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A TECHNICAL STUDY OF RED PAINTS IN THE RETOUCHING LAYER OF SOME WET-COLLODION GLASS PLATE NEGATIVES OF GOLESTAN PALACE PHOTO ARCHIVE

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ABSTRACT

This study presents a part of a research project on retouching wet Collodion and dry gelatine glass plate negatives from Golestan Palace photo archive in Tehran, Iran, dating from the mid-19th century. The collection belongs to Qajar era. This is a case study on the use of red paint in retouching wet collodion glass plate negatives and aims to help the understanding of retouching material and their application. Red paints in four retouched negatives, and also their binder, identified in this study by means of, micro Fourier transform infrared (µ-FTIR), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and stereo microscopy technique. Elemental analysis performed with (SEM-EDS) revealed the presence of Lead (Pb), and Iron (Fe) elements in the paint. Thus, red Iron & red Lead pigments were identified as the red paints. The results confirmed by micro Fourier transform infrared (µ-FTIR), and a natural resin (probably gum Arabic) is identified as the binder of all paints as well. Red Lead, is realized as a paint to cover the boundaries, create more brightness, and as a binder to adhere masking papers, to the intended areas. Red Iron, is also found as a paint to correct emulsion defects and, make a perfectly clear and clean sky or background. Apparently, all these choices have been made consciously. It is believed that this study will contribute much to better understanding of retouching materials and the need to preserve them.

Keywords
Retouching; Photography; Collodion; Glass Plate Negatives; Red Paint

1. INTRODUCTION

The invention of photography as a technological advancement was presented at the Academy of Sciences in Paris, in 1839, and not a long time after, in 1842 the camera entered Iran, during the Qajar Dynasty (1785-1925) [1,2].

Photography in 19th century was a series of technical and practical challenges with long-time exposure needed, and lots of shortcomings. To overcome these and other weaknesses an extra-photographic contribution that consisted of several skills, techniques and materials, was required. Retouching has been an integral part of photography almost since of the beginning of photography.

In the days of glass plate negatives, retouching was still a need. Since collodion glass plates were not as sensitive as late gelatine glass plates and they were suffering from more defects, the number of retouched plates, the variety of retouching techniques, and materials was greater in gelatine types. However, there was a subtractive technique (performed with a knife, scalpel, needle or any sharp object), that was specific to gelatine emulsions and was never used on collodion glass plate negatives [3].

Today's retouching has nothing to do with the 19th century practice of elaborately recreating negatives with watercolor, gouache, pencils, and abrasives to remove unsightly features of the image, or change the background or the subject [4].

Glass plate negative retouching in 19th century was a set of manual processing techniques used by the photographer to correct the results of imperfect spectral sensitivity, poor technical manipulation and improving the general appearance of the subject.

This was done by covering defects such as scratches, anomalous specks, or blocking some unwanted objects in the image, as well as covering areas with a lack of emulsion (in the corners of glass plate negative, which is common in collodion types). Retouching was also being used to improve or modify the composition, contrast, proper lighting, framing of the subject or changing the artistic expression of photographer.

There have been always different approaches to retouching; not only in terms of its legitimacy and relationship to other arts, but also in terms of techniques and materials. This can be said based on the on the comparison Iranian and also non-Iranian old manuals.

For example, to correct emulsion insensitivity defects in glass plate negatives, streaked and dirty backgrounds, and to intensify certain parts of the image, in different old manuals, different materials and techniques are recommended [5-12].

Despite the numerous retouching detractors, retouching of glass plate negatives became an extended practice and an important part of the work of 19th century photographers, bringing the fashion approach and extending itself as a more part of the studio work. This ability, although very common, took a long time to be revealed in a written way, because it was only possible in secret, without being admitted by the majority of professionals who were using it. Therefore, it is a good reason to study the techniques and materials used in retouching.

The principles and details of retouching can be found not only by reading old manuals, but also by observing the negatives themselves under different lights (reflected light: Standard, Specular, and raking and also transmitted light), comparing them with their positive versions, reading scratched notations in the emulsion, as well as the written information on the original enclosing paper sleeves or envelopes [13].

But one of the most important measures that can be taken to identify retouching materials is to study them through scientific analysis. Despite many recent articles on retouched glass plate negatives [13-16, 3 & 6], there are still few studies have been conducted to identify retouching materials, especially on collodion glass plates, as most of the studies mentioned are conducted on gelatine dry plates.

Pictorial reservoir of Golestan Palace which is located in Golestan Palace (inscribed on UNESCO’s world heritage list in 2013) Tehran, the capital of Iran. Golestan Palace photo archive is regarded as the second-best reservoir of old photographic materials after the album house of the Royal Museum of Britain and can be considered as one of the best resources for historical research of the time. This reservoir contains 1040 photo albums (nearly 42500 photos), more or less intact, about 9000 glass plates (collodion and gelatine), almost all taken by famous Iranian photographers who lived from 1789 to 1925, as well as many other different photographic materials including motion pictures, cameras and so on.

Glass plate negatives are the oldest images in this collection. The information presented here focuses on some collodion glass plate negatives (CGN) retouched with red colors which is part of the sub-project of studying collodion and gelatine retouched glass plate negatives, from the main project on study of glass plates of Golestan Palace.

2. MATERIALS AND METHODS

2.1 Study object

The objects of study were a selection from Golestan Palace photo archive collection glass plate negatives prepared at 19th century, codenamed of GP005379, GP005375, GP005378 and GP005378. The selected items consisted of two 18 × 24 cm negatives (GP005375 and GP005261) and 13 × 18 cm negatives (GP005379 and GP005378).

All four negatives were selected from the Golestan Palace photo archive collection, and were manufactured in Iran. They were all retouched in different shades of red color, and different types of retouching. The retouching was in the form of painted masking paper, red opaque paint in dark and light shades and tincture in dark red (Figure 1). The first three (Figure 1. (a, b, and c)) are retouched on the emulsion side, there is almost no retouching on the glass side, and the last (Figure 1. (d)), is retouched only on glass side.

Figure 1 – Two different red colors used in retouched collodion glass plate negatives under reflected: on the glass side; a) GP005379; b) GP005375 (1883); c) GP005378; & on the emulsion side: d) GP005261: (Photographer Agha Reza 1870)

The application of dark and light red color in selected samples, was almost similar to the rest studied retouched collodion glass plates in the collection.

Image of GP005379, is the image of Haji Musa Khan, as it was written on the negative. Image GP005375 depicts the pool house in the mansion of Yar Mohammad Khan Soham al-Dawla Bojnurdi in Bojnourd, belonging to 1883. Image GP005378, is the image of Khosrogerd Minaret, but no specific date or photographer is available. The photographer of image GP005261 is Agha Reza, and the image is related to the year 1870.

In the first three images (Fig.1; a, b, & c), two shades of red colors were used to retouching the image. In images GP005379 & GP005378 (Fig.1 a & c), light red color was used to draw the outlines, but dark red color was used for the background. According to what was seen on negatoscope in these two images, the areas painted in dark red color was more transparent than in bright red color. Image GP005375 was outlined in bright red color, and dark red color was used to overcome the defects of emulsion due to scratches in some parts. In the last image (Fig.1; d), dark red color was used to cover the defects resulting from scratches, of the emulsion.

2.2 Methodology

A set of minimally invasive analytical techniques was developed to identify the red paints, and their binders, if any.

The methodology included observations using optical microscopy (OM), chemical evaluation by Field Emission Scanning Electron Microscope-Energy-Dispersive X-ray Spectroscopy (FE-SEM-EDS), and chemical evaluation by Fourier-transform infrared spectroscopy (FT-IR).

Most samples were collected from the back of papers adhered as masking papers to the glass plates or from the damaged parts of retouched parts of the plates.

2.3 Instrumental

Stereo microscopy

Leica Wild Heerbrugg M8 stereo zoom Microscope, made in Switzerland, with maximum 50X magnification, was used to study the texture and details about the paints.

µ-Fourier-transform infrared spectroscopy (µ-FTIR)

µ-Fourier-transform infrared spectroscopy (µ-FTIR) was used to identify binder of paints, if any, and to study the potential presence of mineral compounds with a complex anion functional group. This method is not only applicable for the minimum amount of the sample, but also enjoys suitable levels of speed, precision and accuracy and is not expensive. Analyses were performed using a Nicolet 510P spectrometer with IR microscope (MCT/A detector cooled by liquid nitrogen). Interferograms were collected in 64 scans, at a resolution of 4 cm^{-1} in the spectral range 4000–650 cm^{-1}, in transmission mode.

Due to many advantages, μ-FTIR has become an essential analytical tool available to cultural heritage scientists:

1. Relatively fast and simple to use: Little or no sample preparation required for spectral acquisition.
2. Sensitive method that requires very little sample.
3. Non-destructive or micro destructive.
4. Sample manipulation under magnification
   - Isolate areas of interest for interrogation
   - Work with very small samples
5. Multiple sample environments: Samples in the form of liquid, gas, powder, solid, or film can be tested

Field Emission Scanning Electron Microscope Energy-Dispersive X-ray Spectroscopy (FE-SEM-EDS)

Due to the small amount of the samples, Field Emission Scanning Electron Microscope (FE-SEM) with high magnification and separation was used for elemental analysis. Developed by Czech company, Tescan Mirall, the instrument is equipped with advanced Energy-Dispersive X-ray (EDS) features for semi-quantitative element analysis. The microscope used is a field emission that enjoys much higher field depth and separation capability compared to the ordinary scanning electron microscope. The magnification of this microscope is 700,000 times (700,000X).

3. RESULTS AND DISCUSSION

3.1 Stereo microscopy

Visual examination and morphologic evaluation were performed with a precision wire-account magnifier and a stereo microscope to obtain more in-depth information on damages, emulsion abrasion, discolorations, and some other details.

Dark red paints were detected with an opaque look, and not very fine texture, almost intact, except some areas with finger prints and little abrasion and scratches (Figure 2).

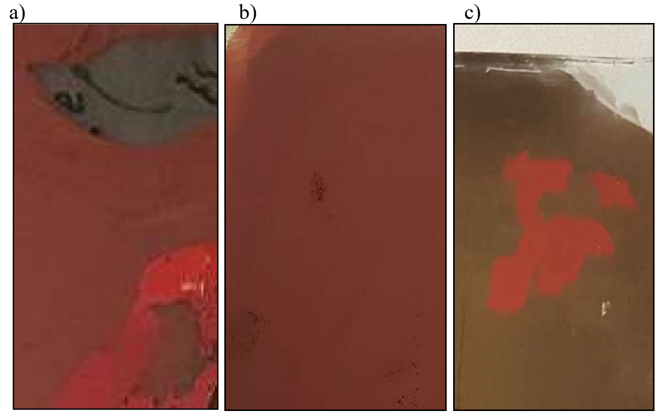

Figure 2 – Dark red almost intact paints used in retouched collodion glass plate negatives on the glass side; a) GP005379; b) GP005378; & on the emulsion side: c) GP005261

Light red paints appeared with an opaque look, dense and fine-textured, and good hiding power. Scratched, peeled, and abraded areas, as well as remnants of retouching papers were also seen in various parts of the paints (Figure 3).

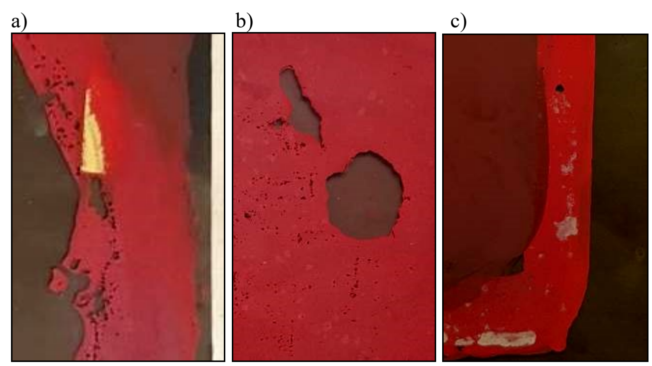

Figure 3 – Light red damaged paints with remnants of peeled masking paper used in retouched collodion glass plate negatives on the glass side: a) GP005379; b) GP005375; c) GP005378

Considering this fact, and extra papers found in the enclosures of these glass plate negatives, it was realized that almost all of bright red color painted areas, had been covered with the paper. While no sign of paper coverage was observed in the areas that were painted with dark red color.

Obtained details helped to present three hypotheses for further studies:

1. Given that red lead, as a common red color used at that time, may darken and turn brown due to the formation of brown lead dioxide in result of exposure to humidity and light [17 &18], it can be hypothesized that red lead is the only red color that had been used, and darkened in uncovered parts due to the exposure. However, a clear gap and sometimes overlapping (figure 2: a) of two shades of red colors (dark and light), was seen under microscope. Given this fact and given that the red lead pigment in the oil binder would be fairly permanent and also has good hiding power and creates relatively opaque colors in this media, another hypothesis is presented:
2. It is possible that these two different shades of red color have same pigment but different binders.
3. The last and the most probable assumption is that the two different shades of red color, were chemically different from the beginning.

Therefore, to prove any of the aforementioned hypothesis, further analysis was needed.

3.2 Field Emission Scanning Electron Microscope Energy-Dispersive X-ray Spectroscopy (FE-SEM-EDS)

The EDS elemental analysis for light red paints confirmed the presence of Pb atoms in all light red paints (Fig. 4: a, b & c) and Fe atoms in all dark red paints (Fig. 5: a, b, c & d), as the main component. This result is consistent with the last hypothesis.

Based on the EDS elemental analysis for light red paints (Figure 4), Lead (II, IV) oxide, 2PbO.PbO_2 (historically, Pb_3O_4), more commonly known under the name "Red lead", identified as the light red color compound used in the studied retouched glass plates. However, sample GP005375 is more contaminated than two others (i.e. sample GP005379 and GP005378).

Red lead pigment which was also a favourite of Persian illuminators, is thought to have been one of the first artificially produced pigments, but due to its toxicity and discoloration, it is no longer manufactured for artists. Red lead is liable to discoloration in the presence of air pollutants such as hydrogen sulfide. Red lead may photo-oxidize, in presence of humidity and light, and discolor to a light pink or darken to a brownish red, depending upon the environmental influences. For this reason, it is recommended not to use in watercolor painting [19-22].

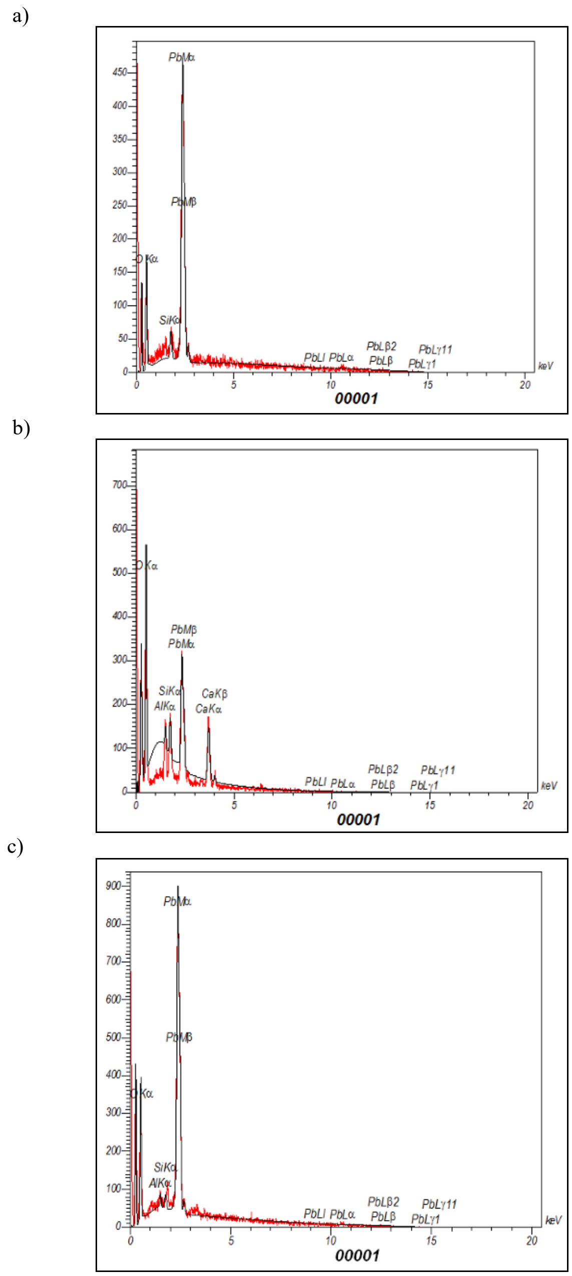

Figure 4 – EDS analysis on light red paints of; a) GP005379; b) GP005375, and c) GP005378, showing the presence of Pb atoms as the main colorant component.

The EDS results for dark red paints (figure 5), confirmed that the main component of dark red paints is Fe atoms. As a result, all the dark red paints are kind of Iron red color, (iron (III) oxide: (Fe_2O_3)), probably red bolus ($Fe_2O_3 \cdot xSiO_2 \cdot yAl_2O_3$) or red ochre ($Fe_2O_3$), with some fillers or impurities.

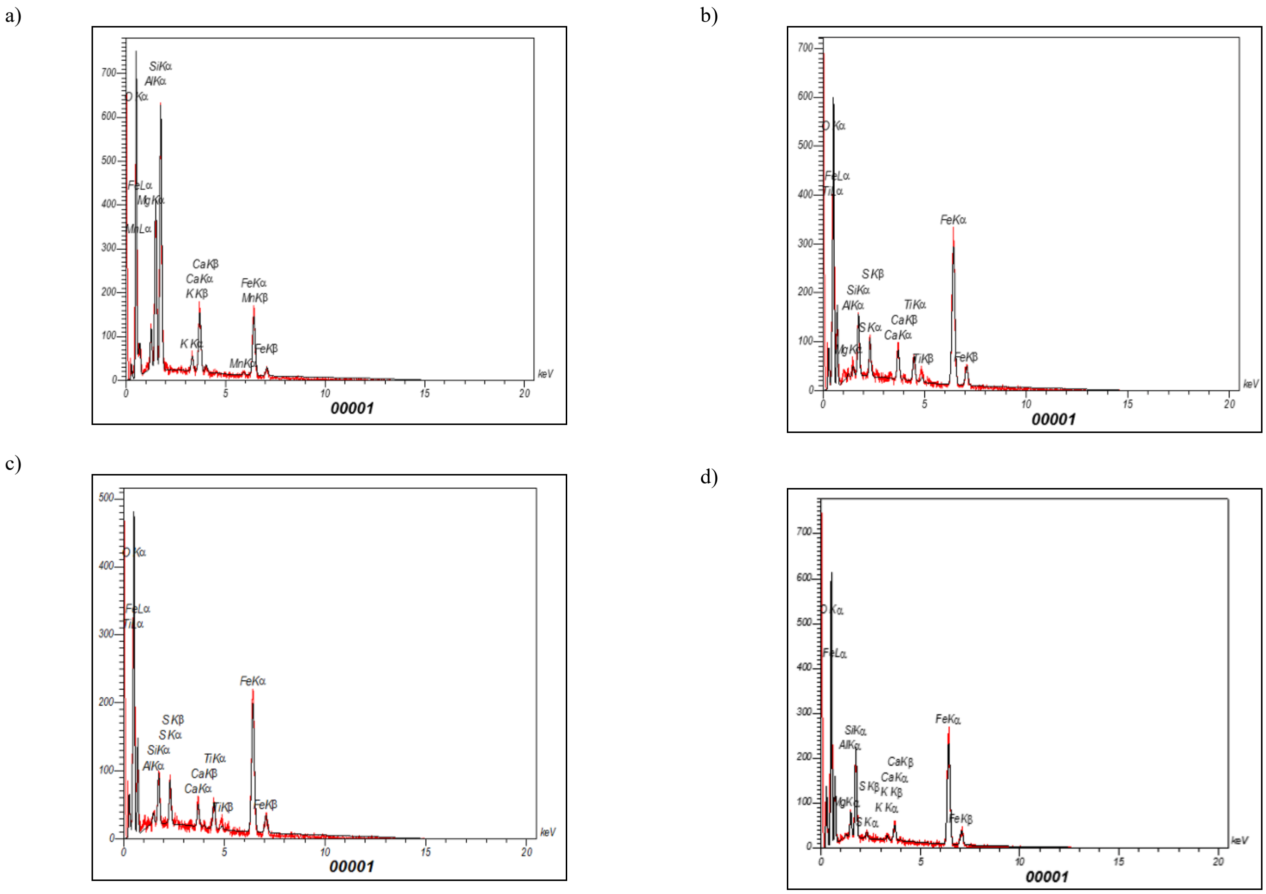

Figure 5 – EDS analysis on dark red paints of; a) GP005379; b) GP005375; c) GP005378; and d) GP005261, showing the presence of Fe atoms as the main colorant component.

Natural red iron (III) oxide can be defined as earthy, metal oxide-rich impure deposits, containing a mixture of mineral components, commonly quartz, carbonate, clays and/or micas as well as metal sulphides; which can be seen in side elements in EDS analysis [23].

3.3 Micro Fourier-transform infrared spectroscopy (μ-FTIR)

μ-FTIR analysis, was used to detect the presence of binder of paints, and to identify them; also, as a complementary analysis method to best identification of the pigments.

For this purpose, after sampling, the samples (500 μg) were mixed with KBr, pulverized, and formed into a disk-shaped transparent pellet.

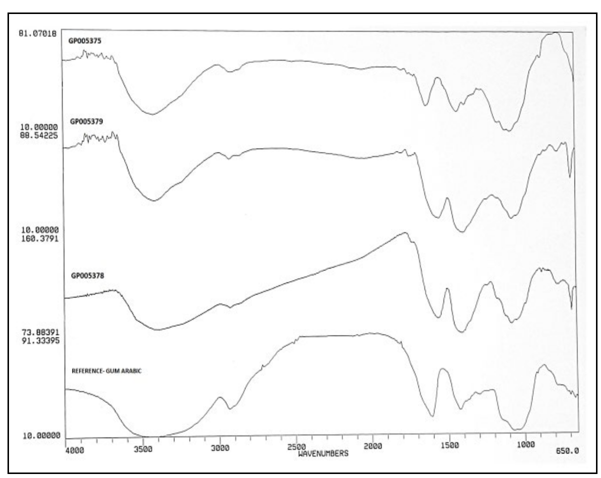

Figure 6 – General μ-FT-IR normalized spectra of light red paints of; GP005375, GP005379, GP005378 confirming the use of natural gum as the binder.

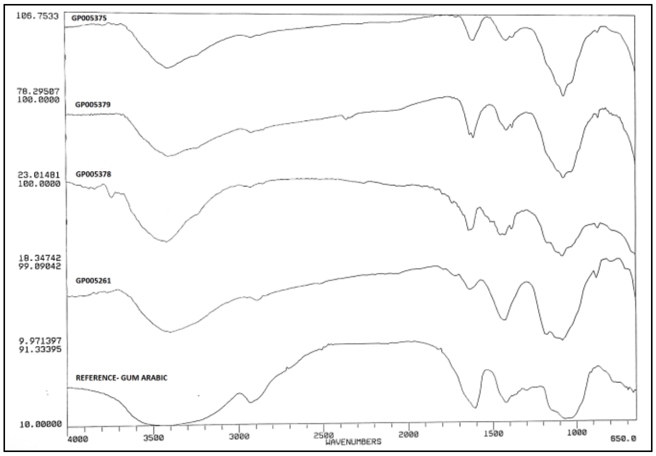

Figure 7 – General μ-FT-IR normalized spectra of dark red paints of; GP005375, GP005379, GP005378 & GP005261 confirming the use of natural gum as the binder.

The use of a type of natural gum, possibly gum Arabic, as binder of the all analysed colors (Fig. 5 & 6) with absorption bands at 3000-3600 cm^{-1} (O-H), 3000-2800 cm^{-1} (C-H), 1600 cm^{-1} (COO) and 1421 cm^{1} (C-H), 1143 cm^{-1} (C-C), 1075 cm^{-1} (C–O–C ether group of the ring), 1037 cm^{-1} (C-C), & 979 cm^{-1} (C-H), was confirmed in all spectra [24].

This is while in some old retouching instructions, it is recommended to avoid adding gum to the color, as it would adhere to paper and spoil the negative [5]

Gum Arabic is a complex polysaccharide, either neutral or slightly acidic, found as a mixed calcium salt of polysaccharide acid.

The high solubility of gum Arabic makes it particularly suitable as a painting medium. The use of plant gums as binding media appears to had been widespread in old photography materials based on several old Iranian manuals [7].

Since there was no sign of oil presence in any spectrum, the second hypothesis was rejected. Considering the physical nature of the colors and also that no other signs of the presence of any other organic material were detected in the spectra of the studied samples, it can be concluded that the colors are all mineral pigments, without any other organic additives.
The FTIR spectra of the light red colors presented in Fig. 6 shows the absorption bands in low frequency regions of 682 cm^{-1} which is characteristic of lead oxide.

The FTIR spectra of dark red color in all four analysed samples (Fig. 7), represent the absorption bands at 1000 cm^{-1} and 900 cm^{-1}, which can be attributed respectively to Si–O–Si, and Si–O stretching bands in red bolus ($Fe_2O_3 \cdot xSiO_2 \cdot yAl_2O_3$) color [25].

4. CONCLUSIONS

This study comprises the identification and application evaluation of two different common red paint, in retouching of 19th century collodion glass plate negatives. In this research two shade of red color were examined, in four collodion glass plate negatives belonging to Golestan palace photo archive. The application of red paints in the selected glass plates was almost similar to the other retouched collodion glass plate negatives in the collection.
The light red colors were applied to trace the outlines of the figures; which is common in collodion glass plate negatives, in portrait and also landscape photography. In portrait photography, it often happens when photographer is confronted with a portrait negative which is perfect in other respects but has a very streaky and dirty background. In landscape photography of blue-sensitive negatives, sky has to become in greater contrast with either the subject or the rest of the image.
In such cases the subject has to be outlined with a thick coat of opaque paint with a good hiding power, and the rest of the background or sky should be covered with a thin coat of opaque paint and or by applying a paper mask.

Based on this study, all the four, light red paints were red lead (Pb_3O_4) with gum Arabic binder; good hiding power and ease to use for outline the boundaries. Moreover, red lead is toxic; and this is probably one of the reasons why it has been used with the paper masks in retouching.
Moreover, in negatives with some emulsion defects (ex. spots of dirt, physical damages like scratches, etc), spotting was needed. In the selected sample and almost all the other retouched collodion glass plate negatives in the collection, dark red color were used in such cases.
According to this study, the main composition of dark red paints used, is hematite (Fe_2O_3) and gum Arabic

binder, which is match any photographic tone nearly enough for general work. This paint has less hiding power than red lead.

According to the obtained results and considering the materials used in retouching glass plate negatives of this era, it should be noted that retouched glass plates need more serious protection measures.

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