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ANALYTICAL AND CONSERVATION TECHNIQUES FOR GENERAL ARRANGEMENT PLAN - SCREW YACHT "SAFA-EL-BAHRE" ON TRACING PAPER

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Abstract:
This study aims to investigate, analyze and conserve the general arrangement plan of the Egyptian royal yacht "Safra El-Bahr" from the National Archives of Egypt's tracing paper collection. The yacht was specifically designed for Abbas II, the khedive of Egypt in 1894 A.D. The following analytical techniques were used for this study: pH value measurement, fungal testing, XRD, ATR-FTIR and SEM-EDX. Results revealed that the pH value of the plan paper is 6.5. Fungal testing proved the presence of Aspergillus Niger and Penicillium sp. The crystallinity index of cellulose in the historical paper increased compared to modern tracing paper indicating the occurrence of deterioration. The ATR-FTIR spectrum of the studied tracing paper revealed the presence of gelatin as a sizing material. The SEM investigation showed the effect of the natural ageing and surrounding environmental conditions on the surface morphology of the fibers. The EDX analysis revealed the use of kaolinite $Al_2Si_2O_3(OH)_4$, Cl, NaOH and $CaCo_3$ in paper manufacture. Copper carbonate ($CuCO_3$) was used for the blue color. Conservation treatments conducted on the object included cleaning, removal of pressure sensitive tape, removal of adhesive residues, tear mending and lining. These processes revealed the aesthetic value of the general arrangement plan - screw yacht "SAFA-EL-BAHRE.

1. Introduction

Tracing paper was commonly used for architectural, engineering, and design drawings due to its translucency and low cost which allow for the simple production of multiple copies. Kojima and Kaneko, Lizuka, and Askeland et al. [1-3] explained that the paper becomes translucent by replacing or reducing the air between the paper fibers, which enables light to penetrate through the paper without refraction according to the Snell Refractive Law and the theory of mathematician Francesco Maria Grimaldi at the Bologna Univ., Italy. This mechanism was achieved through three techniques according to the historical development of the tracing paper industry. The first technique involved submerging paper sheets in materials that have a similar index of refraction as cellulose such as oil, resin, and varnish. The resultant paper is known as vellum paper or impregnated paper as explained by many authors [4-10]. The second technique involved compressing fiber web of the paper sheet to reduce the air between the paper fibers by submerging paper sheets made from cotton, linen or pure bleached wood pulp in strong acid for seconds to obtain short fibers that are randomly linked. This paper is known as genuine vegetable parchment tracing paper. This method has been used since the mid-19th century as mentioned by Bachmann as reported by some authors [11-14]. The last technique involved the prolonged beating of chemical wood pulp in order to obtain short and randomly linked fibers. This paper, commonly known as overbeaten tracing paper or modern tracing paper, has been used since the end of the 19th century as explained by some authors [6,8-10,15,16]. Weidner [17], Yates [18], Bicchieri et al [19] and Wang et al. [20] stated that there are many factors which lead to the deterioration of paper-based cultural heritage objects (e.g. tracing paper). These factors include its short fibers, inappropriate housing, improper surrounding environmental conditions, improper treatments and frequent use. Prior to performing any conservation treatment, several analysis and investigations should be carried out in order to identify its components and explain the mechanism of its degradation, and thus make correct choices with regard to conservation materials and methods. This study aimed to examine, analyze and conserve the general arrangement plan - screw yacht “SAFA-EL-BAHRE" from the National Archives of Egypt’s tracing paper collection in order to enhance the understanding of the deterioration process of tracing paper and indentify the components used in its manufacture. Many analytical techniques were used for achieving this aim. pH value measurement was carried out to detect the acidity of the tracing paper. Fungal testing was performed to isolate and identify fungal species that maybe present as well as to investigate occurring microbiological deterioration. X ray diffraction was carried out to study the effect of degradation on cellulose crystallinity. ATR-FTIR was used to identify the sizing material used in paper manufacture and to study paper deterioration. SEM was used to investigate the surface morphology of the plan. Furthermore, EDX analysis was carried out to identify the fillers and colors which were used in the manufacture process [21-28]. Analysis and investigation results with regard to the condition of the plan confirmed the need for conservation. Conservation is vital for all cultural heritage materials. Abdel-Maksoud et al. [25] stated that cleaning is extremely significant since it reduces or stops potential damage, reveals the aesthetic value of the object, improves the readability of the drawing or writing and increases the chemical stability. It is also an essential preliminary measure for performing further treatments. It was also reported that cleaning is very complicated since the substance of the object may be very similar to dirt. Becker et al. [29] mentioned that dry cleaning is vital to remove dust and dirt. Page [30] stated that tape can be mechanically removed using a thin metal spatula, while adhesive residues can be removed using moist cotton swabs and blotting paper for drying. Abdel-Maksoud [31] reported that many different conservation techniques are necessary such as disinfection, cleaning, repair, mending, tape removal, etc. He also clarified that the main aim of these techniques is to remedy all forms of deterioration found on the object and to recover the imperfect object to its original condition as much as possible. In this study, selected conservation treatments included cleaning, removal of pressure sensitive tape, adhesive residues removal, tear mending and lining.

2. Materials and Methods

2.1. *Materials (Object description)*

The general arrangement plan - screw yacht "SAFA-EL-BAHRE" from the National Archives of Egypt's collection dates back to 1894 A.D. and was drawn on tracing paper. This rare plan was produced by A & J Inglis Ltd. Company, Glasgow, Scotland, which was a shipbuilding company founded by Anthony Angeles and his brother Tony in Glasgow, Scotland in 1862. The company had specifically designed this yacht for the Khedive of Egypt, Abbas II in Alexandria, Egypt; hence its historical significance. The plan was drawn using black ink, blue, red and yellow pencil colors and measures 151×72 cm^2.

2.2. *Aspects of deterioration*

The plan was stored as a roll for a long period of time. It was found to suffer from several forms of damage such as dust accumulations, fig. (1-a), yellowing of the pressure sensitive tape used to mend tears, fig. (1-b), surface dirt stains, fig. (1-c), several tears in the center and edges of the plan, fig. (1-d) and severely decayed edges, fig. (1-e); all of which made conservation a vital requirement to prolong the lifespan of such rare object of significant historical value.

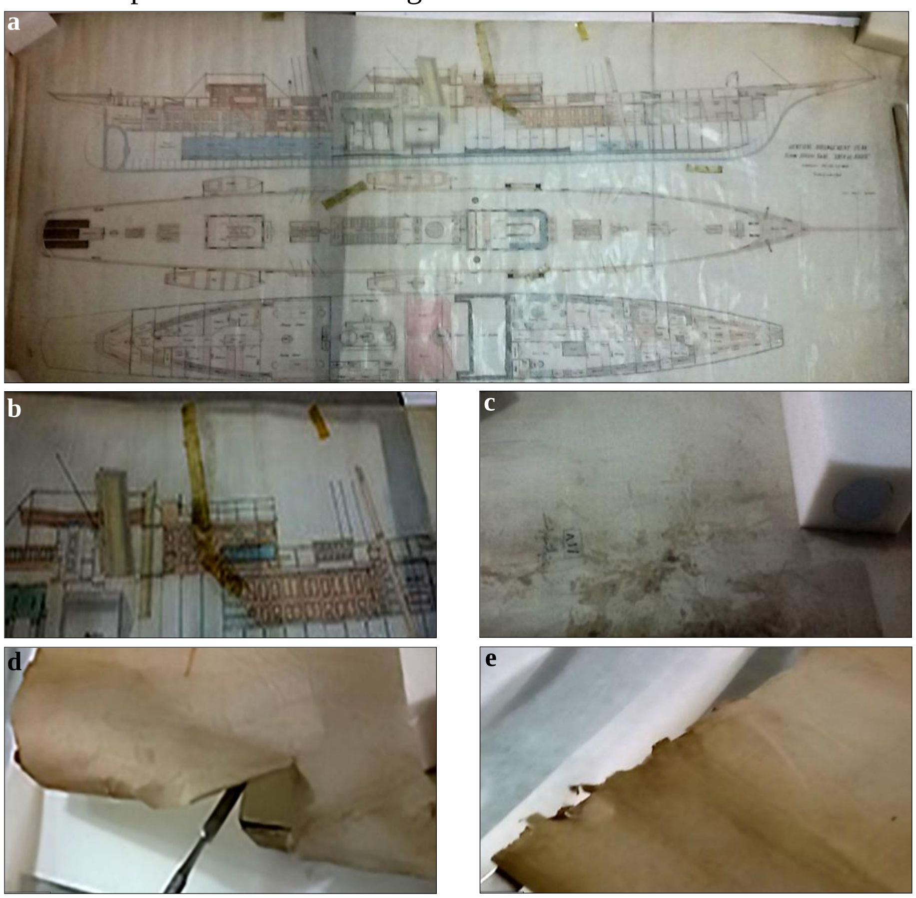


Figure (1) Aspects of deterioration of the plane; a. the screw yacht "*SAFA-EL-BAHRE*" plane, b. yellow pressure sensitive tape on tears, c. dirt on paper surface, d. tear in the edge, e. decay of edge.

2.3. *Analysis and Investigations*

2.3.1. The pH value measurement

The pH value was measured using a Lutron pH meter model pH- 211. The procedure was carried out at the Conservation Center at the National Archives of Egypt. The pH meter was calibrated with known buffer solutions before use (i.e. buffers of pH 7 and pH 4 are usually selected). The electrode of the pH meter was rinsed with distilled water and then immersed in the buffer solution contained in a beaker [32, 33]. The pH measurement was carried out in accordance with the standard Tappi 529 om-99 1999. A flat electrode was placed on a drop of distilled water which was added to the surface of the plan. The paper was backed with a polyester film. The pH value was recorded after 10 min [34].

2.3.2. Isolation and identification of fungi

The isolation of fungi was carried out following the steps used by Sabatini et al. [35], Engelkirk et al. [36]. The process involved using cotton swabs to carefully wipe the surface of the paper, more precisely, the surface dust found on the paper. The cotton swap was then cultivated in Sabroud dextrose agar (SDA pH 5.6) medium containing (62g) of Sabroud Dextrose Agar, (5g) of Agar powder pure, and (1000 ml) of distilled water in the Petri dishes. After 7 days of incubation at 25 ºC, the fungi species were identified according to Gaddeyya [37], Alsohaili [38] by observing the colony features (i.e. shape, color, size and hyphae), and also microscopically by examining a slide-mounted with a small portion of the mycelium under a compound microscope with a digital camera using. Isolation and identification were carried out at the Conservation Center, The National Archives of Egypt.

2.3.3. X- Ray diffraction analysis

This technique was used for determining the crystallinity of cellulose. It was performed using a Panalytical X' pert PRO Theta/2 Theta Diffractometer, Cu-radiation (λ= 1.542 A°) at 45 K.V., 35 M.A. and scanning speed 0.04°/ sec. Two samples were used for this analysis (i.e. the historical plan paper, and a modern sample of tracing paper). The procedure was carried out at the Egyptian Mineral Resources Authority Laboratories (E.M.R.A.), Dokki, Giza, Egypt. The crystallinity index of cellulose was measured according to some scientists [27,28,39] using the Segal equation: CI = {(I002- I am)/(I002)} X100. Where CI = crystallinity index, I002 = intensity at about 22.6° 2ϴ, and I am = intensity at about 19° 2ϴ.

2.3.4. Attenuated total reflectance fourier transform infrared spectroscopy

ATR-FTIR spectra were obtained using a Nicolet 380 FT-IR Spectrometer with ATR crystal, in the frequency range of 4000-400 cm^{-1}, in reflectance mode. The procedure was carried out at the National Institute of Standards (NIS), Cairo, Egypt. Two samples were prepared: a modern tracing paper from Rotring, 72 g/m^2 and a modern tracing paper from Rotring, 72 g/m^2 sized with gelatin (3%) dissolved in warm water. The purpose of this study was to compare the functional groups of both samples with that of the historical plan paper sample with the aim of evaluating the degradation of the latter and to identify the sizing material used in the paper manufacture. The modern tracing paper sample from Rotring, 72 g/m^2 and Gelatin were used.

2.3.5. Investigation of surface morphology by SEM- EDX

Scanning electron microscopy was used to investigate the surface morphology of the plan paper. The samples were coated with gold using a PIRANI 10-S150 Sputter Coater. The samples were then scanned using a QUANTA FEG 250 scanning electron microscope with an EDX unit (i.e. Energy-dispersive X-ray spectroscopy). EDX was used to identify the fillers and the blue color used. Analysis was only performed on the blue color since a few loose samples were found. On the other hand, the other colors used on the plan are strongly adhered to the surface, thus sampling is not possible without damaging the surface. Portable analysis instruments were not available at the National Archive of Egypt; and therefore, the authors preferred not to carry out further analysis in order to preserve the aesthetic value of the plan. The procedure was carried out at the National Research Center, Dokki, Giza, Egypt.

3. Results

3.1. *The pH measurement*

It was clear that the measured pH value of the tracing paper was 6.5 pH. It very close to neutral level of pH.

3.2. *Identification of fungi*

The fungi testing results, fig. (2) revealed the presence of Aspergillus Niger and Penicillium sp. on the surface dust; however, no signs of fungal growth were noticed on the surface of the paper.

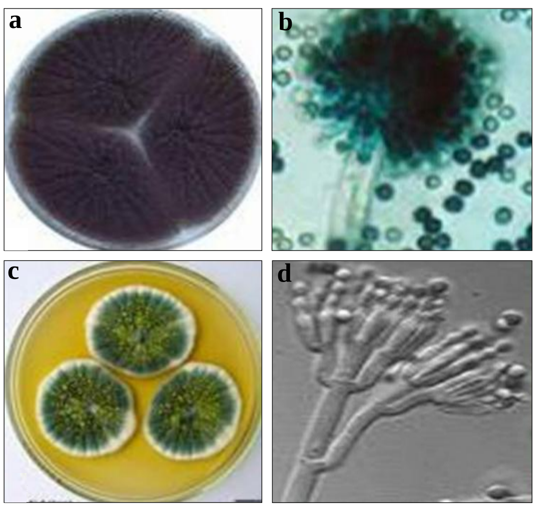
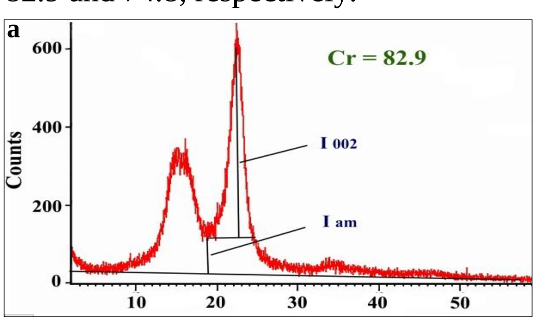


Figure (2) Shows the identified fungi; **a.**, **b.** *Aspergillus Niger*, **c.**, **d.** *Penicillium sp*.

3.3. *XRD analysis*

The results of XRD analysis used for determining the tracing paper crystallinity, fig. (3) revealed that the crystallinity index of the cellulose in the historical paper and the modern tracing paper samples was 82.9 and 74.8, respectively.



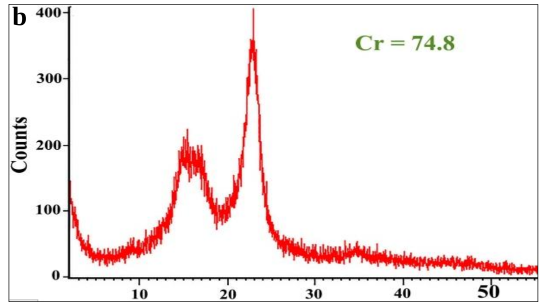


Figure (3) Shows X-Ray diffraction analysis for determination of paper crystallinity, **a.** the historical tracing paper sample, **b.** the modern tracing paper

3.4. *ATR-FTIR*

The results obtained, fig. (4) stated that the sizing material used in the historical tracing paper was identified as gelatin by comparing the functional groups in the historical tracing paper with the gelatin-sized modern tracing paper from Rotring 72 g/m^2. The comparison showed the presence of the 1540 and 1623 cm^{-1} bands, tab. (1) assigned to the amide I and amide II bands, respectively. Amide I and amide II are the most prominent vibrational bands of protein (i.e. gelatin, glue, etc.). The results also showed that the historical tracing paper suffered from deterioration which was due to the loss of water molecules caused by natural ageing.

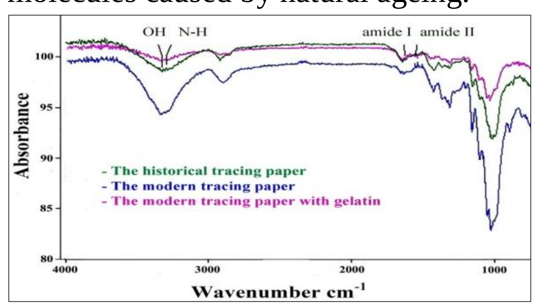


Figure (4) Shows FTIR-ATR of historical and modern tracing paper samples

Table (1) FTIR analytical results of object paper, modern tracing paper, and modern tracing paper with gelatin

Functional groups	Assignment	Historical tracing paper		Modern tracing paper		Modern tracing paper with gelatin	
		W. number cm⁻¹	*Absorbance*	*W. number cm⁻¹*	*Absorbance*	*W. number cm⁻¹*	*Absorbance*
- OH stretching	Cellulose	3336	99	3339	94	3325	99
- N-H stretching	Gelatin	3328	99	---	---	3302	100
-CH stretching	Cellulose, gelatin	2919	100	2894	97	2919	100
		2860	100	2862	98	2871	100
C=O Stretching	Cellulose, gelatin	1650	100	1640	98	1637	99
		1623	100			1668	100
C-N-H banding bands	Gelatin	1540	100	---	---	1540	99
CH- banding bands	Cellulose, gelatin	1432	99	1427	96	1437	99
		1370	99	1369	95	1374	99
		1315	99	1315	95	1313	99
C-O	Cellulose	1155	97	1159	92	1162	98
		1105	96	1106	89	1111	97
		1027	92	1051	84	1052	95
		-	-	1026	82	1033	95

3.5. *SEM-EDX investigation*

Investigation of the surface morphology of plan paper using SEM, fig. (5-a) revealed the effect of natural aging on the paper fibers, which appeared to be deteriorated in some areas. SEM images also revealed the presence of gaps, and proved that the plan paper was made by the beating technique. The results of EDX spectroscopy, fig. (5-b, c) revealed the presence of Al, Si, O, Cl, a small percentage of Na, Ca, C and Cu elements.

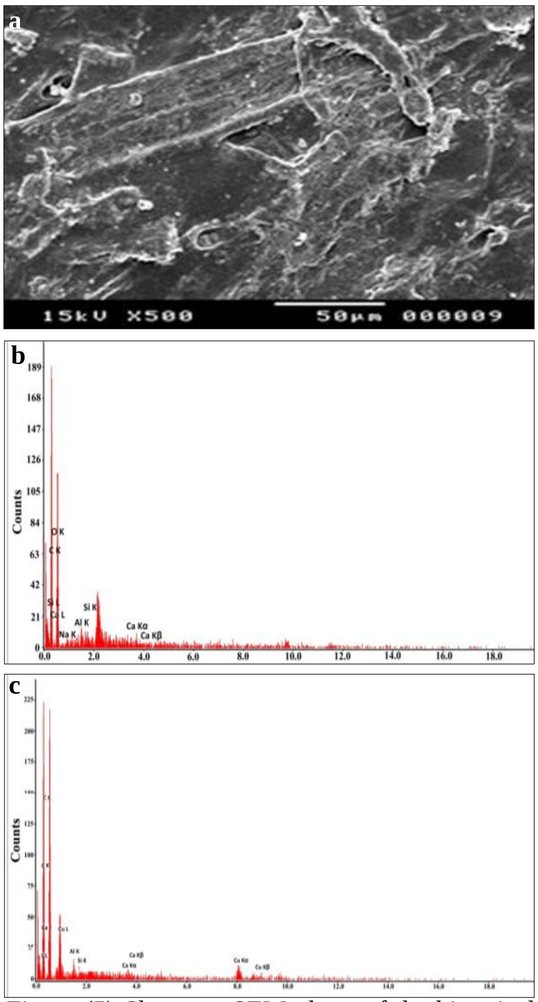


Figure (5) Shows **a.** SEM photo of the historical tracing paper sample, **b.** EDX analysis of the historical paper sample, **c.** EDX analysis of blue color

4. Discussion

It was clear from the measurement of pH value that the pH of the tracing paper was very close to the neutral level (6.5 pH). Accordingly, the tracing paper did not require a de-acidification procedure. This may be due to the use of calcium carbonate in the paper manufacture. A slight decrease in the pH value may have been caused by the occurrence of slight acid hydrolysis or oxidation of cellulose as a result of improper surrounding environmental conditions such as acidic compounds from air pollutants (sulfur dioxide [SO_2], and nitrogen oxides [NOx], temperature and relative humidity (RH) levels (Malešič [40]; Mochizuki et al. [41]; and Drougka et al. [42]). In addition to the scission of chemical bonds between monomeric glucose units which resulted in a decrease of the cellulose chain length (i.e. the degree of polymerization), the formation of free radicals and carbonyl, carboxyl, and hydro peroxide, lead to the decrease of pH of paper [27,34,43-45]. It was clear from the identification of fungi that the common fungi isolated from the surface dust were *Aspergillus Niger* and *Penicillium sp*. This results confirmed by Sahab et al. [46] who reported that These microorganisms can be carried by dust particles into the indoor archive repositories by means of the people and the air ventilation systems. Fouda et al. [24] reported that archival materials like manuscripts are susceptible for biodeterioration especially fungi. They also explained that there are some factors that can cause biodeterioration, which are the components of manuscripts or from particulates from surrounding environmental conditions (such as dust). It became clear from the results obtained that the crystallinity of historical tracing paper was higher than the modern tracing paper. This results was confirmed by many authors [47-54] explained that paper is composed of fibrous polysaccharide cellulose, which is composed of glucose units linked together by a β-Linkage at a carbon atom 1, and 4 in the sugar molecule in long and straight chains. The increase in the crystallinity index of the cellulose in the historical paper was due to acid hydrolysis, or cellulose oxidation, which occurred during natural aging, causing the formation of free radicals and carbonyl, carboxyl, and hydro peroxide, and the breaking of hydrogen bonds that link cellulose chains together. The amorphous regions of cellulose were more susceptible to deterioration than the crystalline regions as confirmed by Beyene et al. [55], Xie [56], and Kusmono [57]. It was clear from ATR-FTIR analysis that the sizing material used in the historical tracing paper was gelatin compared to modern tracing paper sample. The results were confirmed by Derric et al. [58] and Gorassini [59] who reported that reported that band at 1623 cm^{-1} and 1540 cm^{-1} referred to amide I and amide II, which are characteristic of gelatin. The ATR-FTIR spectrum of the historical paper compared to that of the modern tracing paper proved that the plan suffered from deterioration. There was a decrease in the intensity of the OH band and a slight decrease in the intensity of the C=O at 1641 cm^{-1} due to the loss of water molecules [60-62]. The study also stated that there was an increase in the intensity of the CH_2 vibrations at 1432-1427 cm^{-1} associated with the increase in the amount of the crystalline structure of cellulose; this was a result of natural aging. The decrease in the intensity of the C-O vibrations at 1155-1026 cm^{-1} is a result of the decrease in the polymerization of cellulose chains due to natural aging [63-66]. The investigation by SEM revealed that gaps found in the tracing paper may due to poor sizing during manufacture, or may be due to the effect of the deterioration factors in the surrounding environmental conditions. It was also clear that the beating technique was used in the manufacture of the plan studied, since the fiber composition is unclear; and this is consistent with the pattern of overbeaten tracing paper, where the pulp is beaten for long period with a high content making the fibers very short and randomly linked. The other techniques dealt with the surface layer of the paper sheet which made the fibrous composition partly clear as mentioned by Der Reyden et al. [4]. EDX analysis revealed that the presence of Al, Si, O may be due to the use of kaolinite $Al_2Si_2O_3$ $(OH)_4$ as a filler in paper manufacture. This result was confirmed by Bundy and Lshley [67], and Hubbe and Gill [68]. The presence of Cl may be due to the use of chlorine compounds for bleaching paper in the manufacture process [69,70]. The presence of a small percentage of Na and O may be due to the use of caustic soda (NaOH) in the pulp preparation process [71]. The presence of Ca, C and O may be due to the use of $CaCo_3$ as an alkaline filler for paper to improve the paper [72-74]. The increase of Cu, O and C percentage in the blue color sample may be due to the use of copper carbonate $CuCO_3$ as a blue color source [75].

5. Conservation Processes

5.1. *Dry cleaning*

The first step of the conservation treatment was dry cleaning, fig. (6-a, b). The paper surface was surface cleaned using a soft brush and a natural sponge to remove dust, dirt, and stain caused by improper handling from the paper surface in accordance with Johnson, Greuter [75,76].

5.2. *Disinfection*

The disinfection of the paper surface was a vital process to protect the object from future fungal growth. The identified fungi from the surface dust were *Aspergillus Niger* and *Penicillium sp.* Ethyl alcohol 70% had been used for disinfection according to Westin, Nittérus, Bacílková and Sequeira et al [77-80].

5.3. *Pressure sensitive tape removal*

The removal of pressure sensitive tape from the paper surface was done using a thin metal spatula, fig. (6-c). Acetone was used for the removal of adhesive residues [7,30].

5.4. *Tear mending*

Tear mending, fig. (6-d) was carried out using Archibond Texicryl/Paraloid with acetone. Archibond® is a 100% manila fabric covered with a layer of acrylic adhesive and weighs 9.5 g/m^2. It is the preferred choice for the restoration of transparent papers due to its high quality and speed of application. It can either be applied using heat or solvents [76].

5.5. *Decayed edges completion*

The decayed edges, fig. (6-e) were completed using Japanese paper (Arakaji 32 g/m^2) with Klucel G adhesive 4% dissolved in acetone. This method was selected due to the sensitivity of tracing paper to moisture and water [16,30].

5.6. *Lining*

Lining process was vital to consolidate and support the plan. The first step was the preparation of the work station by placing a layer of Reemay on the tabletop**.** The object was laid on top of the Reemay layer with the object facing downwards. Then, a layer of thin Japanese paper (i.e. Kuranai paper roll 5 g/m^2) was laid on the back of the object. The Klucel G adhesive 4% dissolved in acetone was applied on the Japanese paper layer using a soft brush moving from the center outwards. Excess adhesive was removed by covering the object's back with a layer of Reemay and applying pressure on it using a ruler, also moving from the center outwards [18,19,30]. Then, the blotting paper was placed on the Reemay layer, and a P.V.C. board was place on the top to apply pressure on the object for the purpose of flattening. The blotting paper was changed several times until the object became completely dry. The excess Japanese paper was cut. After finishing all the conservation processes, the historical tracing paper object became more strengthened and its aesthetic value becomes clear, fig. (6-f).

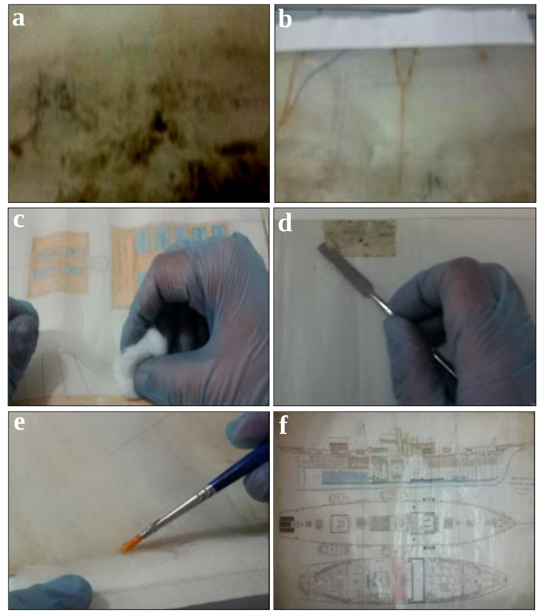


Figure (6) Shows conservation processes of the plane **a.** before cleaning, **b.** after cleaning, **c.** removal of pressure sensitive tape, **d.** mending tears, **e.** completion the decayed edge, **f.** the historical tracing paper object after all conservation processes

6. Conclusion

Many publications have discussed the conservation of paper-based objects; however, a few are dedicated to tracing paper, hence the significance of this study. The general arrangement plan of the Egyptian royal yacht "Safra El-Bahr" from the National Archives of Egypt's tracing paper collection was selected for its historical value since it dates back to 1894 A.D. and is associated with the khedive of Egypt, Abbas II. Correct diagnosis of the condition of the object greatly assists in making correct treatment choices. Accordingly, the following techniques were used to study the composition of the object as well as evaluate its state of preservation: pH value measureement, fungal testing, XRD, ATR-FTIR, and SEM-EDX. Analysis results revealed that the pH value of the plan paper is 6.5. The fungi found in the surface dust were identified as Aspergillus Niger, and Penicillium sp. XRD results showed the increase of the crystallinity index of the cellulose in the historical paper compared to the modern tracing paper as a result of the deterioration process. ATR-FTIR results of the plan paper showed the presence of gelatin as a sizing material. The SEM results showed the effect of natural aging process *on the fibers, which appeared to be severely decayed in some areas. The EDX analysis revealed that kaolinite $Al_2Si_2O_3(OH)_4$, (Cl), (Na OH), and $CaCo_3$ were used in the manufacture of the paper. Copper carbonate ($CuCO_3$) was used for the blue color. All selected conservation treatments (i.e. surface cleaning, removal of pressure sensitive tape, adhesive residue removal, tear mending and lining) applied on the historical tracing paper object revealed the aesthetic values of the object and increased its strength.*

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