

Cairo University
Faculty of Archaeology
Conservation Department



Experimental and Applied Studies on the Effects of Selected Remedial Conservation Treatments on the Chemical and Physical Properties of Silver Gelatin and Chromogenic Prints

A thesis presented to
Cairo University/Faculty of Archaeology
In fulfillment of the requirements for the degree of
Doctor of Philosophy in Conservation of Antiquities

Submitted by

Maha Ahmed Ali Ahmed
Assistant Lecturer at the Conservation Department
Faculty of Archaeology - Cairo University

Supervisors

Prof. Dr. Mona Fouad Ali

Professor of Conservation
Former Vice Dean
Former Head of the Conservation Department
Faculty of Archaeology - Cairo University
Principle Supervisor

Prof. Dr. Mohamed Osama Saker

Professor of Photography
Former Head of the Photography,
Cinematography and Television Department
Faculty of Applied Arts/Helwan University
Co-Supervisor

Prof. Dr. Sawsan Sayed Darwish

Professor of Chemistry
Conservation Department
Faculty of Archaeology-Cairo University
Co-Supervisor

Cairo, May 2016

In the name of Allah, the Most Compassionate, the Most Merciful...

“Learn as if you were to live forever”

Mahatma Gandhi

ABSTRACT

Photographs are an essential part of the Egyptian cultural heritage both for their artistic and documentary value. The existence of large quantities of photographic records in archives and libraries has created problems of preserving these records that are, to some degree, comparable to conventional paper objects, but also have special requirements due to their particular nature. A major objective of conservation treatments is to increase the physical and chemical stability of the object being treated. Cleaning and consolidation treatments often form a significant part of the stabilization process. Many studies have dealt with these remedial conservation treatments; however, photographs continue to require educated choices about their conservation and care, particularly since there are no established parameters for the use of these treatments in this field. The research included in this thesis addressed these two major photograph conservation treatments via theoretical, experimental and practical approaches. The study was only applied on silver gelatin and chromogenic prints since they are the classic forms of black and white and color photography, respectively. Evaluated cleaning treatments include: mechanical cleaning (i.e. vinyl erasers), aqueous cleaning (i.e. distilled water, distilled water and ethanol 1:1), and solvent cleaning (i.e. acetone, ethanol, isopropanol, and toluene). The study further evaluated the effectiveness of four consolidants in reinforcing damaged gelatin binder in black and white silver gelatin prints, three of which are frequently used by conservators to consolidate flaking binders and paint (i.e. Klucel E, gelatin, and Funori). And a new consolidation method with gelatin nanoparticles (GNPs) was introduced and evaluated. Changes promoted in the photographs, as a result of these treatments were measured and registered in order to evaluate the benefits and potential problems of each treatment and estimate if they can be used without unacceptable change in the original image now and in the future. The following investigation and analysis methods were used for the evaluation process: USB microscope, Atomic force microscope (AFM), densitometer, spectrophotometer, Fourier transform infrared (FTIR), pH of the binder, and dynamometer. The applied section included the conservation of El-Shenawy Palace photographic collection consisting of five black and white prints documenting one of the most valuable structures of architectural heritage in the city of El-Mansoura, El-Shenawy palace. The collection was studied using visual inspection, SEM-EDX, FTIR, XPS, pH measurement and fungal testing. The conservation of the photographic collection was effectively performed following several interventive treatments: disinfection treatment, mechanical cleaning, minor solvent cleaning, removal of previous secondary supports, deacidification, consolidation and reunification of paper supports, minor retouching, and finally framing.

KEYWORDS

Silver gelatin prints

Chromogenic prints

Surface cleaning

Consolidation

DLS

SEM

TEM

AFM

FTIR

Color change

SUMMARY

Photographs are an essential part of the Egyptian cultural heritage both for their artistic and documentary value and as a record of the history of photography, as a technique as well as a form of artistic expression. Due to their significance, the interest in photographs is growing worldwide and institutions are making great efforts to increase access to photographic collection, as well as preserve originals for future generations. The threats to photographs are many. They are very sensitive to fluctuating temperatures and relative humidity, frequent handling, air pollution, light, and improper storage and display.

Deteriorated silver gelatin and chromogenic prints present a very challenging problem in the conservation field due to their complex nature. Since photographs are in high demand due to their numerous applications: for study and research, publications, exhibitions, etc., they often suffer from physical and chemical damage from improper and frequent handling. Particulates, which may be greasy, grimy, abrasive, and chemically or biologically active, settle on shelves and on collection materials and create dust that is spread to other materials when they are handled. Another serious problem in photograph conservation is gelatin binder decay. Severely deteriorated gelatin photographic prints are a very common, complex, and challenging problem in conservation. Considering the varied structure of a silver gelatin print and the difference in composition of the layers, it is unsurprising that flaking or cracking occurs.

Unlike other paper objects, photographs have special conservation requirements due to their complex and unique nature. Therefore, this thesis mainly aimed at assessing the current conservation practice of cleaning and consolidation of silver gelatin and chromogenic prints, techniques adapted from paper conservation. Many studies have dealt with these remedial conservation treatments; however, photographs continue to require educated choices about their conservation and care. It further evaluates the use of gelatin nanoparticles in the consolidation of damaged photographic binders. The research included in this work consists of eight sections dealing with both black and white developed-out silver gelatin prints and chromogenic prints.

1. Introduction

This section is intended to provide a brief overview of how photography was introduced to Egypt and it also address the importance of safeguarding historical

Summary

photographs. It further highlights the main research problem which is to what extent do consolidation and cleaning procedures affect the surface of the photographic binder altering its sheen and state of preservation? And to what extent does different degradation affect treatment selection?

2. Aims of Research

This section discusses why in particular was the previous research problem selected and also lists the general aims of the present work.

3. Literature Review

Several studies dealing with photograph conservation, particularly cleaning and consolidation treatments were pointed out in this chapter.

4. Background

This section is divided into six main sections. *Section 4.1* discusses the history of photography and the stages of its development. Photography was invented with the progress of two distinct scientific processes combined together (i.e. optical and chemical processes) and the contribution made by so many scientists, researchers, and artists. When photography was first introduced in the early 19th century, it brought amazement with its ability to capture the true living world. Soon, inventors and photographers in America and Europe invented many processes. However, despite the wide variety of black and white photographic processes, they are all missing one vital element, and that is color. Modern color photography's basic principles were first demonstrated in an experiment related to the theory of color vision by James C. Maxwell in 1861. The first commercially successful color process was the Lumière Autochrome process introduced in 1904. The Autochrome process was soon followed by other types.

Section 4.2 deals with the chemistry and technical background of black and white and color photography. Photographic chemistry involves the study of the nature of light sensitive layers used, of the changes induced in them by the action of light, of the nature of development, and of the properties of the final image. Understanding the nature of the chemicals involved in the different stages of photography will lead to better understanding of why and how silver gelatin and chromogenic prints deteriorate as well as help make correct conservation and preservation choices.

Summary

Section 4.3 is intended to provide a basic understanding of the structure of silver gelatin and chromogenic prints and their characteristics. The complexity and multiplicity of elements that make up silver gelatin and chromogenic prints, give them a unique layer structure that is to a large extent responsible for their long-term stability characteristics. Consequently, it is extremely essential to consider the nature of each element to better understand their role in the deterioration cycle.

Section 4.4 focuses on the different deterioration agents and mechanisms affecting the permanence of silver gelatin and chromogenic prints. The forms of damage found in each type are well illustrated.

Section 4.5 is dedicated to conventional cleaning and consolidation treatments applied in photograph conservation. Discussed cleaning treatments are surface cleaning, aqueous cleaning, solvent cleaning, ultrasonic cleaning, and enzyme cleaning. Consolidation using gelatin is the typical treatment used with damaged photographic binder.

Section 4.6 lists the different studies dealing with accelerated aging tests. There are several international and national standards, such as:

- ISO-standards from the International Standards Organization.
- ASTM-standards from the American Society for Testing and Materials.
- ANSI-standards from the American National Standards Institute.

5. Experimental Section

This section examines the effects of cleaning treatments on the properties of silver gelatin and chromogenic prints. The following cleaning treatments were investigated: dry cleaning (i.e. vinyl erasers), aqueous cleaning (i.e. distilled water, distilled water and ethanol 1:1), and solvent cleaning (i.e. acetone, ethanol, isopropanol, and toluene). The study presented here is inspired from a project developed at the Kent Workshop (1998). Furthermore, the effects of selected consolidation treatments on the properties of silver gelatin prints were also evaluated. Tested consolidation treatments included Klucel E, funori, gelatin, and gelatin nanoparticles. The tests are based on the consideration of the following criteria: changes in surface characteristics through digital imaging and atomic force microscopy (AFM); changes in optical density through densitometric measurements; changes in the chemical structure of the gelatin binder through attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR),

Summary

changes in color and gloss through spectrophotometric measurements; changes in pH of the paper support and the binder; and changes in the mechanical properties of paper. Data obtained from naturally and artificially aged samples were compared with those of the control samples. This study consists of two main sections as follows:

- Section one: preparation of gelatin nanoparticles (GNPs).
- Section two: scientific evaluation of cleaning and consolidation treatments.

6. Case Study: Conservation Treatment of a 20th Century Photographic Collection, Mansoura, Egypt

A private collection was selected for this study. The collection consists of five black and white photographic prints documenting one of the most valuable structures of architectural heritage in the city of El-Mansoura. This section describes the forms of deterioration present in the collection through documenting the preservation status of El-Shenawy palace photographic collection. It also describes the conservation treatments carried out to prolong their lifespan. Prior to treatment, the photographs were characterized and studied by visual inspection, digital camera, Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Scanning electron microscope (SEM) provided with an energy dispersive X-ray spectroscopy unit was used to identify the components of the photographs, assess their preservation status, as well as study the morphology of the paper fibers in both the primary and secondary supports. Microbiological studies and pH measurements were also carried out. The results of the investigations revealed that image silver in most cases suffered from sulfiding, the secondary supports suffered from both oxidation and hydrolysis, and the gelatin binder also showed signs of degradation. Based on the results of previous studies, the following interventive conservation procedures were selected and carried out: disinfection, cleaning, dismantlement of the secondary support, deacidification, tear mending and compensating for losses, remounting, retouching, and rehousing.

The thesis ends with the following sections:

7. Conclusion

8. Recommendations and Future Work.

TABLE OF CONTENT

Keywords	I
Summary	II-V
Table of Content	VI-X
List of Figures	XI-XXIX
List of Tables	XXX -XLI
Abbreviations	XLII-XLIII
Acknowledgments	XLIV- XLVII
Dedication	XLVIII
1. Introduction	1-2
1.1 Overview	1-2
1.2 Description of the Problem	2
2. Aims of Research	3
3. Literature Review	4-9
4. Background	10-141
4.1 History of Photography	10-35
4.1.1 The Beginning of Photography	10-15
4.1.2 Transition to the Era of Modern Photography	15-19
4.1.3 Transition to the Era of Color Photography	19-35
4.2 Basic Principles of Photographic Chemistry	36-68
4.2.1 Light-Sensitive Materials	36-50
4.2.2 Silver Halide Technology	51-68
4.2.2.1 Photographic Processing Chemistry	54-68
4.2.2.1.1 Black and White Processing Chemistry	55-61
4.2.2.1.1.1 Development	55-58
4.2.2.1.1.2 Halting Development	58
4.2.2.1.1.3 Fixation	58-60
4.2.2.1.1.4 Washing	60-61
4.2.2.1.2 Chromogenic Processing Chemistry	61-68
4.2.2.1.2.1 Development	61-64
4.2.2.1.2.2 Halting Development	64
4.2.2.1.2.3 Bleaching	64-65
4.2.2.1.2.4 Fixation	65
4.2.2.1.2.5 Washing	65
4.2.2.1.2.6 Color Stabilization	65-68
4.3 Structural Analysis of Silver Gelatin and Chromogenic Prints	69 - 85
4.3.1 Structure of Silver Gelatin Developed-out Prints	69-81
4.3.1.1 Final Image Material	69-70
4.3.1.2 The Image Binder	70-72
4.3.1.3 The Primary Support	72-77