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# Experimental and applied studies of various writing inks effects on paper manuscripts and documents, and important methods of treatment & conservation applied on selected objects.

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## Summary

Manuscripts, documents ,covenants, correspondence, and rare historical books Still an important source of many sciences, mathematics, and humanities…….,and reliable supportive, and progress basis for many peoples and countries, including in respect of important and useful information and scientific rules for the various branches of science, as a memory of all that.

For thus, it was necessary for each specialist in this Branch, protecting and studying manuscripts and its ideas , events, and codified knowledge which written using ink of who made it an important heritage after years and decades ago since bringing it ,without disappear challenging factors of time and the futility of who read it , not only its achievement, but also maintenance and treatment, preceded by identifying the causes and phenomena of damage in order to remain compelling each tool or catalyst for deteriorate it , to benefit who means science, originality and substance.

All previous principals were motivation and a cause for the purpose of this study - analysis and experimentation and practice - try to find the causes of damage and genuine ways to get rid of them and treat them or chellate motivational tools to complete the destructive role at least according to what is available tools, methods, techniques, treatments, and in secure borders allowed in this matter.

To achieve all of these attempts has meant research study major causes leading to weakness and dishonor to the paper supports, as a result of oxidation of metallic- Gallo tannin inks and its implications for those inscribed supports, as well as study oxidation phenomena of the ink, especially fading and a low concentration of colored material, besides this to study treatment of damage caused by oxidation like the reduction of the metal ions using antioxidants, and revive the faded writings using natural materials not change the chemical composition of the original, with the assessment and codification of these methods by appropriate measurements, and citing studies and experiences in this regard.

The research involved than previous studies of related subjects, findings, and recommendations and a list of references in three parts consisted of eleven chapters , we can watch very closely to clarify as follows:

## Landmark study: Inks materials; properties, deterioration , investigation and analysis, and treatment of deterioration.

It is composed of two parts encompassed nine chapters as follows:

# First part:Materials & colourants of inks

## Chapter I: Substrates and instruments of writing

Has dealt with a simplified account of the most writing Substrates used to writing ,beginning of the use of ancient papyri, through Ostraka, Palm leaf, textiles, and paper in the middle and modern ages, manufactured from cellulose from various sources like plant worn rags, wood, cotton and other ... and, most important examples in museums, archives and libraries, as well as the most important tools used in the preparation of writing ink and saving it as ink stand ... or used for writing and codification as pens and stylus, with models of it.

## Chapter II: Black inks and writing materials

And in it a detailed account of the most important materials used for the processing of black inks in general, and the advantages and disadvantages of each type when used for filings and write, and structures derived from each type, unlike the distinction between different kinds, the most important mounts, which is renowned for its propensity to receive different types of inks, as well as the historical beginnings to be used for the purposes of writing, encompassing the following types of black inks:

* **Carbon inks**, processed from a pure carbon, including lamp black ink, Black soot, and Indian or Chinese ink..... And others.

* **Carbonaceous inks**, manufactured from organic or inorganic materials contained carbon in its chemical composition unlike sulfur and nitrogen ..., including sepia "squid" ink, and bistre ink.

* **Ink mixture** of carbon-base plus ferrous sulfate to prevent the physical instability of carbon ink, and figuratively is named iron carbon ink.

* **Metallic –Gallo tannin inks**, where they were monitoring all the materials of tannin (gall, sumac, the bark of chestnut....) and tannin Compounds (Gallic acid, tannic acid ... ..) derived from them, other than mineral salts (substances of vitriol of iron salts, copper, silver ....) used in processing inks, and quality of it according to the synthesis of tannin derivative or composite and a particular metal salt and other additives.

## Chapter III: Coloring - writing materials

A review of the materials of coloring inks at length, used for the preparation of coloring ink - so to speak - to codify and decoration of paper and the implementation of miniatures, together with the advantages and disadvantages of each material, the date used, degrees of color, chemical compositions, properties, and evidence used for this purpose and how to prepare the coloring ink amounts selected, and divided according to the nature of organic and inorganic mixtures and other (mixed), has been addressed as follows:

* **Red coloring materials:** non-organic materials, which contained the study: red ochre "hematite", minium (red lead), red vermilion (cinnabar or vermilion) ...., and red organic materials: cochineal, madder red, Brazil wood, logwood, and red anemones (Coquelicot red).

* **Blue coloring materials:** included from non-organic materials; Azurite, blue lapis lazuli or ultramarine, Prussian blue ... ..., organic blue

materials included blue indigo, and wild indigo (woad), and mixtures; Maya blue, and Seri blue.

*** Green coloring materials:** about them research deal from inorganic colorants; green salt or Patina verdigris, malachite green, Atachamite green, cobalt green, Green earth ... .., and from its organic colorants; Sap green, Buckthorn plant ..., as well as mixtures as arsenic mixed with indigo.

*** Yellow coloring materials:** which, as noted above research dealt with the study of non-organic materials: Ochre yellow, king's yellow (Orpiment), Realgar ..., and the most cited of the organic yellows: Saffron, and yellow Turmeric (curcumin) ... and so on.

* In the same vein, discussions dealt with the different types of **brown colorants** as raw and burnt umber (not organic), tannin brown ( organic) as well as a mixture of alum and cochineal. Also dealt with - broke clear - Types of **gold ink** from crushed gold after the dissolving it by one of the methods, and gold-colored ink ever was crushing minium and mixed with gum Arabic, the same approach inks gold goes silver inks are either of pure **silver**, or silver-color ink by mixing black ink with another white. Otherwise foregoing study mentioned item for the **white** pigments used for the preparation of white ink, including white lead, zinc white..... And so on.

## Chapter IV: Innovated and modern inks

this chapter discussed of the study, six types of inks, which innovated by Arabs and Persians and show developing skill of creators and manufacturers of it, which was discussed in terms of material constituents, method of processing, disadvantages and advantages, the date of use, and aspects of their use, and were as follows:

* **Travel ink** (tablets and Ink powders): has been confined to two categories: a category for black ink and perhaps the most famous is iron gallate dried in the form of tablets and powders and provide them with a solvent such as water and used for writing, and the other product in the same manner for processing and use of , except that the color of materials known (above) by color desired.

*** Sympathetic ink:** its scientific basis is to find solutions no color writes in the things that need to be secret, and then used other solutions to show later, in ancient periods inks used vitriol white (silver nitrate), and then wipe it with gall water as an example, and more recently For example, ammonia used as not visible ink shown by cobalt nitrate, other than the chemical reactions and ultraviolet radiation inks.

*** Lighting ink:** is read only in the dark, which consists of half pound of yellow phosphorus and eight pound of cinnamon, add phosphorus to the oil and heat the mixture slowly on a water bath until the mixing, use glass pen when writing.

*** Colour - Changeable ink:** groups of ink from a mixture plus a few other materials, and can change it to red or other according to the desire to separate bottles.

*** Modern inks:** a broad list were addressed included; nigrosine inks (aniline and nitrobenzene), Fountain - pen ink (of black nigrosine, fuschine

brilliant orange, yellow napthal yellow, or diamond green) typewriter inks (aniline blue, or minium according to the desired color), Inks for carbon paper (from the linseed oil+ methyl violet+ glycerol+ graphite), and innovative vehicle Synthetic inks, including vanadium inks, and nickel titanium yellow.

### Chapter V: Media & Solvents of inks

With the exception of the functions of media and solvents in the processing ink, and comparison between the two terms, reviewed in detail through the major items of materials and fluids as solvents and media for inks materials of different kinds, disadvantages and advantages, components, and aspects of their use, and were as follows:

*** Media:**

Which included the gums (gum Arabic, gum tragacanth ...), Glues (skin glue, cartilage & bone glue, etc.), and whole egg (Egg yolk & white).

*** Solvents:**

The discussion dealt with and about them other than the different forms of water (rain water, hard water, and rose water) other solvents are: wine fermented juice of fresh grapes, palm wine, dates, vinegar(acetic acid concentration of 6% or lemonade, or wine) , in addition to evidence of the use of ammonia, urine solvents for inks.

## Part II: Properties, deterioration, examination and analysis, and treatment of ink and paper

The study included in this part of four chapters are detailed as follows:

### Chapter I: Properties of inks materials and its media

This chapter attributes characteristics and behaviors that characterize the materials of inks and pigments, as well as its binding media, and then its disposal and its resistance to destructive mechanisms, which are exposed, as well as the cohesion, stability and diversity of permanence and stability and their susceptibility to engage in various chemical reactions, addressed the qualities and the following characteristics:

•**Properties of inks materials and its colorants:** the study included from properties of materials and colored inks; physical properties (density, refractive index, particle size, and strength of coating), and chemical properties (disposal of materials, and the impact factors of temperature, humidity and light in incidence, and the impact of functional groups in the composition of these materials on the viability and activity to accomplish this and incidence).

• **Physico-chemical properties of media for inks and pigments:** tenor has been discussed for two things: first, in their liquid (rheological properties, stabilization of pigments, wetting agents, and the absorption coefficient of oil and the right concentration), and the second in the solid state (Genesis color film, physical change, chemical reaction, mechanical properties, and optical properties).

• **The forces of cohesion of the color granules:** The discussion touched upon the various forces that bind together particles of the color of the hand and with its support bearer on the other hand, its presence in the material without the other, as well as control over the extent to which these materials can be damaged and its entry in the different chemical interactions ,and its persistence and stability, which are: covalent forces, the forces of polarization, ionic forces, hydrogen binding forces, and Van der waals forces.

• **Good characteristics of inks and pigments:** It has been dealt with qualities that must be met in inks to become classified as good, including black ink, and inks of coloring materials, including: vulnerability of the application, chemical inertness, resistance to color change, color darkness, consistency of friction, viscosity and medium speed of dryness..... etc.

## Chapter II: Physico - chemical deterioration of inks and its influence on paper

It discussed the mechanics of the various different types of damage to inks, without being subjected to explain and dwelling on the factors leading to the emergence of these interactions has little, and it has been reviewing the following operations:

• **Deterioration mechanism of metallic-Gallo tannin inks:** which included a discussion of acidity inks by formation of sulphuric acid by the components of the ink itself and its impact on paper supports written by it, as well as discuss the oxidation of this ink by ions mineral in the composition of it and incentive for these activities ,like Iron & copper ions through "Redox" and "Hamilton - Fenton," addition to reviewing the various oxidation processes, and the interaction of components of the inks with the components of paper, and phenomena of damage resulting from each of those operations.

• **Damage of carbon and carbonaceous inks:** With regard to that issue research was presented to two of them: the first is specialized in physical therapy for the damaged carbon ink, restricted to the appearance of corruption can not be overlooked is the outside of the components of place"bleeding", and the second damage of carbonaceous inks, which handles damage resulting from the contain the inks on tar or bitumen, and the resulting fading of bistre ink, as well as by light.

• **Damage and fading of coloring inks and harm for paper:** This item included damage to several different pigments, which vary due to different chemical composition of a substance to another, and perhaps most important as reported by research in this context that the destructive mechanism of famous green known Verdigris or salt green, which is similar in its way and behavior to acidity of metallic-Gallo tannin inks mentioned above, in terms of impact of burning written or illuminated paper...., other than to review the destroying interactions by the coloring inks contain other active groups as a sulphate, nitrate ...., and manifestations of each type of damage and its implications for paper substrates written by such materials.

## Chapter III: Examination and analysis of inks and

**paper**

Discussions dealt with in this regard, four major items are:

• **Study the chemical composition of writing materials and determine the types**: extensively discussed methods, techniques and materials through which to identify different types of inks and components that defined in qualitative and quantitative form, and the possibility of use in this field, making it clear whether destructive or unfair or not to ink samples being studied, and contained in two items: chemical methods using dyes and reagents, and means of physical methods (tools) using micro-technology, and the various analytical techniques.

• **Age Estimation of manuscripts inks:** Thesis has been adopted in dealing with that point on two axes: factors influencing the estimate age of inks (the case of the ink, chemical composition, paper type used, and storage conditions), and methods and estimation techniques included physical methods as analysis instruments and microscopic technique (microscope Drills scanner), and chemical methods using the above-mentioned reagents, and the latter methods is destructive and depend on reducing the ink and interaction.

• **Reading faded and charred (burnt) documents and detection of fraud manuscripts**: research involved the issue as confined to physical methods (imaging by infrared light, reflected photography, sodium light photography .... etc.) to read the faded and charred documents, but reviewed the types of means: physical tools (micro – laboratory technique of XRF, methods to estimate the age...., etc.), and chemical methods (Chevallier test, and ink reagents), with a review of flaws in any of them and the features that distinguish them .

• **Study techniques of inks deterioration and its effect on paper:** this study singled part for methods and techniques needed to achieve this through four themes: **1 - Methods of study of color change (fading) for writing materials, a three;** methods of color characterization using devices operating in accordance with the CIE Lab system and electrical measurement, micro-technical description and measurement of intensity of color, and using analytical techniques and advances through the ratios of sulfur and iron for example .**2 - Study of the stability of the inks and their sensitivity to liquids and solutions( cationic or anionic), 3 - methods of studying the acidity and oxidation damage to those from inks**, including physical ways and chemical materials, so you can get on observations of color using color indicators to measure the acidity and oxidation rates using chemical methods or certain indicators as change in metal ions content or in the amount of functional groups of paper supports using both of physical and chemical methods, **4 - measurement of mechanical properties of acidic and oxidized paper** such as exploration endurance, and tearing endurance ....., using physical means only, given indications of the extent and vulnerability of the paper damaged by the acidity and the oxidation of metallic-Gallo tannin inks.

## Chapter IV: Treatment & conservation of acidic and

## oxidized paper due to inks

Research involved in dealing with the subject of this chapter on the themes of the various special treat damage caused by the different inks were incorporated into two important studies:

**Treatment of deteriorated writing materials:**

The treatments included three major items:

• **Fixation of inks and writing materials:** it has been reviewed the various fixatives to suit every type of material and colored inks, for example, polyvinyl alcohol suit graphic art and coloring inks, while calaton CA or CB is suitable for most of the metal and colored inks, and mesitol NBS for dyes of anionic sensitive inks as methyl violet and seal inks, with defects and the features and methods of preparation and application of stabilizers as well as the appropriate concentrations of each case.

• **Consolidation of weak inks:** with same previous trend appropriate consolidants reported for each type of ink as methyl cellulose is used together with gelatin to consolidate gouache color in paper drawings and some other coloring materials, and Paraloid B 72 is used to strengthen the various pigments such as hematite red as examples of that.

• **Reviving faded writing inks:** The materials included talk about refreshing that not change the chemical composition of the metallic- Gallo tannin inks such as tannic acid, Fermented gallol tincture, and another change of composition as iodine fumes, and ammonium sulfide, and a third suit coloring material and charred documents, other than the methods of processing, defects and features ... etc..

**Treatment of paper damage caused by the acidity and the oxidation of ink:**

As well as processing methods, defects and features, methods of appropriate application and treatment for cases of damage, without regard to other materials used for various treatments, the discussion dealt with the study and evaluation of the following treatments:

• **Aqueous treatments:** included ways of removing the acidity(deacidification), reduction of metal ions and carbonyl groups from paper, treatment with anti-oxidants (chelating agents) of phytates and others.

• **Non-aqueous treatments:** (removal and neutralization of acidity using materials such as magnesium acetate).

• **Other Treatments:** included chelating agents (anti-oxidant compound)+ deacidification compound, electrolysis (reduction), and the removal of acidity through mass - deacidification.

• **Consolidation of paper:** thesis discussed manual restoration and mechanical restoration, strengthening using solutions and polymers, parylene consolidation, and graft copolymerization as methods for consolidation of acidic and oxidized paper.

## Research methodology and procedures:
## Experimental study and application of research

# results

Thesis examined in this study, the experimental laboratory study to the issue of oxidation of metallic-Gallo tannin inks paper supports and their impact on paper
supports and inks color, as well as appropriate treatments for the manifestations of damage resulting from the ink to paper with both measurements and analysis to monitor the efficiency of methods and materials used, and the successful application of the results to similar situations for the archaeological samples. The research involved all of this in Part III of the study, which consisted of two chapters:

## Chapter I: Experimental study.

This chapter included four studies in his experimental laboratory study:

**• The primary study: a study of discoloration of metallo-gall ink**: .

The study assesses and analyzes the impact of dry thermal ageing and stimulated by metal ions on the color of the ink yielding fading or not, and the role of other components of the ink in discoloring and the different colors of ink of each recipe, the use of color characterization measurements by CIE Lab system to monitor the degree of fading and contrast, as well as ways to prepare combinations of ink for paper supports for this study.

**• The second study: the impact of thermal oxidation on the whiteness of the paper:**

In that study has been discussing the impact of thermal oxidation using dry thermal ageing on degrees of paper whiteness as a separate study and measure these values by system of measurement used to measure the degree of ink fading, as an evidence of components role of paper in the amount of oxidation of those affected with the assessment and analysis of results received in this regard.

**• The third study: The effect of thermal oxidation of iron-gall ink on mechanical properties of paper:**

Other than to talk about ways to prepare samples of inked paper using various recipes, ageing test, measurement techniques and differences of those properties and to evaluate and analyze the results, discussions dealt with the impact of oxidation of iron-gall ink on mechanical properties of paper, the activity of metal ions in catalyzing oxidation of paper cellulose and weaken it, as well as the emergence of carbonyl groups at the expense of reducing the hydroxyl groups of the composition of cellulose and then weakness of paper supports and make it fragile, difficult to be addressed, and the implications of the damage incident, which was invoked in this regard include:

- Measuring the change in enjoyed by the paper from mechanical properties of inked paper before and after the ageing, which included the measurement of bursting force, tearing resistance, and tensile strength.
- Chemical tests such as testing amyloid compound in the oxidized paper, as well as the degree of its water absorption before and after oxidation.
- Change in the content of the paper from the carbonyl groups, as they represent an increase from oxidation of inked paper thermally aged unlike

paper is not aged.

• **The fourth study: Revival of faded metallo- gall inks and using antioxidants:**

The study included in this case, discussion of materials which can be used to revive metallic-Gallo tannin inks are used to writing supports of paper manuscripts, takes into account the selection of materials not change the chemical composition of the original ink faded, like the natural extracts of the materials already used for the preparation of this type of inks , used either alone or with another material, and in both cases, added to half of the quantity of anti-oxidation of calcium caseinate attempt to restrict the activity to stop the resumption of metal ions to catalyze the oxidation process that led to the fading ink currently and in future, and the study has come to the conclusion that used antioxidant have a major role in protecting the ink from the affected operations of oxidation catalyzed by metal ion, and resulted in the concentrated tannic acid solutions tannic acid, concentrated myrobalan,gall and tannic acid solutions, and mixtures of tannic acid & myrobalan gave the best results in terms of tone, coating strength, color energy, , and when it is used for the rehabilitation of faded inks, but it needs to further study and evaluation to make it useful .

## Chapter II: Application

Study also discussed the application of the results of the successful outcome of the experimental studies mentioned above in the treatment of deterioration oxidation of iron inks used in writing the manuscript and the codification of the subject of the application of colors to fade arrived so completely disappeared in some pages, and treatment for those of the weakness of manuscript paper and change the color , and were as follows:

- **Reduction of metal ions from the paper by boiling**.
- **Deposition of alkaline reserve in paper with a solution of calcium hydroxide.**
- **Treatment restriction factors (antioxidants) by using the material** for the deposition of reserve anti-oxidant in the future by chelating iron ions and prevent them from stimulating any oxidation can occur later.
- **Revival of faded writings with a concentration 20% of tannic acid solution**.

Unlike the foregoing has been conducting archaeological documentation of the Application manuscript and to study the chemical composition of paper and manuscript ink and the measurement of oxidation and Acidity incident with damage, and monitoring others as spots and etc. ...., in addition to the following points:

- **Removing binding of manuscript** and prepare it for other processors.
- **Fixating the writings of the manuscript** for its sensitivity to the treatments of water, chemical solutions and cleaning materials used.
- **Remove and clean the bad effects of binding and different spots** of pages of the manuscript, before starting to conduct oxidation and acidity treatments made in advance.
- **Restoration and renovation complete loss in the margins of**

**manuscript** paper and complete the holes are scattered in it, and repair tears.

This, thesis concluded the discussion results, which were obtained for the theoretical, experimental and applied chapters, and to make recommendations that emerged from this debate, then Arab and foreign references made in end of study which from it, all the studies, experiments and applications taken.