non-corrosive iron-gall-ink.

Second Group Experiments

In this group, the paper samples treated with three iron-gall-inks with copper to iron mole ratios of 0.01 (Sample 6), 0.4 (Sample 4) and 0.8 (Sample 5) were analyzed. Sample 1 was used as a reference since there is no any copper in the ink applied. The purpose was to investigate the effect of copper on paper degradation. Colorimetric analysis results of those samples are given in Table 3.12.

Table 3.12 Changes in L* a* b* values of the samples in Group 2

Sample	**Cu/Fe mole ratio**	**ΔL***	**Δa***	**Δb***
4	0.4	-7.9	0.47	15.7
5	0.8	-8.3	0.50	19.2
6	0.01	-7.3	0.31	14.0
1	-	-6.6	0.27	13.6

With increasing copper to iron mole ratio from 0.0 to 0.8, ΔL* absolute values increased but not considerably from -6.6 to -8.3.

Sample 1 had the least change in lightness since there was no copper in ink 1. Although there was much more copper in ink 4 and ink 5 when compared to ink 6, the change in lightness of samples treated with them showed no considerable differences.

This means all three have amount of copper that is already greater than necessary to give high amount of darkness. This required amount might be corresponding to the amount present in ink 6 which is 0.009 g considering the lightness results, copper can be said to have a little effect in the darkening of the paper after ageing.

Copper ions have known to be corrosive for the paper by catalyzing the oxidation of cellulose and it is hard to understand the degree of oxidation from the change in the lightness, oxidation can cause changes in the a and b values. With increasing amount of Cu/Fe mole ratio from 0 to 0.8, the Δa^* values increased from 0.27 to 0.5 which was not a considerable difference. Similar consideration can also be said for the Δb^* values, only a relatively high increment can be seen in sample 5.

Third Group Experiments

In this group, the paper samples treated with three iron-gall-inks with saffron to iron weight ratios of 0.03 (Sample 11), 0.17 (Sample 9) and 1 (Sample 10) were analyzed. Colorimetric analysis results of those samples are given in Table 3.13.

Sample 1 was again used as a reference since there was no any saffron in the ink applied. The purpose was to investigate the inhibitory effect of saffron on iron-gall-ink corrosion. Since saffron can resist a wide range of pH variations. The existence of dicarboxylic acid and its esters (crocin, caretenoid esters and crocetin) and nitrogen compounds in the chemical composition of saffron could be responsible for its high resistance to pH change. Unsaturated di-carboxylic acid involves 16 carbon atoms in the main chain. All carbon atoms and oxygen of carbonyls have sp^2-hybridization; the whole system is conjugated and has a highly stable energy resonance (Barkeshli and Ataie, 2002).

Table 3.13 Changes in L* a* b* values of the samples in Group 3

Sample	**Fe/Sa Weight ratio**	**ΔL***	**Δa***	**Δb***
9	0.17	-1.27	0.11	6.71
10	1	-1.04	0.02	6.53
11	0.03	-2.86	0.15	11.95
1	-	-6.57	0.27	13.64

With increasing weight ratio of saffron to iron from 0 to 1, the change in the lightness decreased. Sample 1 darkened more than the others; samples 11, 9 and 10 seemed to be more durable.

When sample 9 and sample 10 were compared it was seen that the change in lightness was almost same. This may be attributed to the fact that the effect of saffron was highest as in the sample having the ratio of 0.17, increasing the ratio of Sa/Fe to 1 did not make considerable change in the lightness.

Increasing amount of saffron caused decrease both in Δa* and Δb* values. This effect was more pronounced in the Δb* values of the samples.

When the sample 1 and 11 are compared a decrease was observed both in the Δa* and Δb* values but not considerable although the difference in the samples 9 and 10 was more significant. This means that the amount of saffron in ink 11 was not enough to prevent it from being so corrosive.

The Δb* values of samples 9 and 10 were already the same, which contain the optimum about 0.166 g saffron which was the amount advised in historical recipes.(Table 2.4) Above and below this value, its effect was non-obvious.

This effect of saffron can be attributed to the buffer effect of it. The ink samples with saffron have higher pH value than ones without saffron. In strong acid conditions, gallic acid will not form stable complexes with iron. Since at very low pH, most of the ligands remain protonated and the available binding sites decrease for the metal ion (Maqsood, 1991). Also at low pH values, the reduction of Fe^{3+} to Fe^{2+} by the gallic acid (Reaction 3.2) increases. As the amount of Fe^{2+} ions increases, the oxidation of the cellulose increases.

Moreover, in less acidic medium the acidic hydrolysis of cellulose also decreases. Besides its buffer effect, saffron filters the light, thus it can prevent color change of samples due to the light.

Considering the results of this group, it can be said that saffron inhibits the iron-gall-ink corrosion.

Fourth Group Experiments

The paper samples treated with two iron-gall-inks containing different amounts of copper to iron mole ratio and the same amount of saffron; Cu/Fe: 0.4 and 0.17 g saffron (Sample 7), Cu/Fe: 0.8 and 0.17 g saffron (Sample 8) were analyzed. Sample 4 and sample 5 (Table 2. 3) were used as references for samples 7 and 8, respectively. Colorimetric analysis results of those samples are given in Table 3.14.

Table 3.14 Changes in L* a* b* values of the samples in Group 4

Sample	Cu/Fe Mole ratio	Amount of saffron (g)	ΔL*	Δa*	Δb*
7	0.4	0.17	-2.96	0.03	10.84
8	0.8	0.17	-3.71	0.02	12.45
4	0.4	-	-7.90	0.47	15.65
5	0.8	-	-8.30	0.50	19.20

When samples 4 and 7 were compared, it was seen that the change in lightness is greater in sample 4 although they have same amount of copper. This can be attributed to the buffer effect of saffron. The same results were valid for the samples 5 and 8. The results showed that samples treated with saffron containing inks (sample 7, 8) darken less than others (samples 4, 5).

When the Δa* and Δb* values of samples 4 and 7 that have the same amount of copper were compared it can be seen that sample 4 degraded more due to the presence of saffron in sample 7. Similar consideration can be used for the samples 5 and 8.

Samples 7 and 8 seemed to be more stable due to their higher pH. As mentioned before at low pH, both the hydrolysis and oxidation of cellulose increase. However, the value of pH is important, especially for the copper ions. Since interaction of copper ions with cellulose occurs in both acidic and alkaline conditions. Copper is capable of catalyzing the oxidation of cellulose in a wide pH range and cause extensive depolymerization of the cellulose chain (Banik, 1989). At low pH medium, copper ions catalyze the oxidation on the anhydroglucose ring while iron ions catalyze the cleavage of the cellulose β-1, 4-glycosidic bond (Budnar *et al.*, 2004) whereas in alkaline environment, the oxidative decomposition of cellulose catalyzed by copper ions leads to formation of reducing groups which together with copper ions present, react according to Fehling reaction (Banik, 1989). The pH value of about 5.5-6 is the optimum value for both copper and iron ions (Strlic *et al.*, 2003).

Therefore saffron solution can be a good inhibitor for the degradation caused by copper ions since it can resist pH change for a wide pH range.

Fifth Group Experiments

Samples treated with two different iron-gall-inks (Sample 12, sample 13) prepared according to different historical recipes were analyzed. (See Chapter 2.1.1) Colorimetric analysis results of those samples are given in Table 3.15.

Table 3.15 Changes in L* a* b* values of the samples in Group 5

Sample	**ΔL***	**Δa***	**Δb***
12	-5.5	0.15	9.74
13	-2.6	0.08	14.51

Sample 12 showed greater change in lightness than sample 13. The reason for this might be the presence of gum Arabic in ink 12.

The darkening of cellulose may be attributed to the decomposition of gum Arabic. In a study in 2003 (Bleton *et al.*), it is observed that gum Arabic is degraded considerably if it is not alone during the ageing; it is degraded by drastically in the presence of ferrous sulphate. Some degradation products could be galactonic acid and its lactone and the lactone of arabinonic acid (Bleton *et al.*, 2003).

Sample 13 showed greater change in b* value than sample 12. The reason for this might be the presence of gum Arabic in ink 12. Although having said to be accelerating the darkening of cellulose, gum Arabic keeps the pH of the ink solution more stable. Moreover, ink 13 contained alum of about 0.3 g and it may act as an acidifying agent and decreased the pH of the medium. Therefore having lower pH, sample 13 degraded more tha sample 12.

Sixth Group Experiments

In this group, paper samples were treated with two different green inks (sample 14 and sample 15) prepared according to the historical recipes were analyzed. (See Chapter 2.1.1) Colorimetric analysis results of those samples are given in Table 3.16.

Table 3.16 Changes in L* a* b* values of the samples in Group 6

Sample	**ΔL***	**Δa***	**Δb***
14	-43.44	27.51	25.96
15	-34.26	12.66	10.38

The change in lightness in green inks was so drastic. When two samples were compared, the sample 15 darkened less than sample 14. When the Δa* and Δb* values of the samples were compared, it was observed that the sample 15 degraded less than sample 14 but not so considerably.

This difference might be attributed to the buffer effect of saffron providing a less acidic medium and this reduced the degradation reactions of copper ions. But it was obvious those samples treated with both green inks were the most degraded samples that may be due to the corrosiveness of the copper.

Besides the cellulose oxidation catalyzed by copper ions, drastic changes in the chromatic values of the samples may also be due to the acidic hydrolysis of cellulose that caused by the $CuSO_4$ in the ink.

Seventh Group Experiments

Red Ink

Paper sample treated with red ink to prepare sample 16 and it was analyzed. Colorimetric analysis results of the sample are given in Table 3.17.

Table 3.17 Changes in L* a* b* values of the red ink

Sample	**ΔL***	**Δa***	**Δb***
16	-1.21	4.46	6..17

Changes in E* Values

The comparison of the total color difference, ΔE*, values of the all samples can be seen in the Figure 3.37. The change in the E* value shows the changes in lightness (L*), a* and b* value and calculated using the following equation:

$$\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$$

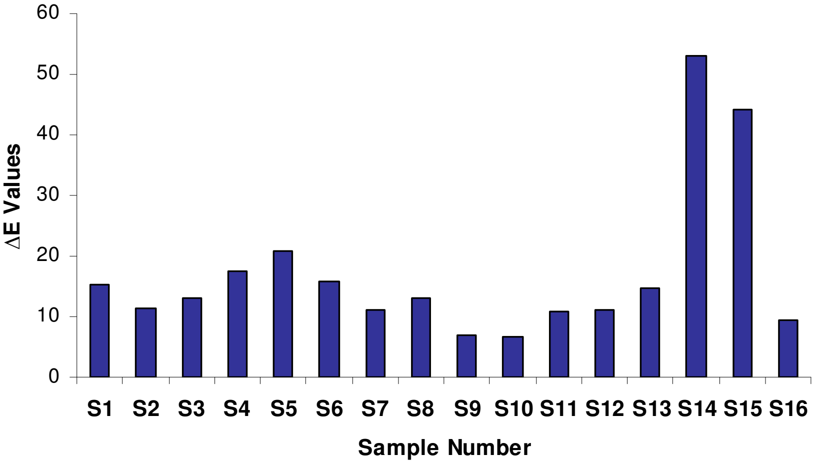


Figure 3.37 ΔE* values of the all of the samples

As can be seen in the Figure 3.37, sample 16 which was treated with the red ink composed of cochineal and alum was the one of the most stable inks together with sample 9 and sample 10. It can be due to the fact that carminic acid the main ingredient of the sample 16 is a stable pigment.

Other stable samples were the ones treated with saffron containing inks (Sample 9, 10, 11, 7 and 8). Sample 2 was also more stable than sample 1 and sample 3 as explained before. In sample 2 ratio of Fe/Ga was 1.5.

The most degraded samples were seen as the samples 14 and 15 which were treated with copper-based green inks. In visual examination, great changes in color were also observed in these samples. Thus, visual results were approved by the CIE L*a*b* results given by ΔE^* values.

3.5 Fourier Transform Infrared Spectroscopic Analysis(FTIR)

Ink-treated Whatman No: 1 filter paper samples were analyzed using FTIR Spectroscopy as explained in Chapter 2.7. FTIR spectra were evaluated to get information about the molecular changes of the paper samples treated with different inks.

FTIR spectroscopy is mainly sensitive to the cellulose oxidation but there are some limitations and difficulties in the interpretation of the spectra, since the cellulose remains as the major component of the sample, small discrepancies can be observed between the pure cellulose spectra and the inked paper before ageing (Remazeilles *et al.*, 2000). In this study, all ink-impregnated papers before ageing gave similar FTIR spectra, very close to pure cellulose spectra. FTIR spectra have some difficulties to interpret the experimental data obtained, because this method may not be sensitive enough to capture the changes in the state of cellulose degradation (Csefalvayovna *et al.*, 2007).

The most informative spectral region of the cellulose spectra has known to be between 1500 cm^{-1} and 1900 cm^{-1} especially for examining degradation of the cellulose (Sivakova *et al.*, 2008). After artificial ageing, small variations in absorption appeared in this region (1550-1850 cm^{-1}). As this region is characteristic of carbonyl groups stretching vibration, the increase in absorption may be attributed to cellulose oxidation products (Rouchon-Quillet *et al.*, 2004).

The C atoms which are the most prone to oxidation occupy the 2, 3, 6 positions (see Figure 1.2) in glycopyranose anomer inside the cellulose chain; and the 1, 4 positions in terminal anomers whose number increases upon hydrolysis and can exist as opened or closed rings. In oxidation, they give a variety of products which can be seen in Fig. 3.38 as functional groups which may appear on the glycopyranose ring at various positions (Lojewska *et al.*, 2005).

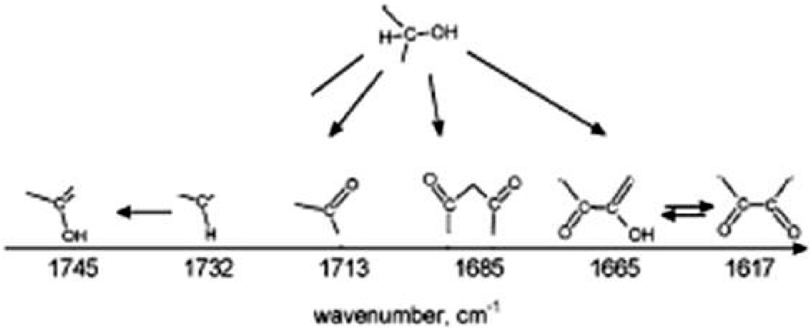


Figure 3.38 Possible products of cellulose partial oxidation presented as functional groups associated with frequiencies of their vibrations (Lojewska *et al.*, 2005)

The most intense absorption maxima were observed between 1730 cm^{-1} and 1620 cm^{-1} which may be attributed to carboxyl/aldehyde groups and conjugated carbonyl groups, respectively. The highest contributions to the band around 1730 cm^{-1} was assumed to become from carboxyl or aldehyde groups and to the band around 1620 cm^{-1} come from conjugated carbonyl groups, respectively (Lojewska *et al.*, 2005).

The band in spectral region of 3330-3430 cm^{-1} corresponds to OH stretching vibrations. Change in the intensity of this band may be related with the acidity in degraded samples. Cellulose oxidation reaction of O-H (hydroxyl) to C-O occurs when the sample is acidic due to the corrosive ink (Sistach *et al.*, 1998).

In addition, the hydration capacity of cellulose and H-bond changes if this molecule is oxidized (Sistach *et al.*, 1998). The decrease in the intensity of this band could reflect the changes of -OH environment (Csefalvayova *et al.*, 2007) and may vary due to the moisture content of the sample.

The band at 2363 cm^{-1} indicates the adsorbed carbondioxide from atmosphere. In all spectra of samples, absorption band for CO_2 adsorption increased upon ageing. This could be due to increasing activity of paper surfaces to adsorb CO_2 from the environment.

Another absorption bands examined in this study is the bands in the 1300 - 1500 cm^{-1} which may be attributed to numerous mixed vibrations rather than to characteristic group frequencies.

Thus, the bands in this range are mixtures of OCH deformation vibrations, CH_2 bending vibrations, CCH and COH bending vibrations (Proniewicz *et al.*, 2001). Also the absorptions in this region (1350-1450 cm^{-1}) may signify the presence of gallic acid (Senvaitene *et al.*, 2006). The bands at 1108 cm^{-1} which indicate the existence of sulphate was also considered in the study.

First Group Experiments

In this group, paper samples treated with three iron-gall-inks with iron to gallic acid mole ratios; 0.17 (Sample 3), 1.5 (Sample 2) and 3.6 (Sample 1) were analyzed before and after ageing in order to investigate the effect of Fe/Ga ratio on cellulose degradation.

The FTIR spectra of the samples for the region of 600-4000 cm^{-1} before and after ageing are presented in Figures below (Figure 3.39, 3.40 and 3.41).

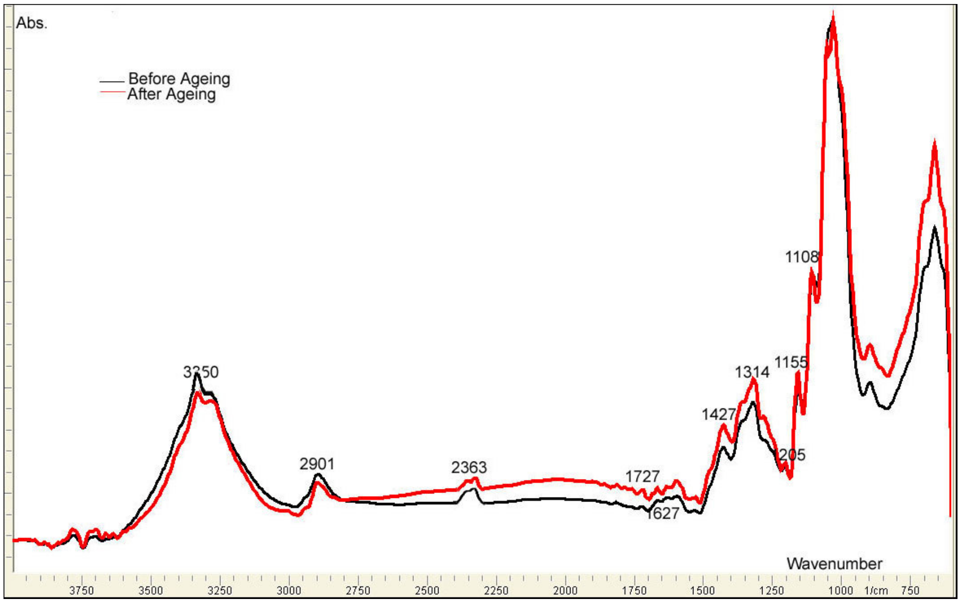


Figure 3.39 FTIR spectra of Sample 1 (Fe/Ga: 3.6) before and after ageing

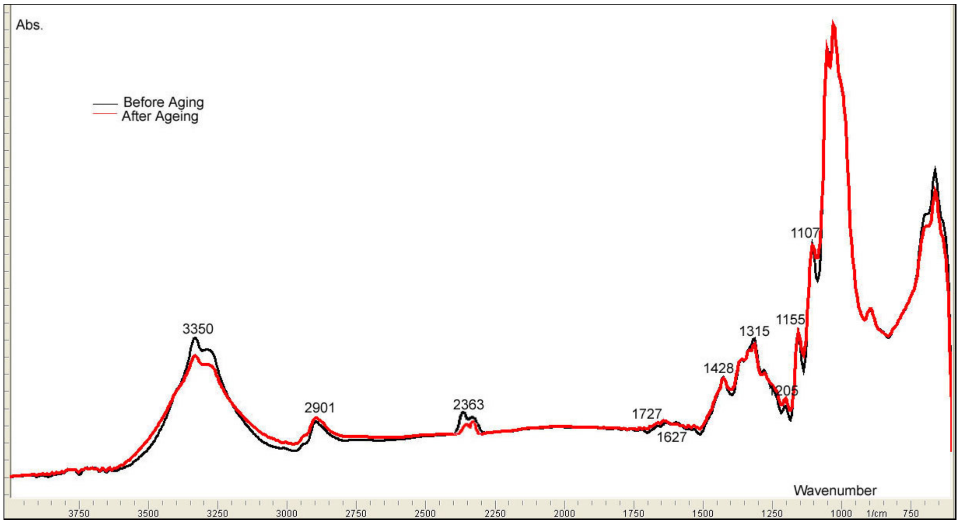


Figure 3.40 FTIR spectra of Sample 2 (Fe/Ga: 1.5) before and after ageing

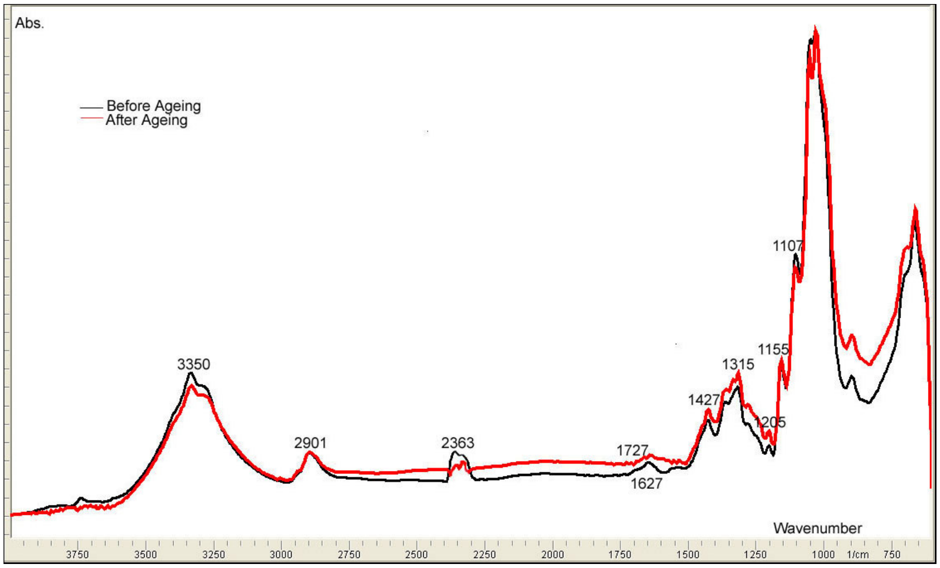


Figure 3.41 FTIR spectra of Sample 3 (Fe/Ga: 0.17) before and after ageing

The FTIR spectra of the samples in Group 1 in the region 1500 cm^{-1}-1900 cm^{-1} are presented in Figure 3.42.

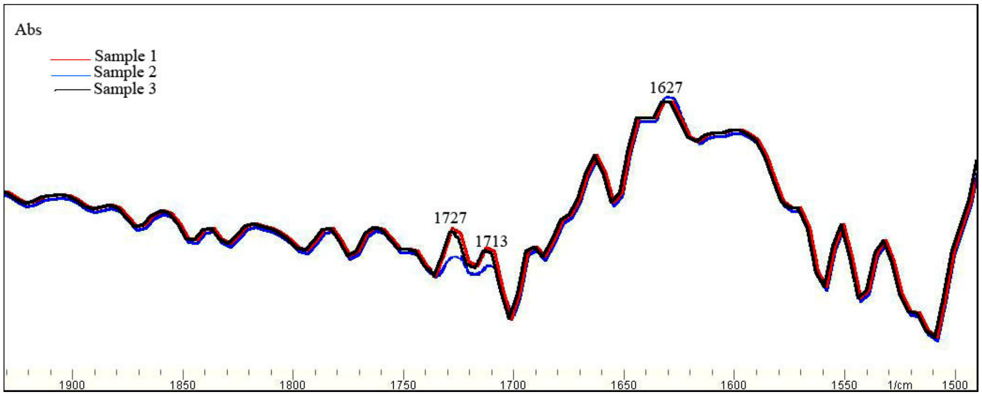


Figure 3.42 FTIR spectra of the samples in Group 1 for the region of 1500 cm^{-1}-1900 cm^{-1} after ageing

FTIR spectra of the filter papers (Whatman No.1) treated with three inks prepared with iron (II) sulphate and gallic acid in different proportions did not show significant difference. However, in the spectrum of sample 2 which have the iron to gallic acid ratio of 1.5, very small differences were observed between aged and non-aged samples. (Fig. 3.40)

The bands at 1108 cm^{-1} and 1155 cm^{-1} may indicate the presence of SO_4^{-2} ion (Ferrer and Sistach, 2005) which comes from ferrous sulphate exist in all three samples and did not change with ageing.

The band at 1427 cm^{-1} may be due to H-C-H and O-C-H in plane bending vibrations while the band at 1315 cm^{-1}may be attributed to C-O-H and H-C-C bending vibrations. Also, the absorptions in this region (1350-1450 cm^{-1}) may signify the existence of gallic acid used in the inks applied to paper samples. New peak formations did not be observed in this region but only the changes in the intensities of the peaks were observed. It is observed that the intensity of these bands shows an increment in Sample 1 and Sample 3 after ageing whereas small variations were observed in the spectrum of Sample 2. (Figure 3.39-3.41)

The band at 1205 cm^{-1} may originate from gum Arabic (Senvaitiene *et al.*, 2005) and this band was valid for all three samples in this group.

The band at 2901 cm^{-1} may be attributed to -CH stretching vibration and did not change much after ageing.

However, there was no so much difference between the aged and non-aged samples of this group. New peak formations were not observed after ageing in the spectra of the samples. However, the significant differences in the intensities of the absorbance were observed especially between 1550 cm^{-1} and 1800 cm^{-1} that is the characteristic region for carbonyl and carboxyl groups. Moreover, a decrease was observed in the bands at 3330-3350 cm^{-1} which corresponds to –OH absorption (Sistach *et al.*, 1998) due to ageing.

The more intensive band formation in the spectrum of the Sample 1 after ageing in the region between 1550 and 1800 cm^{-1} can be explained by the oxidation reaction of cellulose in the presence of excess iron (II) sulphate since free Fe^{2+} ions acts as a catalyst in by catalyzing the formation of hydroxyl radicals. (See R.1.4 - R.1.6)

However, the Sample 3 having the lowest Fe/Ga ratio gives a more intense band at 1727 cm^{-1} and 1712 cm^{-1} when compared to sample 2 after ageing.

This can be attributed to that the excess of gallic acid acts as a reducing agent for ferric pyrogallate complex and then reduces the Fe^{2+} ions which are soluble and can easily be removed from the complex and becomes free. Reduction of Fe^{3+} to Fe^{2+} allows Fenton reaction to be repeated in a cycylic fashion. The reaction that occurs at low pH can be seen in Reaction 3.2. But this effect of gallic acid is valid before ageing or maybe at the beginning of the ageing. Since after ageing, gallic acid degrades and this limits the reducing property of it (Rouchon-Quillet *et al.*, 2004).

Sample 2 after ageing seemed to be less oxidized when compared to other two samples, sample 1 and sample 3. Therefore, it can be said that both the excess of Fe^{2+} and the excess of gallic acid caused more oxidation of cellulose.

The change of band occurs at 3330 cm^{-1} which corresponds to –OH absorption is related with the pH of the samples and may be the moisture content of the samples.

Second Group Experiments

In this group, the paper samples treated with three iron-gall-inks with copper to iron mole ratios of 0.01(ink 6), 0.4 (ink 4) and 0.8 (ink 5) were analyzed. Sample 1 was used as reference since there was no any copper in the ink. The purpose of this experiment was to investigate the effect of copper on cellulose degradation.

The FTIR spectra of the samples for the region of 600-4000 cm^{-1} before and after ageing are presented in Figures 3.43, 3.44 and 3.45.

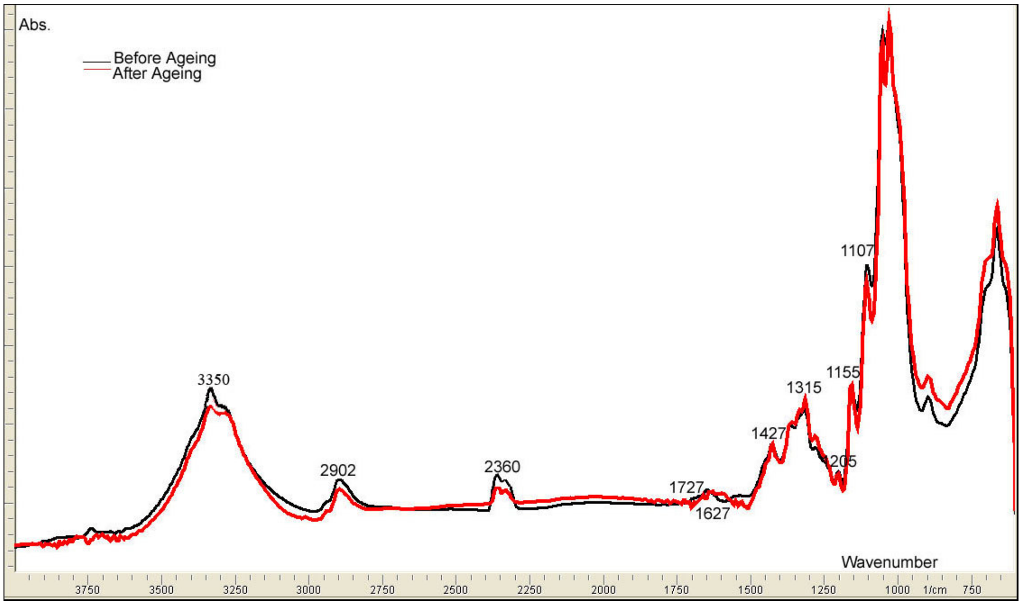


Figure 3.43 FTIR spectra of Sample 4 (Cu/Fe: 0.4) before and after ageing

Figure 3.44 FTIR spectra of Sample 5 (Cu/Fe: 0.8) before and after ageing

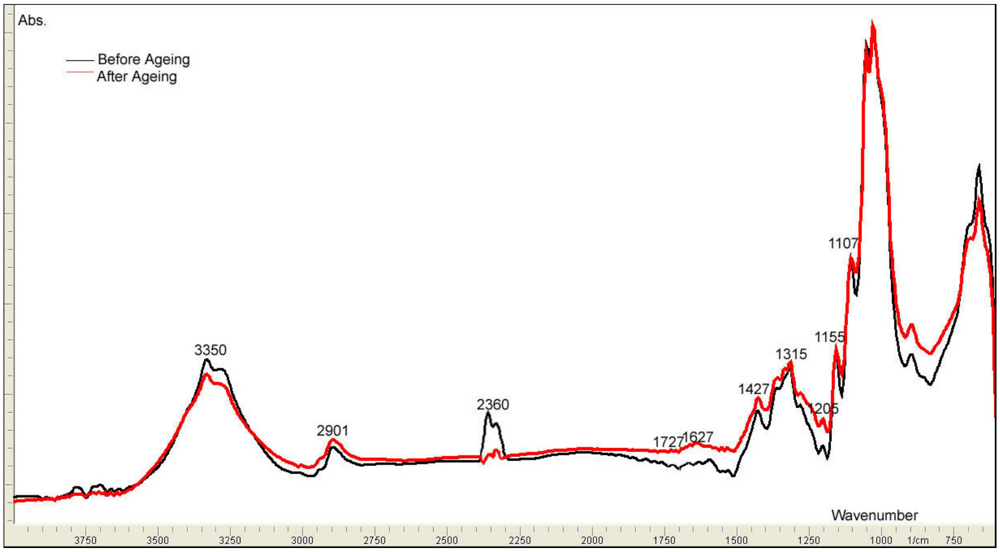


Figure 3.45 FTIR spectra of Sample 6 (Cu/Fe: 0.01) before and after ageing

The FTIR spectra of the samples in Group 2 for the region of 1500 cm^{-1}-1900 cm^{-1} are presented in Figure 3.46.

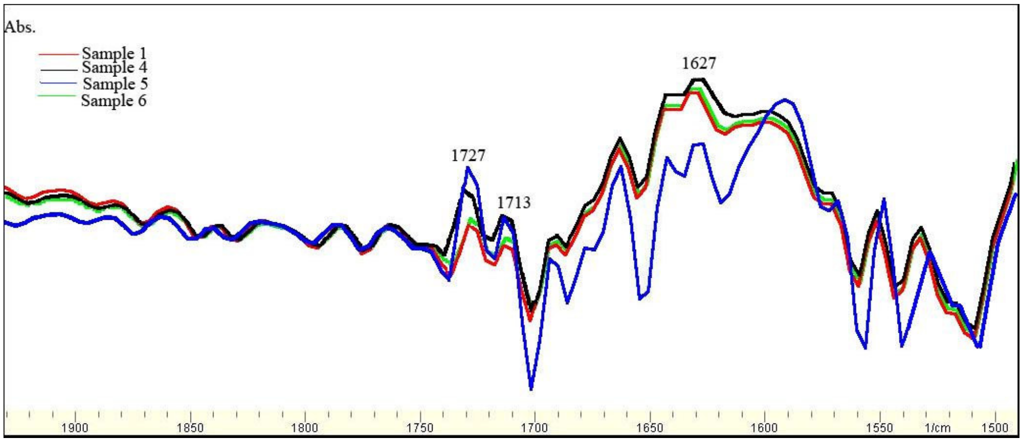


Figure 3.46 FTIR spectra of the samples in Group 2 for the region of 1500 and 1900 cm^{-1} after ageing

The spectra of this group showed similar absorptions to the ones of Group 1. The sulphate bands were observed 1107 cm^{-1} and 1155 cm^{-1} which may originate from ferrous sulphate in all samples.

The bands at 1427 cm^{-1} and 1315 cm^{-1} were observed in all samples in this group. The intensity of these bands showed the most increment in Sample 5. The band at 1205 cm^{-1} which may originated from gum Arabic was observed in all three samples as in Group 1 samples and did not change on ageing.

The band around 2900 cm^{-1} was attributed to -CH stretching vibration and did not change much after ageing.

More significant band formations were observed at 1727 and 1713 cm^{-1} in sample 5 (Figure 3.44) when compared to the spectra of the other samples.

A decrease was observed in the bands at 3330-3350 cm^{-1} which corresponds to –OH stretching vibrations on ageing due to the decrease in the pH of the samples or may be to the loss of moisture on ageing.

Third Group Experiments

In this group, the paper samples treated with three iron-gall-inks with saffron to iron weight ratios of 0.03 (sample 11), 0.17 (sample 9) and 1.0 (sample 10) were analyzed. Sample 1 was again used as a reference since there was no any saffron in the ink applied on it. The purpose of this experiment was to investigate the effect of saffron on iron-gall-ink corrosion.

The FTIR spectra of the samples for the region of 600-4000 cm^{-1} before and after ageing are presented in Figures 3.47, 3.48 and 3.49.

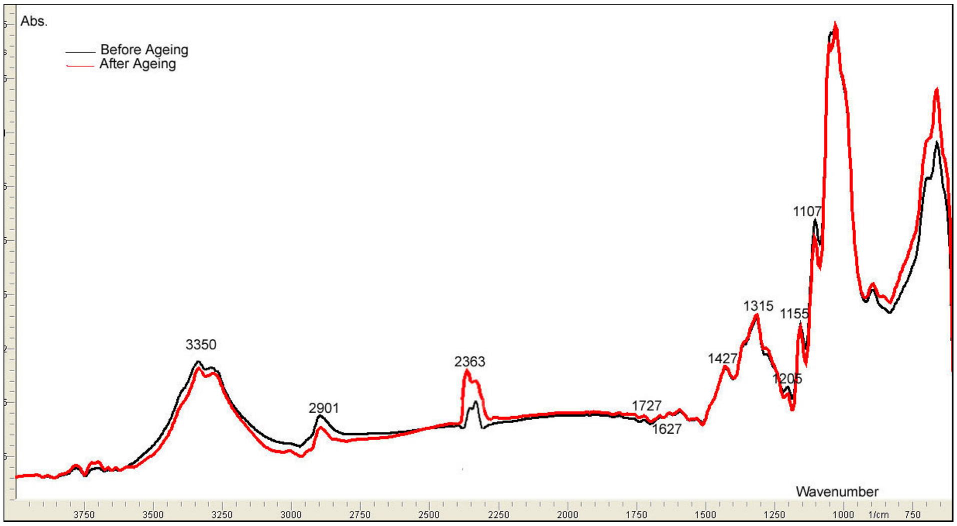


Figure 3.47 FTIR spectra of Sample 9 before and after ageing

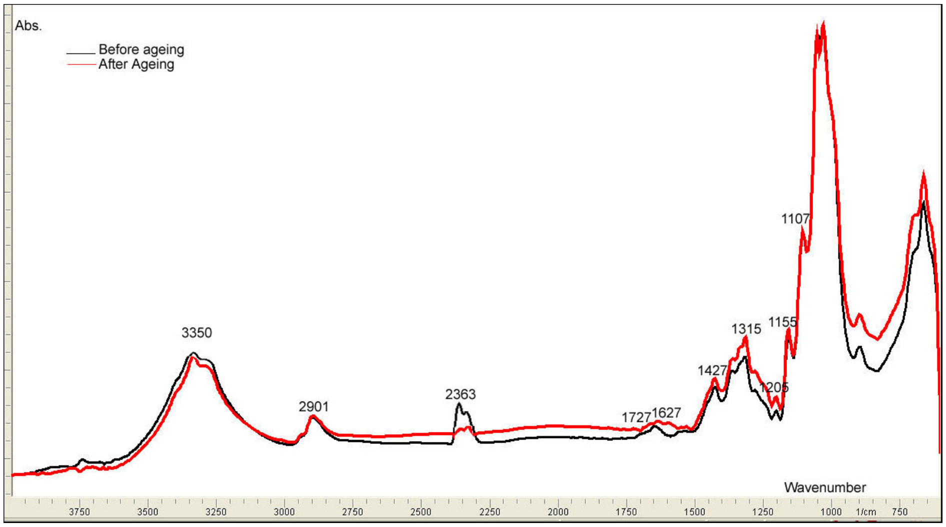


Figure 3.48 FTIR spectra of Sample 10 before and after ageing

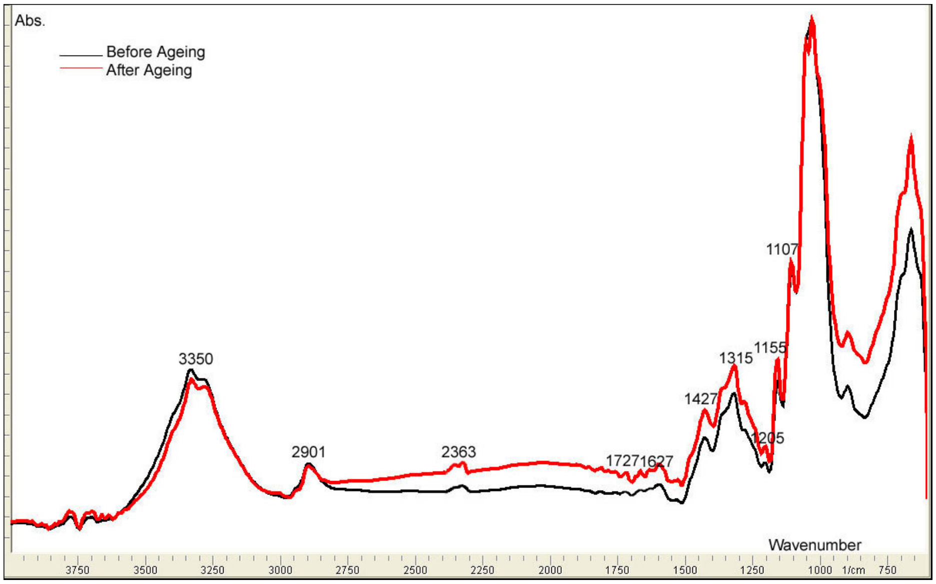


Figure 3.49 FTIR spectra of Sample 11 before and after ageing

The FTIR spectra of the samples in Group 3 between 1500 cm^{-1}-1900 cm^{-1} are presented in Figure 3.50.

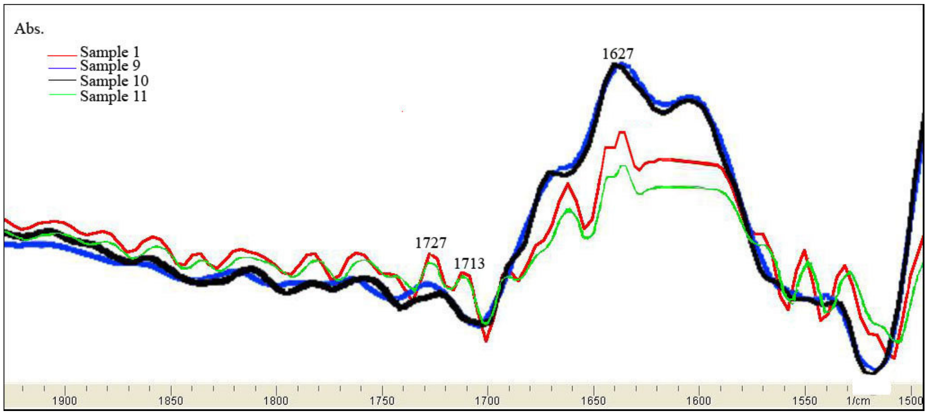


Figure 3.50 FTIR spectra of the samples in Group 3 for the region of 1500-1900 cm^{-1} after ageing

The sulphate bands at 1107 cm^{-1} and 1155 cm^{-1} were observed (Ferrer and Sistach, 2005). The bands at 1427 cm^{-1} and 1315 cm^{-1} were observed in all samples of this group. The intensities of these bands showed the most increment in Sample 11 and the least change was in sample 9.

The band at 1205 cm^{-1} which may originate from gum Arabic was observed at the spectra of all the samples. The band at 2901 cm^{-1} that indicates the -CH stretching vibration was observed in all three samples and showed no significant change on ageing.

The most significant differences were observed between 1550 cm^{-1} and 1800 cm^{-1} which is the characteristic region of carbonyl and carboxyl groups stretching vibration in the samples in other groups. As can be seen from the spectra, especially sample 9 and sample 10 showed no significant changes in this region due to the presence of saffron in the inks applied to them while in the spectrum of sample 11 more intense bands were observed in this region.

The same situation was valid for the absorptions in the region between 3330-3350 cm^{-1} which corresponds to –OH absorption but due to pH stabilizing effect of saffron especially in samples 9 and 10 there was no so significant change in the absorption intensity after ageing.

Different band formations were not observed in the spectra of the samples in Group 3 which may indicate the presence of saffron.

With increasing amount of saffron, the intensity of the bands decreased in the region of 1500 cm^{-1} and 1900 cm^{-1} after ageing. Considering the change in the vibrations in this region, it can be suggested that saffron acts as an inhibitor in the oxidation of cellulose due to its buffering effect.

Fourth Group Experiments

The paper samples treated with two iron-gall-inks containing different amounts of copper to iron mole ratio and constant weight ratio of Sa/Fe of 0.17; Cu/Fe: 0.4 (Sample 7), Cu/Fe: 0.8 (Sample 8) were analyzed. Sample 4 and sample 5 were used as references for ink 7 and ink 8, respectively.

The FTIR spectra of the samples in the region of 600-4000 cm^{-1} before and after ageing are presented in Figures 3.51 and 3.52.

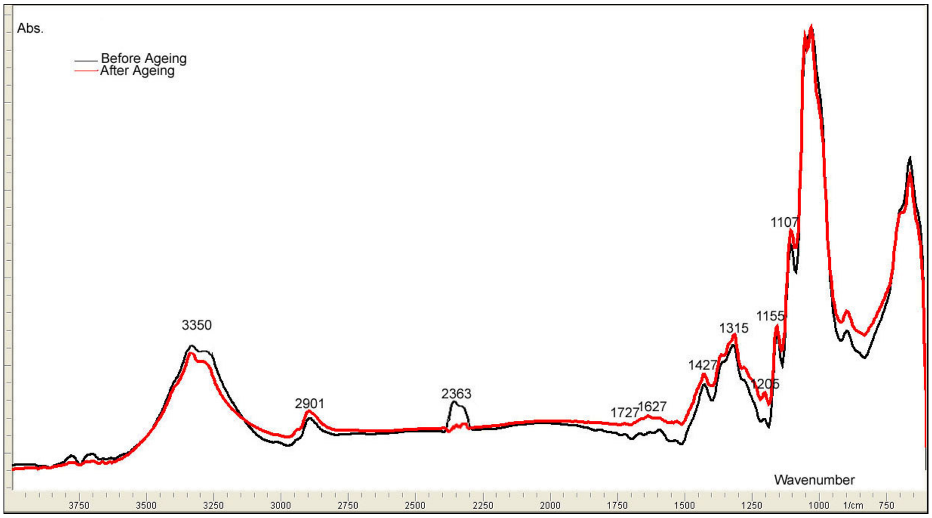


Figure 3.51 FTIR spectrum of Sample 7 before and after ageing

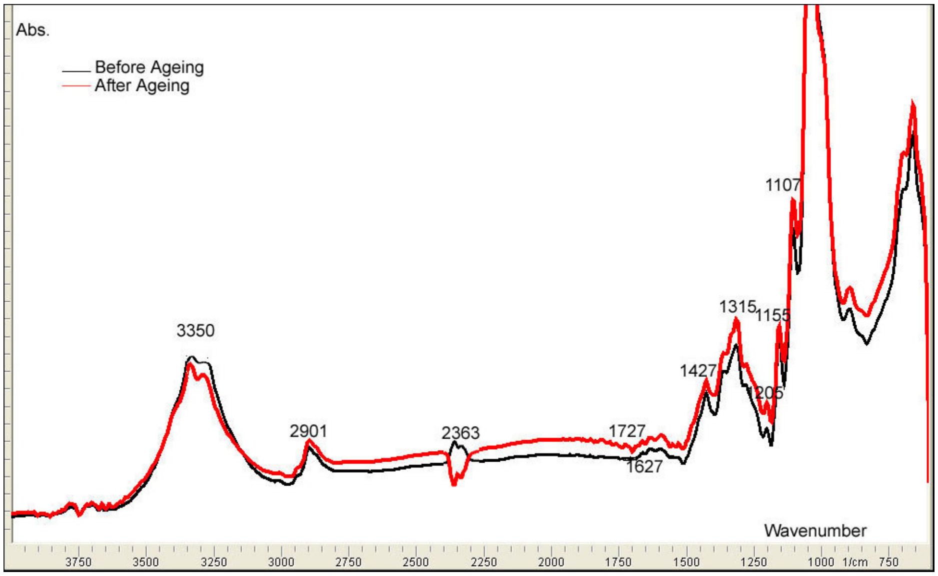


Figure 3.52 FTIR spectrum of Sample 8 before and after ageing

The FTIR spectra of the samples of Group 4 for the region of 1500 cm^{-1}-1900 cm^{-1} are presented in Figure 3.53.

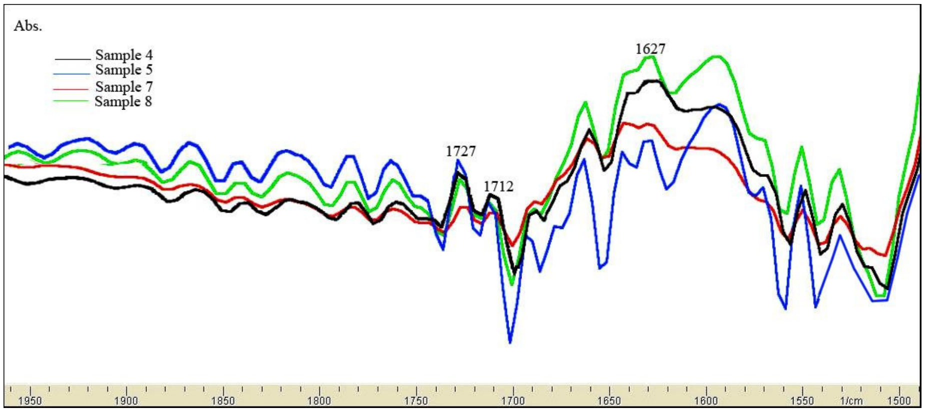


Figure 3.53 FTIR spectra of the samples of Group 4 between 1500 -1900 cm^{-1} after ageing

The sulphate bands were observed at 1107 cm^{-1} and 1155 cm^{-1} in the spectra of the samples 7 and 8. The bands at 1427 cm^{-1} and 1315 cm^{-1} were observed in all samples of this group. The intensities of these bands showed more increment in Sample 8 than Sample 7.

The band at 1205 cm^{-1} may signify that gum Arabic is present in all samples. The -CH stretching vibration band at 2901 cm^{-1} was observed in the spectra of all samples and did not change much after ageing.

The region that the most significant differences occurred was between 1550 cm^{-1} and 1800 cm^{-1}. Sample 8 showed more significant changes than Sample 7 after ageing in this region. (Fig.3.51, 3.52)

The same situation was valid for the absorptions in the region of 3330-3350 cm^{-1} which corresponds to –OH absorption. There was no significant change in the absorption in this region due to the presence of saffron in sample 7 and sample 8.

Fifth Group Experiments

In this group of experiments, the samples treated with two different iron-gall-inks (sample 12, sample 13) prepared according to different historical recipes (Senvaitienë *et al.*, 2005) were analyzed.

The FTIR spectra of the samples 12 and 13 for the region of 600-4000 cm^{-1} before and after ageing are presented in Figures 3.54 and 3.55.

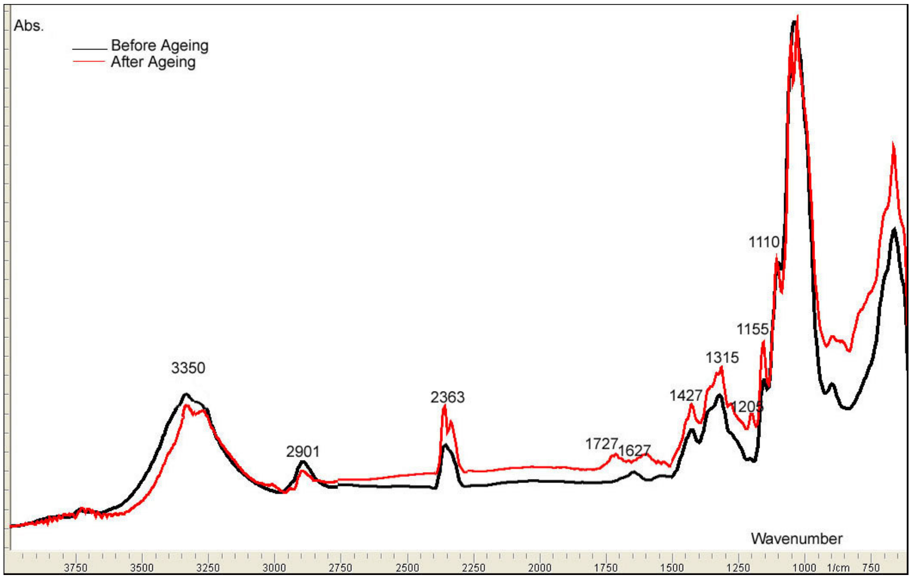


Figure 3.54 FTIR spectra of Sample 12 before and after ageing

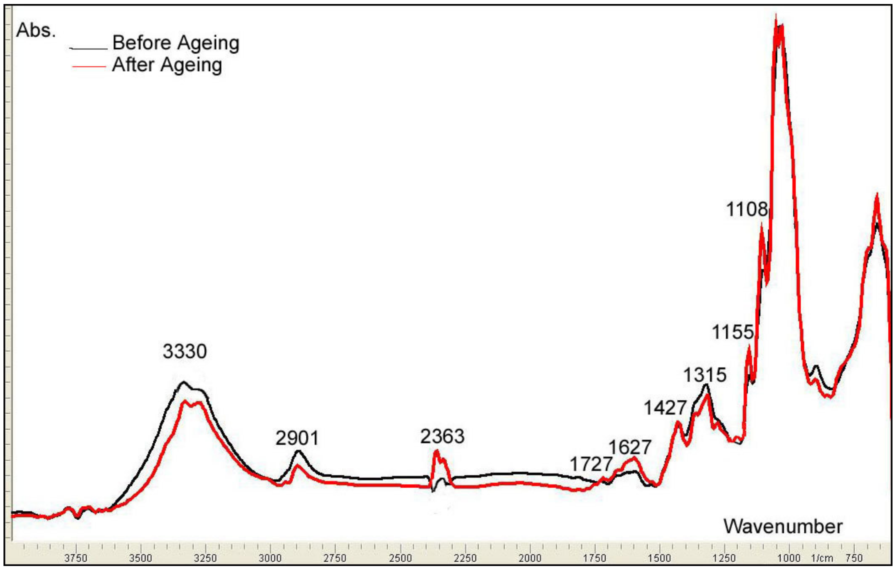


Figure 3.55 FTIR spectra of Sample 13 before and after ageing

The FTIR spectra of the samples in Group 5 for the region of 1500 cm^{-1}-1900 cm^{-1} are presented Figure 3.56.

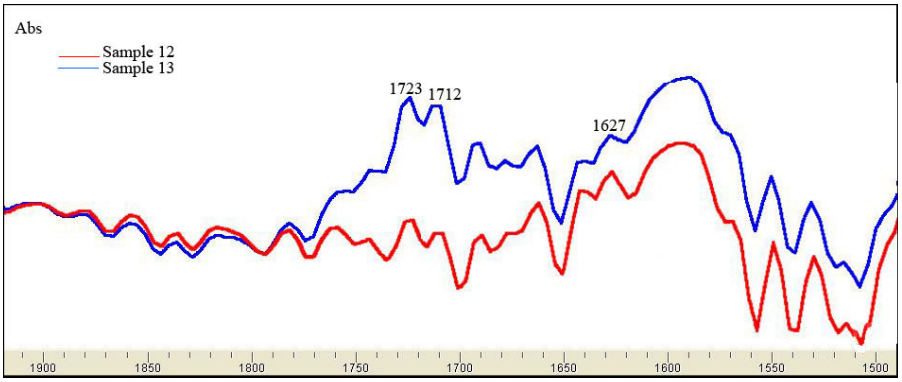


Figure 3.56 FTIR spectra of the samples in Group 5 for the region of 1550-1900 cm^{-1}

The sulphate bands at 1108 cm^{-1} and 1155 cm^{-1} were observed in both samples. The bands at 1427 cm^{-1} and 1315 cm^{-1} were observed in both Sample 12 and Sample 13. The intensities of these bands were more in Sample 12.

The band at 1205 cm^{-1} may originate from gum Arabic this band was not observed in the spectrum of Sample 13 since there was no any gum Arabic in ink 13. The bands at 2901 cm^{-1} that may be attributed to -CH stretching vibration which were also observed in both samples before and after ageing.

As in other groups, the most significant differences were observed in the region of 1550 cm^{-1} and 1800 cm^{-1} which is the characteristic region of carbonyl and carboxyl groups stretching vibration occur. As it can be seen from the spectra, sample 13 showed more significant changes at the bands at 1713 and 1727 cm^{-1} than sample 12 after ageing.

The same situation was valid for the absorptions in the region between of 3330-3350 cm^{-1} which corresponds to –OH absorption since the pH of sample 13 was smaller than the pH of the sample 12. The reason for this might be due to the presence of gum Arabic in ink 12 besides; ink 13 contained alum instead of gum Arabic. Gum Arabic keeps the pH of the ink solution rather constant. But, alum in ink 13 may act as an acidifying agent and decreased the pH of the medium. Therefore having lower pH, sample 13 degraded more drastically than sample 12.

Sixth Group Experiments

In this group, paper samples treated with two different green inks prepared regarding historical recipes (Nefeszade, 1938) were analyzed (ink 14 and ink 15).

The FTIR spectra of the samples in the region of 600-4000 cm^{-1} before and after ageing are presented in Figures 3.57 and 3.58.

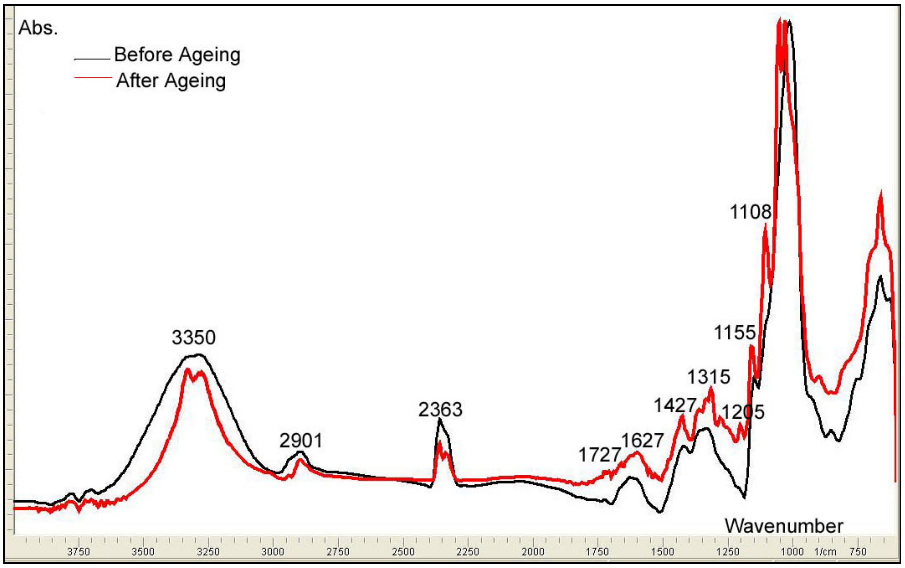


Figure 3.57 FTIR spectra of Sample 14 before and after ageing

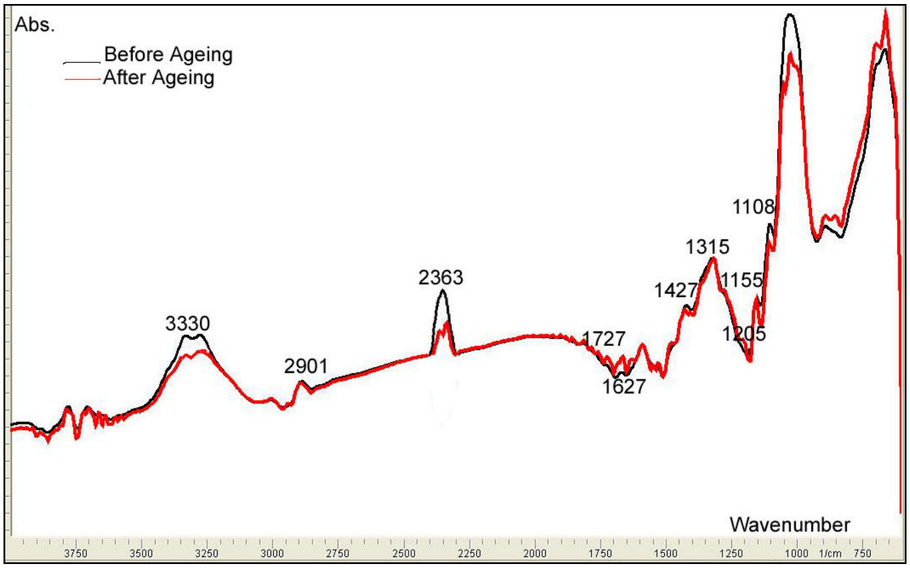


Figure 3.58 FTIR spectra of Sample 15 before and after ageing

The FTIR spectra of the samples in Group 6 in the region of 1500 cm^{-1}-1900 cm^{-1} are presented in Figure 3.59.

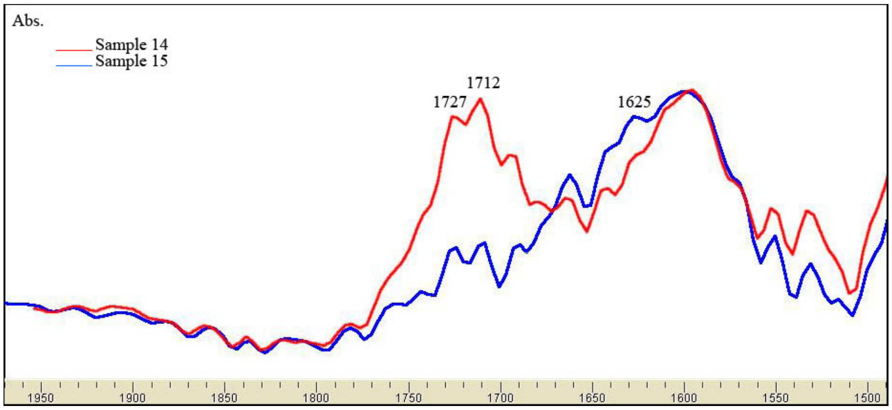


Figure 3.59 FTIR spectra of the samples in group 6 in the region of 1500-1900 cm^{-1} after ageing

The sulphate bands at 1107 cm^{-1} and 1155 cm^{-1} were observed which may originate from copper sulphate. The bands at 1427 cm^{-1} and 1315 cm^{-1} were observed in both samples. The intensities of these bands were more significant in the spectrum of sample 14. This may come from the absence of gallic acid in Sample 15.

The band at 1205 cm^{-1} may originated from gum Arabic was also observed in the spectra of both samples. The band at 2901 cm^{-1} may be attributed to -CH stretching vibration and did not change much after ageing especially in Sample 15.

However, the most significant differences were observed in the region of 1550 cm^{-1} and 1800 cm^{-1}. When the spectra of the sample were examined in this region it was seen that Sample 15 seems to be more stable than sample 14.

When the absorptions in the region of 3330-3350 cm^{-1} were examined which corresponds to –OH absorption, significant changes were observed in the spectra of sample 14 and 15 due to the changes in the pH of the samples.

It is understood that the sample 15 degraded less than Sample 14. This difference might be attributed to the buffering effect of saffron providing a less acidic medium for sample 15 and this reduced the degradation reactions of copper ions.

Red Ink Experiments

In this group, one paper sample (Sample 16) treated with red ink prepared regarding a historical recipe (Nefeszade, 1938) was analyzed.

The FTIR spectra of the samples for the region of 600-4000 cm^{-1} before and after ageing are presented in Figure 3.60.

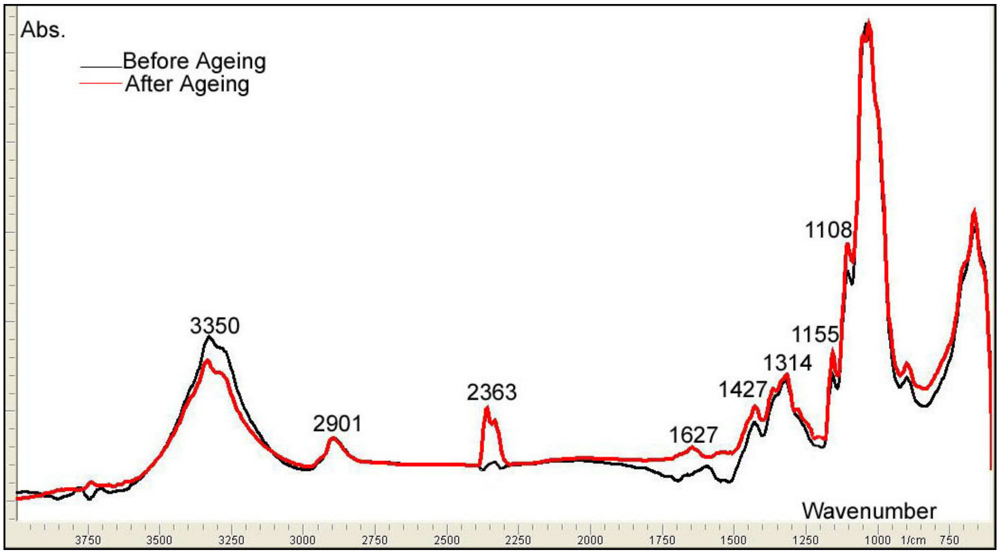


Figure 3.60 FTIR spectrum of Sample 16 before and after ageing

The FTIR spectrum of the red ink sample for the region of 1500-1900 cm^{-1} are presented in Figure 3.61.

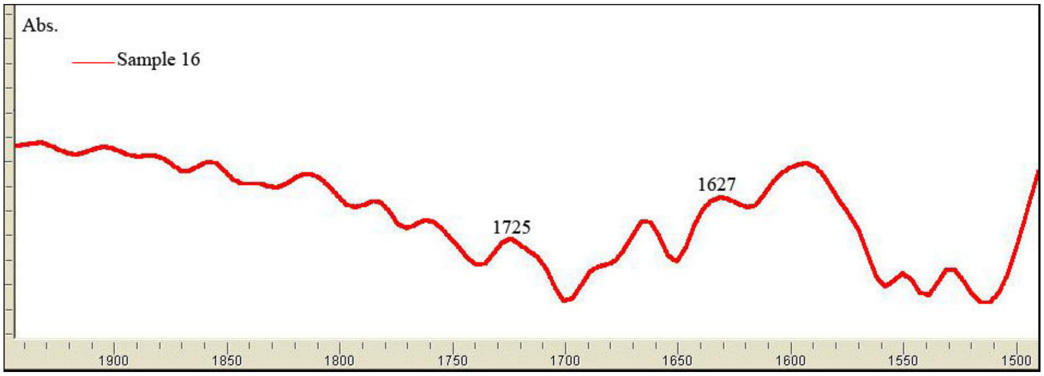


Figure 3.61 FTIR spectrum of sample 16 in the region between 1500 and 1900 cm^{-1} after ageing

The sulphate bands were observed at 1108 cm^{-1} and 1155 $cm^{-1)}$ which may come from alum; $KAl(SO_4)_2.12H_2O$. The bands appeared at 1314 and 1427 cm^{-1} were also observed in the spectra of sample 16.

There was no absorption band observed at 1205 cm^{-1} that may originate from gum Arabic since there was no gum Arabic in sample 16. The band at 2901 cm^{-1} may be attributed to -CH stretching vibration and did not change much after ageing.

The most significant differences were observed between 1550 cm^{-1} and 1800 cm^{-1} where the characteristic region of carbonyl and carboxyl groups stretching vibration. But not much change occured in this region.

In the absorptions for the region of 3330-3350 cm^{-1} which corresponds to –OH absorption the intensity showed a decrease after ageing due to pH lowering and/or loss of moisture.

The cochineal pigment is a stable pigment and non-corrosive. Therefore, no much change was observed in the spectrum of the sample 16 in the carbonyl vibration region.

CHAPTER 4

CONCLUSION

In this study, the influence of different historical ink components on the carrier material, paper, degradation was examined. Totally 16 ink samples composed of iron-gall-ink and other colored inks (green and red) were prepared with different compositions and applied on model paper samples and then subjected to accelerated ageing.

In order to evaluate the influence of the inks on cellulose in time, the samples were analyzed using pH measurements, UV-Vis spectroscopy, color spectrophotometry and FTIR-ATR analysis before and after ageing.

The collective results of experimentation of the 16 samples have yielded the following conclusions:

- Copper ions being stronger oxidizing agent than iron ions, slow down the formation of ferrous gallate complex when added in the preparation of the iron-gall-ink solution and do not form any colored complexes with gallic acid. (UV-Vis spectroscopy)

- With different iron to gallic acid ratios different complexes are formed between the gallic acid and iron ions. (UV-Vis spectroscopy)

- The presence of saffron in iron-gall-ink solutions may increase the degree of complex formation between iron and gallic acid adjusting the pH of the medium. (UV-Vis spectroscopy, pH measurement)

- The pH decreasing of paper-ink samples is relevant to the pH value of ink solution. (pH measurement)

- The ideal complex formation ratio of ferrous sulphate and gallic acid for a less corrosive writing ink is 1.49 not 3.6 as suggested by some of the previous studies. The excess of Fe^{2+} ions and the excess of gallic acid increase the oxidation of cellulose. (Color spectrophotometry, FTIR-ATR spectroscopy)

- Saffron which was advised in historical recipes for stable inks is observed to inhibit the iron-gall-ink corrosion. (Color spectrophotometry, FTIR-ATR spectroscopy, pH measurments)

- Green inks containing copper ions degraded significantly due to corrosive action of them. (Color spectrophotometry, FTIR-ATR spectroscopy)

- Vis spectrophotometry may provide information on the effect of different ink ingredients on the formation of the colored complexes, interactions in the ink whereas Color spectrophotometry and FTIR-ATR techniques may provide information on the influence of inks on the degradation of cellulose. The results of colorimetry are approved by the results of the FTIR- ATR analysis.

- The colorimetric analyses provided better correlating data comparing with FTIR ATR technique for examining the degradation of cellulose.

- The study also showed that even the little changes in the chemical composition of the inks on the writing media (paper, parchment, etc.) results in great changes in the degree of degradation of the carrier material. (UV-Vis spectroscopy, Color spectrophotometry, FTIR-ATR spectroscopy)

- The study may help to understand that in order to apply the appropriate conservation treatment for the paper degradation it is vital to understand the influences of different inks on cellulose.

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The ink corrosion website
http://www.knaw.nl/ecpa/ink/make_ink.html
August 2008

APPENDIX A

MICROGRAPHS OF HISTORICAL PIGMENTS

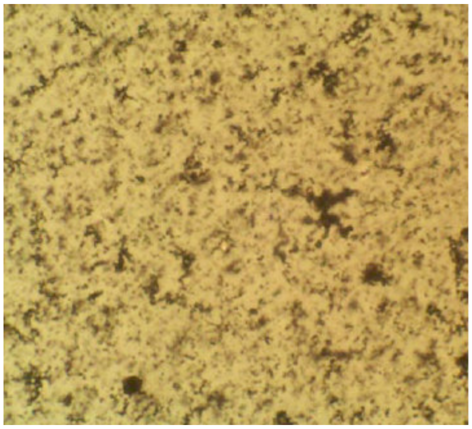

Figure A.1 Micrograph of lampblack at x 500 mag.[4]

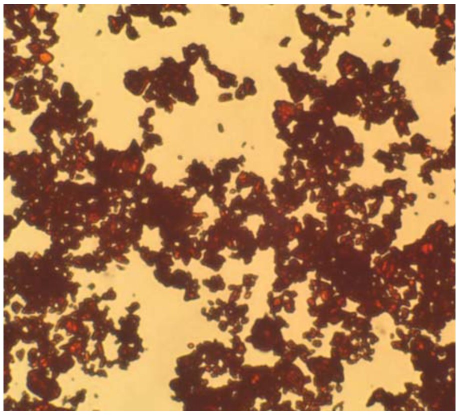

Figure A. 2 Micrograph of vermillion at x 500 mag[5]

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[4] "A Pigment Particle & Fiber Atlas for Paper Conservators", Cornell University Library , Department of Preservation and collection maintenance Publication

[5] "A Pigment Particle & Fiber Atlas for Paper Conservators", Cornell University Library , Department of Preservation and collection maintenancePublication

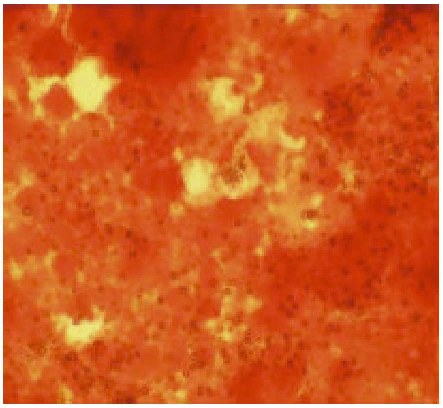

Figure A.3 Micrograph of cochineal carmine at x 500 mag.[6]

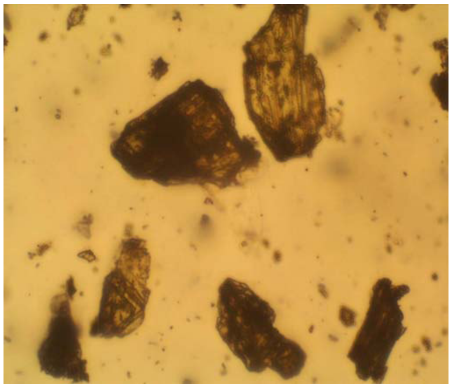

Figure A.4 Micrograph of orpiment at x 500 mag.[7]

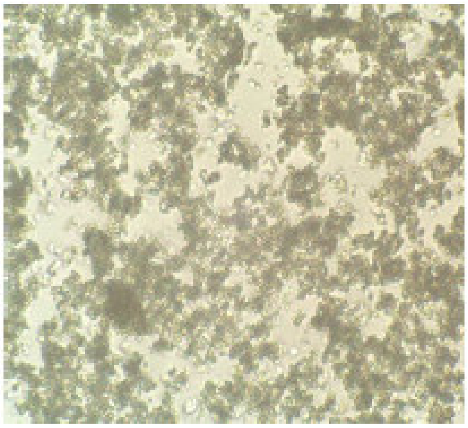

Figure A.5 Micrograph of lead white at x 500 mag.[8]

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[6] "A Pigment Particle & Fiber Atlas for Paper Conservators", Cornell University Library , Department of Preservation and collection maintenancePublication

[7] "A Pigment Particle & Fiber Atlas for Paper Conservators", Cornell University Library , Department of Preservation and collection maintenancePublication

[8] "A Pigment Particle & Fiber Atlas for Paper Conservators", Cornell University Library , Department of Preservation and collection maintenancePublication

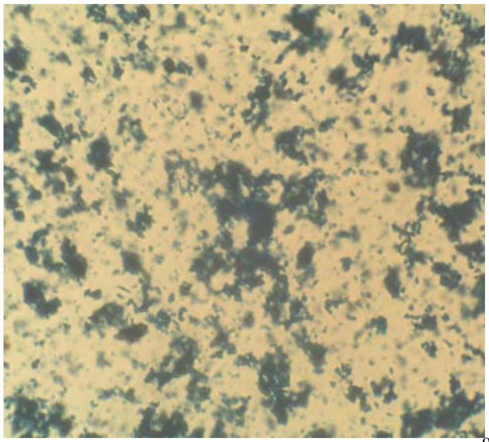

Figure A.6 Micrograph of indigo at x 500 mag.[9]

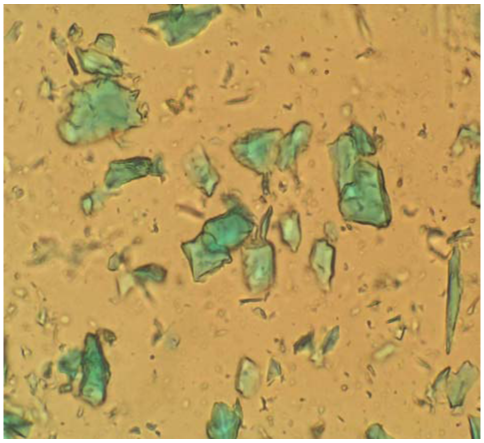

Figure A.7 Micrograph of verdigris at x 500 mag.[10]

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[9] "A Pigment Particle & Fiber Atlas for Paper Conservators", Cornell University Library , Department of Preservation and collection maintenancePublication

[10] "A Pigment Particle & Fiber Atlas for Paper Conservators", Cornell University Library , Department of Preservation and collection maintenancePublication