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Study of Disappearing Ink Writings on Different Types of Documents

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DISAPPEARING inks are used in textile industry such as dressmaking crafts and as a kind of teaching material; for example, printed questions are visible and the spaces for an answer exhibit invisible disappearing ink. The answers only become visible using a coloring assistant. This research was conducted on the preparation of disappearing inks using different concentrations of thymolphthalein (Th-ph) and O-Cresolphthalein (O-Cph). The prepared inks were applied to different types of handwriting papers. It was found that the handwriting stability increased by increasing thymolphthalein (Th-ph) and O-Cresolphthalein (O-Cph), or alkali concentration. Deciphering of the faded documents was evaluated by different methods. Commercial paper C2 surfaces gave the more handwriting stability than other paper, the order of stability were C2 ≥ C1 > Azhar >Xerox > C3 > C4 > Edfo. All the faded documents were visible when treated with alkaline solution. When the faded documents surfaces are exposed to the thermal effect there is no change in all the faded documents.
Disappearing inks have been used in different fields, but it may be abused in forgery and counterfeiting.

Keywords: Forensic medicine; Questioned Documents; Disappearing inks; Fading time;Thymolphthalein; O-Cresolphthalein

Introduction

Ink is a liquid or paste containing colorant used mostly for writing, printing and drawing. Certain inks are available on the market which disappear without leaving any trace with the passage of time

Disappearing ink is used in the textile industry such as dressmaking, and as a kind of teaching material with which the answers are rendered invisible using the faded disappearing ink printed next to the visible questions [1]. The answers only become visible using a coloring assistant. Disappearing ink is also used as paints for example, it is difficult to determine which parts of an existing coat of white paint are not covered by a new paint of a similar shade especially under poor lighting; disappearing ink can solve the problem [2,3].

Disappearing ink is a substance that is prepared from various chemicals with the purpose of having the ink visible for only a certain period. The determination of the fading of an ink entry from a questioned document is often a major problem and a controversial issue in forensic sciences. Therefore, it is important to understand the aging process of the ink to evaluate the possible application of the method to forensic examination of documents [4].

The disappeared or invisible inks are fluids used to for secret writing. These types of inks are revealed by heat, chemical reaction and UV

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light. Disappearing inks are acid base indicators showing different colours at different pH. Writing with this type of ink disappears after about 65 h. These inks could be used for forging the documents such as agreements cheques, property documents and other important documents. Many destructive and nondestructive methods are available for forensic decipherment of these disappeared writing. In present communication, a simple nondestructive method is applied for decipherment of disappeared signatures on share transfer agreement and other related documents [5].

The scope of this research was conducted on the preparation of disappearing inks from O-Cresollphthalein (O-Cph) and Thymolphthalein (Th-ph) dyes. Some factors effectiveness on fading disappearing inks solutions such as a basic substance, and concentration or pH of the dye were studied.

Materials and Methods

Materials

Chemicals

O-Cresolphthalein and Thymolphthalein were obtained from Aldrich chemical co. ltd., Absolute ethyl alcohol (purity 99%), Glycerin (purity 95 %), Potassium hydroxide (from Aldrich chemical co. ltd.), and Sodium carbonate (from Aldrich chemical co. ltd.)

The papers used were from the following suppliers:

-White paper (80 g/m^2) supplied by Azhar, Xerox. -Lined paper (60 g/m^2) supplied by Edfo and different types of commercial documents (C1,C2,C3and C4).[C1 Commercial document : Contract Rent Blue, C2 Commercial document : Contract Amana Blue, C3: Commercial document : White Contract, C4 Commercial document : Blue Delivery Mzarksh]

Dry felt-tip pen, 1 mm point. The pen was composed of a fiber filter, a felt tip, a plastic housing, a plastic cover and a plastic cap.

Methods:

Different concentrations of thymolphthalein or O-Cresollphthalein (0.157,0.471, 0.785,1.099 and 1.57x10^{-2} M) were dissolved in 60 mL of absolute ethyl alcohol, and the solution was shaken until complete solubility. Then, 6 mL of glycerin was added to the solution and was shaken again. Finally, complete to 100 mL with distilled water. The ink was prepared by adding the previously prepared solution to a calculated amount of different concentrations of alkali (potassium hydroxide and sodium carbonate (0.1, 0.5,0.7 and 1 N). The ink was used for writing by filling a dry felt-tip pen. The writing was blue in the case of thymolphthalein, violet in the case of

O-Cresollphthalein, and the fading time was studied. The absorbance of the inks was measured in the ultraviolet–visible region between 190 and 900 nm by Model T60 spectro photometer, United Kingdom spectrophotometer. The initial handwriting surfaces in our work of papers were examined by a scanning electron microscope (SEM) (JEOL JSM-5400 SEM - Tokyo, Japan,) and was operated at 20 kV. Before the examination, the samples were prepared on an appropriate disk and coated by a spray of gold to make the samples conductive to electrons. The pH of the prepared inks was measured using a pH meter (Satorius Model PB-11) combined with glass electrode and was used for other all experiments and the pH of the used papers was measured according to TAPPI standards [6]. The phrase ‘‘With the Name of researcher’s sons in Arabic (Ahmed Hassan Yusuf, احمد حسن يوسف) was written on each type of the papers used. The handwritten phrases were observed by visual examination.

Results and Discussion

Preparation of disappearing inks from O-Cresollphthalein(O-Cph) and Thymolphthalein (Th-ph) dyes by using KOH and Na_2CO_3

The inks can be considered a mixture of dyes dissolved or dispersed in a solvent with characteristics that allow a continuous and homogenous flow from the pen to the paper. Because of the disappearing effect of this type of ink, it has been used in several instances. For example, in some cases the disappearing ink is used on private documents that only need to be visible for a certain period [2].

Disappearing inks typically rely on the chemical reaction between indicator dyes and a basic solutions. Disappearing ink were prepared by dissolving different concentrations ranging from 0.157 X10^{-2} M to 1.571X10^{-2} M of thymolphthalein (Th-ph) or O-cresolphthalein (O-Cph) indicator dyes in ethyl alcohol. Then, glycerin was added to the solution and shaken, followed by dilution with distilled water at 25^{o}C. Solutions of KOH or Na_2CO_3 within a concentration range of 0.1 to 1.5 M were added to the previously prepared solutions. Upon addition basic solutions the color of ink appears. The color of all ink's samples was examined by naked eye in daylight. The blue and violet color is obtained for (Th-ph) and (O-Cph) respectively, Fig. 1.

UV-Vis Spectrophotometric analysis of prepared inks solutions

UV-Visible Spectrometry is a technique used to identify the components of the prepared inks. The analysis involves scanning of prepared ink solutions from Th-ph and O-Cph dye (conc. 0.157 X10^{-2} M) in presence of 0.5 M KOH or 0.5 M Na_2CO_3 at 25^{o}C . The absorbance spectra for Th-ph and O-Cph ink solutions was measured between 200-1200 nm and record in Figs. (2 and 3). Th-ph and O-Cph indicator dyes change their color in the presence of acidic and alkaline medium. The three benzene rings in Th-ph and O-Cph for example, are not conjugated in acidic solution so it only absorbs in the UV region, and is colorless. The absorbance peaks at 254 and 297 nm for Th-ph and O-Cph dyes respectively are due to $\pi \rightarrow \pi^*$ transitions in the benzene. The addition of basic ions removes protons from the hydroxyl groups and breaks a C-O bond which changes the hybridization of the central carbon atom from sp^3 to sp^2. This allows the π electrons in the benzene rings to be delocalized throughout the whole molecule. Visible spectroscopy is the study of the interaction from the visible part (λ=380-750 nm) of the electromagnetic spectrum with a chemical species. Colored compounds are colored because of the absorption of visible radiation. The Th-ph and O-Cph dyes have their maximum absorption at 600 and 555nm, respectively. The color of substances, whether in the solid form or in solution, is determined by the location of their dominant absorption of light within the visible spectrum. Their color is complementary to the color of the light they absorb. The ink solution which prepared from O-Cph have appears violet because of its predominant absorption of green-yellow light. Ink solution which prepared from Th-ph have dark blue color because its ions strongly absorb yellow- orange photons of light.

The absorption of visible light by an absorbing molecule produces an electronically excited species. The amount of energy associated with the photon exactly corresponds to the energy required to promote an electron into a higher energy state. Quantum mechanics states that only certain electronic transitions are allowable. The energy of these transitions (and the energy of the photon) can be calculated using the equation:

$$E = hc / \lambda$$

where E is the photon energy in joules, h is the Planck's constant (h = 6.626 x 10^{-34} Js), c is the light velocity (c = 3x10^{10} cm/s) and λ is the wavelength of the incident light Table (1).

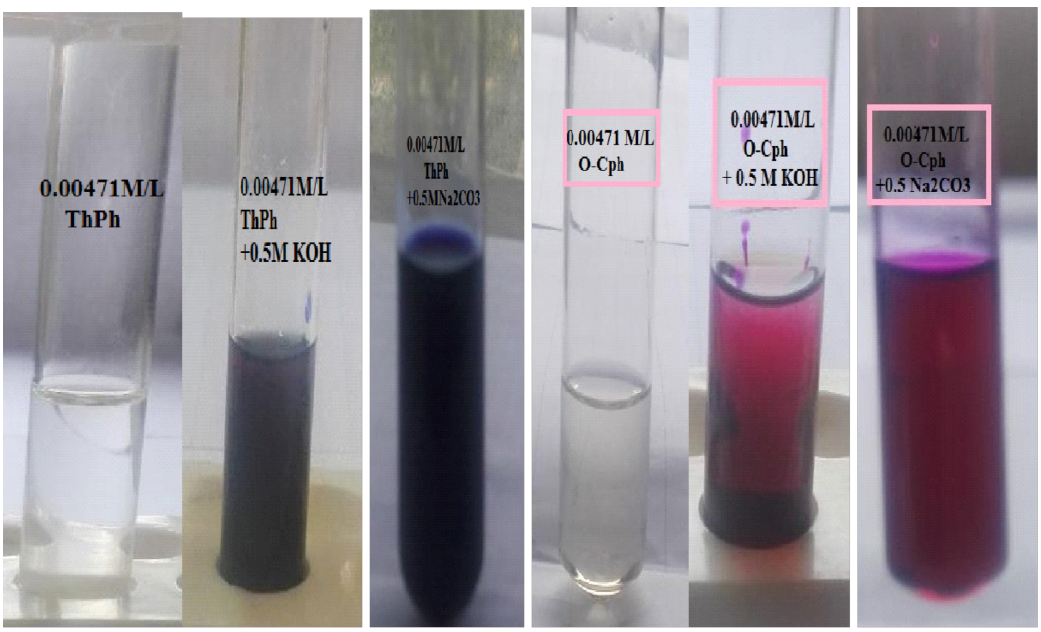

Fig. 1. Preparation of disappearing ink from (Th-Ph)and (O-Cph)

TABLE 1ز Calculation of photon energy in joules from maximum wavelength.

Type of alkali	λmax (cm)		E (Joule)	
	Th-Ph ink	O-CPh ink	Th-Ph ink	O-CPh ink
0.5 M KOH	$611x10^{-9}$	$567\ x10^{-9}$	18330	17010
0.5 M Na_2CO_3	$600\ x10^{-9}$	$548\ x10^{-9}$	18000	16440

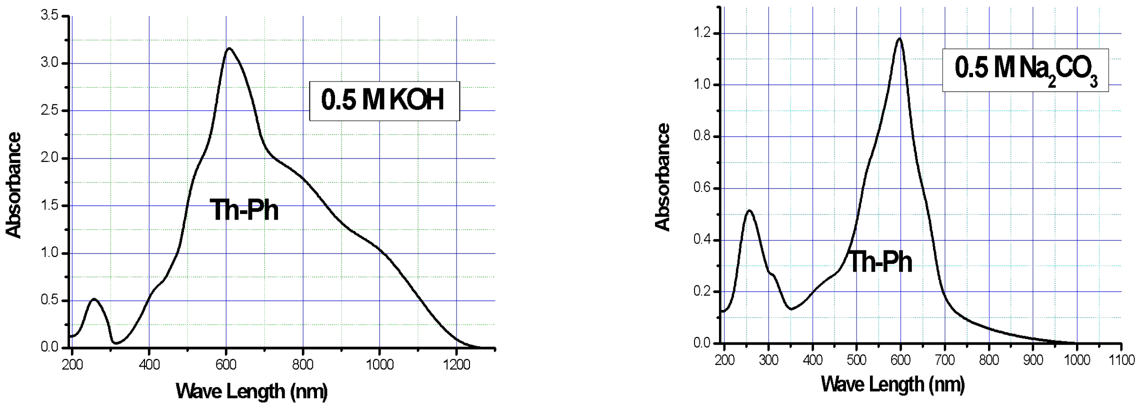

Fig. 2. Full spectra of Th-Ph ink [$0.157x10^{-2}$M dye and 0.5 M KOH or 0.5 M Na_2CO_3].

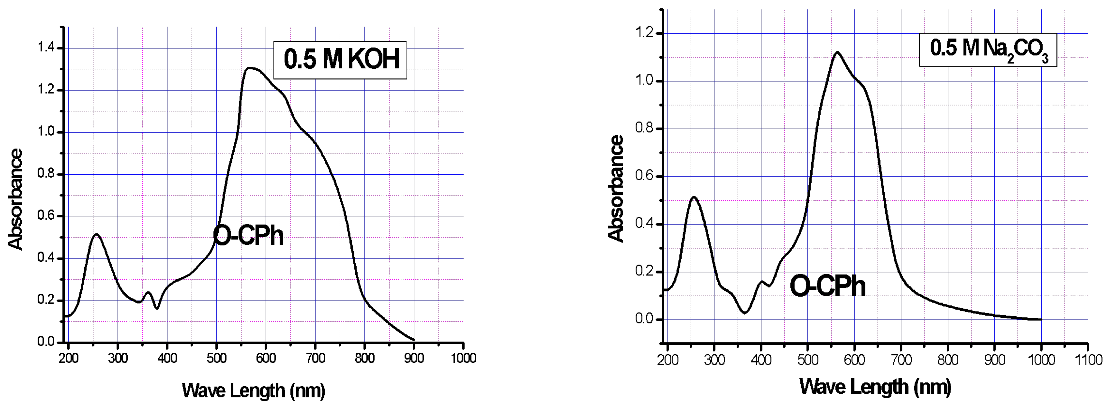

Fig. 3. Full spectra of O-CPh ink [$0.157x10^{-2}$M dye and 0.5 M KOH and 0.5 M Na_2CO_3]

pH of prepared disappearing ink solutions

The pH plays an important role in preparation of disappearing inks. One such ink can be prepared by dissolving solid indicator dyes in ethanol and water. Upon basic solution were added the color of the indicator dye is apparent. The reason of more coloring ink in presence of basic solution was due to the presence of phenolic groups in ink dyes which reacted with alkali. Th-ph exists in two different forms an acid form HTph, which is colorless, and a corresponding conjugate base form Th-ph-, which is blue, Fig. **4.** The color transition range for an acid–base indicator depends on the strength of the weak acid HTph. O-cresollphthalein is a weak organic acid that behaves as an acid–base indicator. It exists in two different forms—an acid form HO-Cph, which is colorless, and a corresponding conjugate base form O-Cph-, which is violet. The color transition range for an acid–base indicator depends on the strength of the weak acid HO-Cph [7], **Fig. 5.**

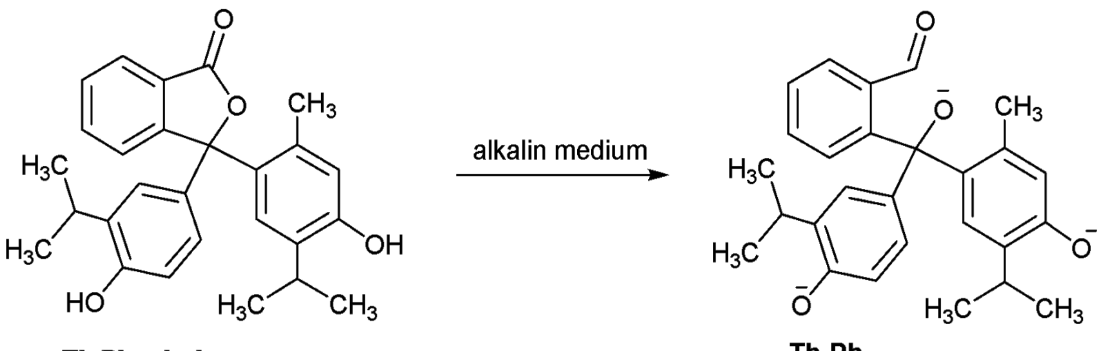

Fig. 4. Structure form of thymolphthalein (Th-ph).

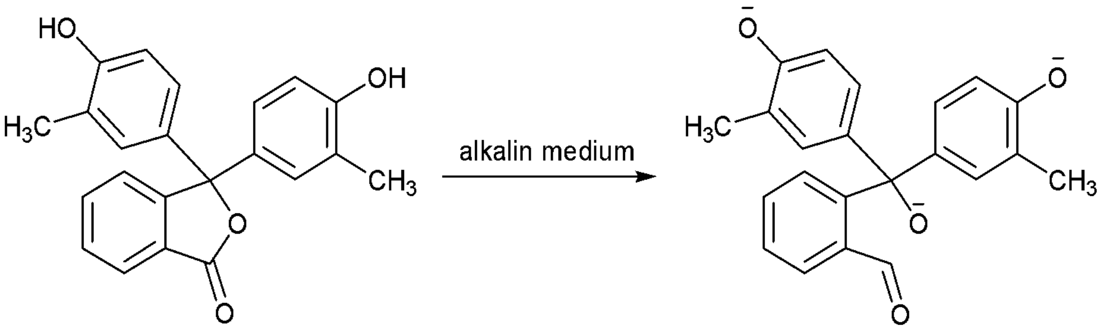

Fig. 5. Structure form of O-Cresolphthalein (O-Cph).

The pH of the prepared ink solutions was studied under laboratory conditions at 25°C. The pH of ink solutions can be measured in different alkaline medium and different dyes concentrations. As soon as KOH and Na_2CO_3 added to colorless ink solution, the solution to become a colored. The most common pH indicators for the ink are thymolphthalein (Th-ph) turns blue in basic solution. While O-Cresolphthalein (O-Cph) turns to violet. KOH and Na_2CO_3 solutions of various concentration (range from 0.1 – 1.5 M) were used to change the pH value of dyes system in various concentration (range from 0.157 to 1.57 x10^{-2} M). It can be seen from the results that the ink solution should maximum color strength at pH 10.5 and 9.8 for Th-ph and O-Cph ink respectively. The relative color strength gradually decreased up to pH 9.3 and 8.2 for Th-ph and O-Cph ink respectively. The ink color change is due to the changing proportion of the indicator molecules in the acid or base form. When the indicator is in a solution where the H^+ concentration equals the equilibrium constant for dissociation of the weak acid, there are almost equal numbers of molecules in the acid form (colorless). The ink molecules are colorless under neutral conditions. When the basic solution is neutralized, the acidity of the alcohol changes the "ink" to colorless. Once the ink solution has been exposed to carbon dioxide in the air, the pH level drop which makes the color disappear. While the ink molecules in the base form (color), and the color is pale (intermediate between colorless and color) once pH value is the exact middle of the transition range for the indicator.

Th-ph has more methyl substituents, which are electron donating [8]. Hence, compared to O-Cph, there will be a slightly larger negative charge in the conjugated system. The bond between the proton and oxygen of the hydroxyl group will be stronger and thus deprotonation will be more difficult. This is reflected experimentally with the observation that a slightly more alkaline medium is needed to allow for deprotonation and therefore the color shift is between pH 9.3 and 10.5 instead of pH 8.2 and 9.8 as for O-Cph and Th-ph respectively.

Application the prepared disappearing inks on writing surface

The prepared disappearing inks can be applied on writing surface with a writing instrument. Th-ph and O-Cph inks with concentration ranging between 0.157 to 1.57 x10^{-2} M in presence of Na_2CO_3 and KOH with concentration ranging between 0.1 to 1.5 M were investigated. The prepared disappearing inks were applied separately on different types of handwriting papers (white paper, Xerox, Azhar , Edfo , C1 , C2,C3 and C4). The pH of ink solutions > 7.0 at 25°C. The ink is used in handwriting by filling a dry 1-mm-point felt-tip pen, Fig. **6.** The phrase (احمد حسن يوسف) was written on each type of paper used. The handwritten phrases were observed continuously by the naked eye in daylight. The mobile camera was then ready to take a picture of handwriting papers, Fig. **7, 8** for Th-Ph ink and O-CPh respectively.

Ink molecules enter the structure of fibers where they are fixed mechanically and by physicochemical links. Among the ink molecule bonding forces are created such as Vander Waals bonds, London bonds, Keson interactions, hydrogen bonds, ionic chemical bonds and rally scarcely even chemical covalent bonds. The color of the writing was blue in case of (Th-ph) and violet in case of (O-Cph) inks then disappeared with time. In some cases, when the Th-ph ink is light blue in color and has pH < 10, colorless writing is obtained. In other cases, when the Th-ph ink is dark blue and produced blue writing, the writing turned colorless after period. The relative color of the writing strength for each ink gradually increase with increase Th-ph and O-Cph and basic concentration. When ink is applied on paper, the ink composition begins to change qualitatively and quantitatively: the solvents migrate into the paper and evaporate, the dyes fade, and the resins polymerize [9].

Fig. 6. The components of the felt tip pen.

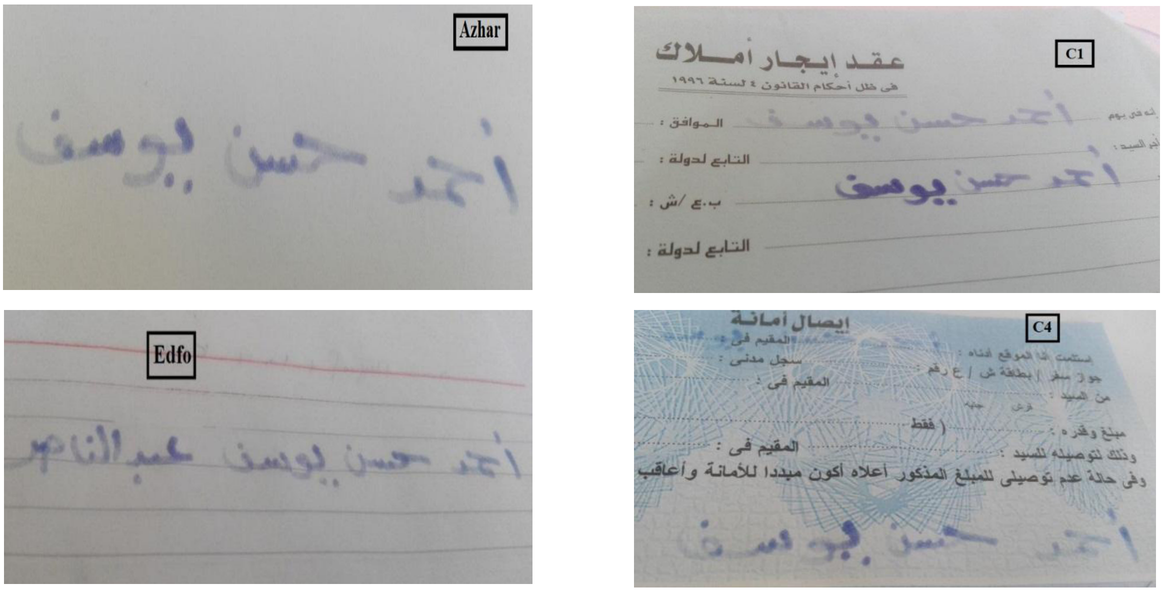

Fig. 7. Deposition of 0.471x10^{-2} M/L Th-ph ink on different types of papers under investigations in presence of 0.5 mol/L Na2CO3 at 25°C.

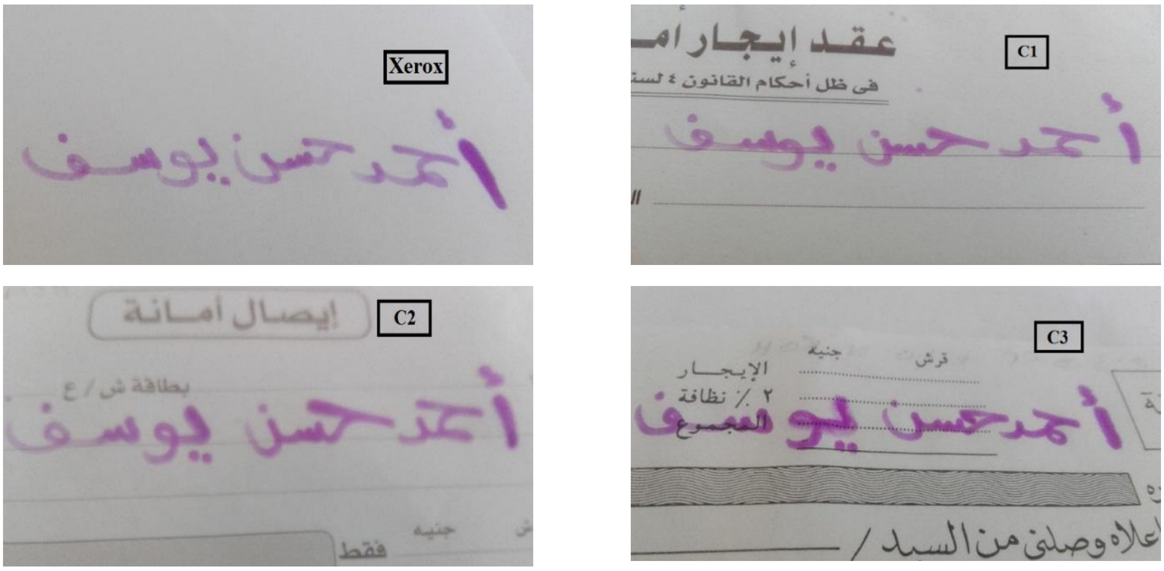

Fig. 8. Deposition of 0.471x10^{-2} M/L C-Oph ink on different types of papers under investigations in presence of 0.5 mol/L Na2CO3 at 25^{o}C.

It is clear from that adding alcoholic Th-ph and O-Cph to alkaline solution causes the mixture to become a colored quinoid form of Th-ph and O-Cph rapidly. The handwriting Th-ph and O-Cph inks stability decreased with time; this could be attributed to the formation of carbinol form (colorless) **Fig. 9,10** . From photos investigation which leads to differences in fading time and attained the result is writing stability of the paper following this order: C2 ≥ C1 > Azhar >Xerox > C3 >C4 > Edfo document.

Characterization of different types of paper by Scanning electron microscopy (SEM)

Scanning electron microscopy energy dispersive spectrometry (SEM–EDX) was used to study the homogeneity of the samples. The results are shown in Figures (11-17). Scanning electron microscopy (SEM) is known as an efficient technique for investigation and evaluation of the surface morphology. SEM were used to analyze the morphology and chemical groups of the paper. SEM of white paper, Azhar, Xerox ,Edfo,C1,C2,C3 and C4 before and after treatment with ink shown in Fig. (11-17).

Fig. 11. shows regions with particles agglomeration within cellulose fibers can be observed. Those particle regions are rich in calcium as white spots in figure. Some authors attributed the presence of calcium due to chemical treatment of cellulose source to produce paper and filler for reinforcement [10] and shows a lot of filler & sizing materials which lead to reducing of ink absorption and hence inhibits a decrease in of pH. The results show that pH of the used documents following this order : Azhar pH (8.4) >Xerox pH (8.2)> C3 pH (7.2) >C4 pH (7.1) > C1 pH (6.95) >C2 pH (6.93)> Edfo pH (6.9).

Fig. 12, shows presence of polymer coating on the surface of the fibers. The pitting on the surface of the fibers are coated with the polymer. This may reduce ink absorption and hence the surface inhibits a decrease in the pH. (Fig. 13-17) shows the fibers of bagasse pulp and aggregation of the filler and the sizing agent. The pitting appears clearly on the surface of the fibers, which could cause fast absorption of the ink (or other materials applied on the surface). However, the paper sheet looks dense with many fibers per unit area and few voids exist between the fibers.

From the results of the surface scanning and pH measurement of document C1 and C2 may be gave writing stability greater than C3 and C4 although its pH of C1 and C2 is less than C3 and C4 pH,s, this is because the physical properties of this type of paper (highly absorption paper for stencil printing). C1 and C2 Microscopy Scanning shows that the size of pits obviously large which may lead to high absorption of ink and hence accelerate pH decreasing differences in fading time can be explained. The fading time (writing stability) of the paper following this order: C2 ≥ C1 > Azhar >Xerox > C3 >C4 > Edfo .

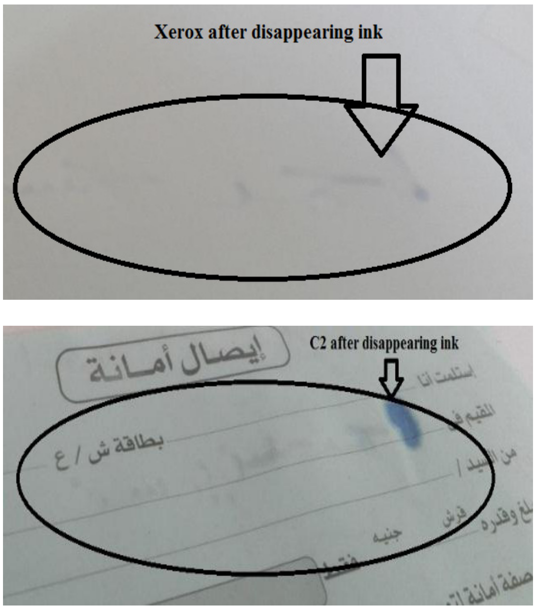

Fig. 9. Disappearing of Th-ph ink from xerox and C2 as an example of papers under investigations.

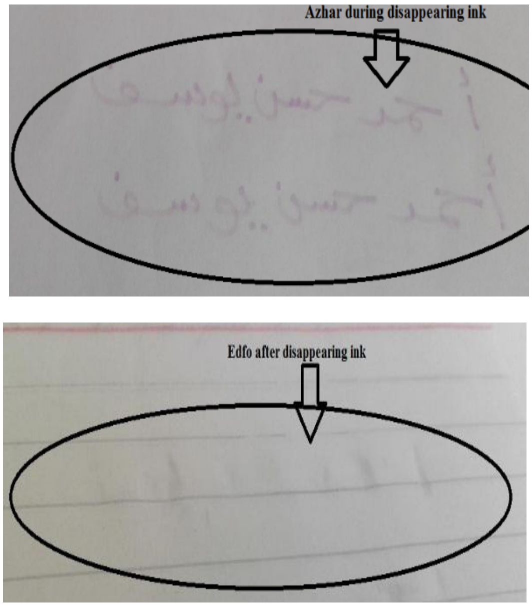

Fig. 10. Disappearing of O-Cph ink from azhar and edfo as an example of papers under investigations.

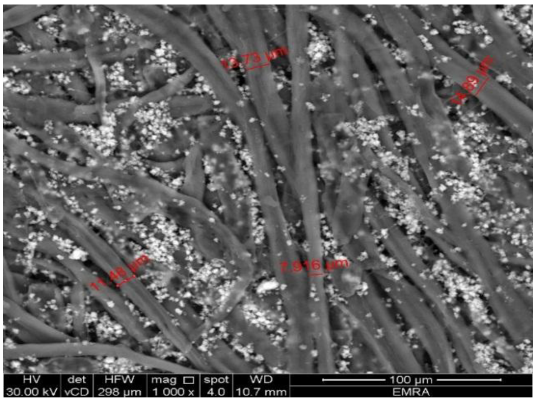

Fig.11. SEM of Azhar document 1000 x.

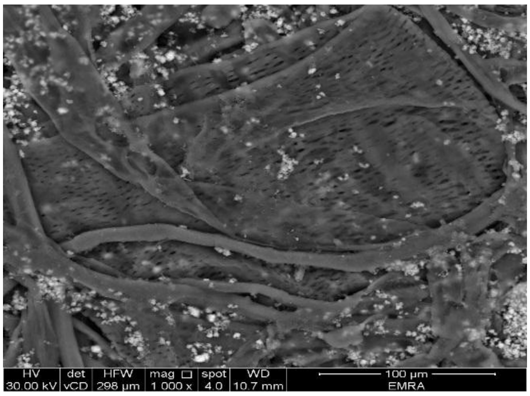

Fig.12. SEM of Xerox document 1000 x.

Fig.13. SEM of Edfo document 1000 x.

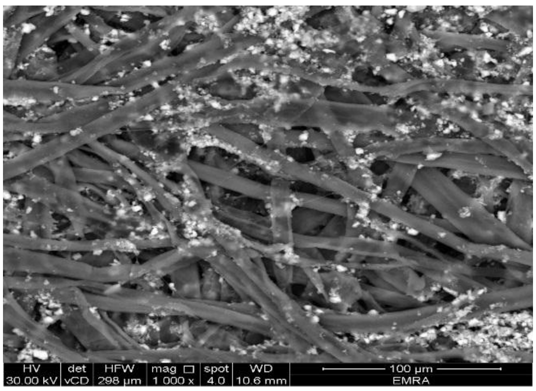

Fig.14. SEM of commercial document, C1.

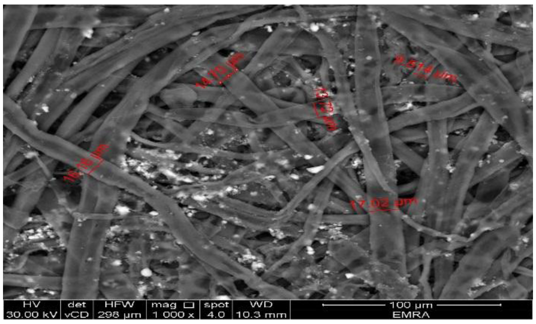

Fig. 15. SEM of commercial document, C2

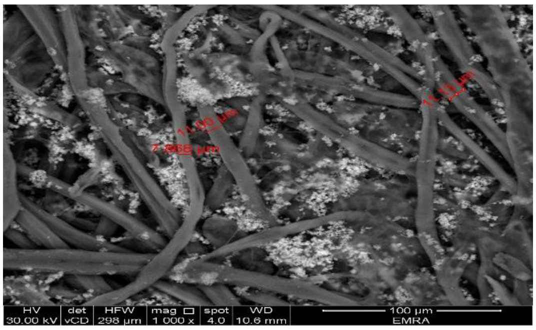

Fig. 16. SEM of commercial document, C3

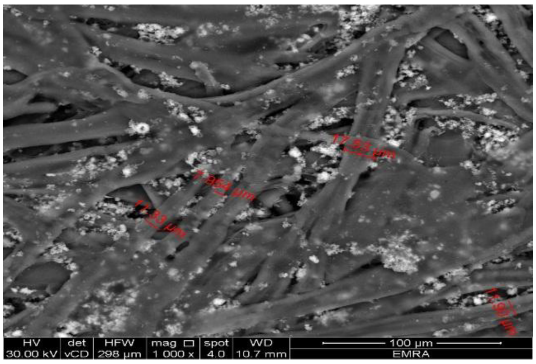

Fig.17. SEM of commercial document, C4.

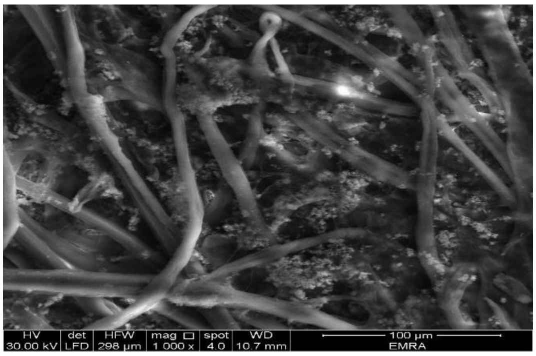

Fig.18. SEM of document C2 after treatment with O-Cph ink.

SEM of white paper C2 after treatment with ink shown in Fig. 18. The color of the white paper was white, and its fibrous structure looked complicated, while the colors check was black, and their structure looked rigid. It is clearly seen that the surface of check is coarse and rough with some cavities (micro-pores) that contributed to deposition of ink on paper while white paper appears to have a smoother surface with homogenous creases with some cavities (micro-pores) that contributed to deposition of ink. It is evident from these images that the surfaces of check have retained their original shape and distribution leading to little or unnoticeable changes. Fig.18 illustrated that Scanning electron microscopy

Writing stability (Time of Fading)

The determination of the time fading of an ink entry from a questioned document is often a major problem and a controversial issue in forensic sciences. Inks start to age once deposited on the paper surface. Upon aging, the ink stroke dries through solvent loss, fading dye and hardens through resin polymerization. Document examiners have been highly interested to study these phenomena, because the possibility of dating documents by age determination would greatly help in the investigation of backdating frauds [11]. The main problem arising in the attempt of determining the age of an ink is the dependence of aging on many factors such the type of paper, and the initial ink dye concentrations. For these reasons it has been long considered that dating a document was to compare two ink thymolphthalein (Th-ph) and O-Cresolphthalein (O-Cph) entries from the same pen on the different paper and under the same conditions.

Effect of initial ink dye concentrations

Dating time depend on quantitative measurements of physical (e.g. motions) or chemical (e.g. reactions) changes of the ink. The fading processes measured must be reproducible under given conditions to insure a correct determination of the date of entry. An ink solution contains different concentration ranging between 0.157 to $1.571X10^{-2}$ M from (Th-ph) or (O-Cph) in presence of 0.5M and 1.0 M KOH or Na_2CO_3 at 25^{o}C were applied on white paper and seem as good disappearing ink. The phrase حسن (احمد يوسف) starts out blue and violet color for (Th-ph) and (O-Cph), respectively. The colored alkaline (Th-ph) and (O-Cph) unfortunately tends to fade away with passage of time due to chemical changes. The evaluation results of the prepared Th-ph and O-Cph inks through studying the faded handwriting on different surfaces are shown in Tables (2 to 5) .The original phrase is highly colored, with passage of time varying up to 2 and 3 h for 0.471 x10^{-2} M Th-ph or O-Cph respectively tends to fade. Fading ink will vary with the pH where pH of a medium will control the magnitude of electrostatic charges in molecules [12]. Colorant fading may be caused by light. The excited dye molecule reacts with the adjacent molecule or free radical and the reaction runs according to the following reaction. The overall reaction of dye fading is determined by reaction.

Dye + hv → dye*

dye* + X → products of decay, Where X = oxygen, water and hydroxyl radical.

The stability of 0.157x10^{-2} M Th-ph ink color on white paper in in presence of 0.1 M KOH or 0.1 M Na_2CO_3 were 0.5 min and 0.25 min respectively. The stability of 0.1571 x10^{-2} M O-Cph ink color on white paper in in presence of 0.1 M KOH or 0.1 M Na_2CO_3 were 1 and 0.75 min respectively. Colorant light fastness of the whole system, it is influenced by the nature of the dye. The acidity or basicity of the ink depend upon the nature of ink dye. The presence of hetero atoms such as oxygen, which can form phenols, ethers, lactones ketone and carboxyl. Synthetic dyes are characterized by different lightfastness depending on their chemical and physical properties. Chemical structure which directly influences the lightfastness, consists of two parts: the fundamental skeleton and other substituents. Within the framework of one basic skeleton it has been found that the presence of hydroxyl groups decreased lightfastness while the presence of carboxyl groups increased it. Intra molecular hydrogen bonds as well as dye molecule symmetry, also increase its lightfastness. From Tables (2 to 5) when the concentration of dye increased, the stability of Th-ph or O-Cph ink color on the two type of paper increased may be due to dye aggregation. The dye in colored fiber is present in different sizes from single or separate molecules to large aggregates. The dyes containing larger aggregates show grater lightfastness.

TABLE 2. Effect of concentration of Th-ph ink dye on its stability (time of fading) in presence of KOH.

Conc.of Th-ph ink X10^2 M	C2 paper		Edfo paper	
	Time of fading		Time of fading	
	0.5M KOH	1.0MKOH	0.5M KOH	1.0MKOH
0.157	15 s	27 s	3 s	8 s
0.471	40 m	55 m	16 s	90 s
0.785	4 h	11 h	2 h 18m	5h 38 m
1.099	10 h	24 h	5 h	9 h 10 m
1.571	2 days	5 days	10 h 54 m	16 h 30m

TABLE 3. Effect of concentration of Th-ph ink dye on its stability (time of fading) in presence of Na2CO3.

Conc.of Th-ph ink X10^2 M	C2 paper		Edfo paper	
	Time of fading		Time of fading	
	0.5M Na_2CO_3	1.0M Na_2CO_3	0.5M Na_2CO_3	1.0MNa_2CO_3
0.157	6 s	15 s	1 s	9 s
0.471	27 m	35m	10 s	1 m
0.785	1.5 h	7 h 30 m	20 m	30m
1.099	4h	20 h 30 m	1 h	5 h
1.571	12 h	2 day	7 h	12 h

TABLE 4: Effect of concentration of O-Cph ink dye on its stability (time of fading) in presence of KOH.

Conc. of Th-ph ink X10[2] M	C2 paper		Edfo paper	
	Time of fading		Time of fading	
	0.5M KOH	1.0MKOH	0.5M KOH	1.0MKOH
0.157	44m	17 m	3 m	8 m
0.471	2 h 30 m	5 h	1 h	2 h
0.785	5 h 15 m	18 h 5 m	3 h 18m	5h 38 m
1.099	1.5 day	2 day	4 h	12 h 10 m
1.571	2 days	7 days	8 h 54 m	15 h 24m

TABLE 5: Effect of concentration of O-Cph ink dye on its stability (time of fading) in presence of Na_2CO_3.

Conc.of Th-ph ink X10[2] M	C2 paper		Edfo paper	
	Time of fading(min)		Time of fading(min)	
	0.5M Na_2CO_3	1.0M Na_2CO_3	0.5M Na_2CO_3	1.0MNa_2CO_3
0.157	2 m	5 m	2s	30 s
0.471	30m	2h	50s	50 m
0.785	1.5h	9h	30m	2h 10m
1.099	12h	1 day	2h 30m	9h 15m
1.571	18h	1.5 day	6h 40m	14 h 3m

Effects of different documents on fading time

The secret to making ink disappear is carbon dioxide in the air which reacts with the water in the solution to form carbonic acid. The carbonic acid then reacts with the base in a neutralization reaction to form carbonate. This lowers the pH of the solution with the alcohol acting as an acid to turn the ink stain magically disappears.

$$CO_2 + H_2O \longleftrightarrow H_2CO_3$$

$$H_2CO_3 + \text{ink (color)} \rightarrow HCO_3 + \text{ink (colorless)}$$

The ink drying processes were earlier described in the literature as two separated falling rate phases. The first exponential represents the fast falling rate of drying (rapid solvent evaporation and diffusion into the paper) and the second exponential represents the slow falling rate of drying (slower evaporation and diffusion processes) [13].

The fading time (time from writing until disappearance of the color) varied according to the document type. The first 2 h showed a dramatic invisible ink on all paper at low concentration of alkali as KOH or Na_2CO_3. The first 2 h period showed very little change to the ink on the papers. On application of the low concentration of alkaline 0.5 M KOH or Na_2CO_3 solutions, the faded writing becomes visible for a short time (Tables 6 to 9) . With increasing the concentration of the alkaline solution to 1.0 M, the duration of stability of the ink was increased. This procedure was carefully repeated up to 20 times with the same results and with no apparent damage to the paper itself. The most resistant paper for chemical deciphering was paper xerox and azhar as just a single simple dust with the alkaline solution will reveal the faded writing, and once more it will disappear again.

Reconquest of the Faded document

Reconquest of the faded document was carried out with several techniques [14].

Optical Examination

The faded document is examined by Projectina Docucenter 3000 using different light sources and different barrier filters. The faded document did not respond to the different light.

Chemical Reconquest

An alkaline solution was sprayed over the faded document surfaces. All the faded handwriting was visible when treated with alkaline solution [15]. A camera was employed to take pictures quickly before fading again. The fading time of the deciphered writing depends on

TABLE 6. Effect of different documents on Th-ph ink dye stability (time of fading) in presence of KOH.

Type of handwriting paper	0.471x10^{-2} M		1.571X10^{-2} M	
	Time of fading		Time of fading	
	0.5M KOH	1.0MKOH	0.5M KOH	1.0MKOH
C2	40 m	55 m	2 day	5 day
C1	32 m	50 m	1 day 18 h	4 day 20 h
Azhar	25 m	45m	1 day	3 day
Xerox	20m	40m	18 h	2 day
C3	5 m	20m	14h	23h
C4	1m	17m	12h	19 h
Edfo	16 s	90 s	10h 54 m	16 h 30m

TABLE 7. Effect of different documents on Th-ph ink dye stability (time of fading) in presence of Na_2CO_3.

Type of handwriting paper	0.471x10^{-2} M		1.571X10^{-2} M	
	Time of fading		Time of fading	
	0.5M Na_2CO_3	1.0M Na_2CO_3	0.5M Na_2CO_3	1.0M Na_2CO_3
C2	27 m	1h 35 m	12 h	2 day
C1	25 m	1 h	11 h	1.5 day
Azhar	15 m	40 m	10 h	1 day 7 h
Xerox	12 m	34 m	9 h 20 m	1 day
C3	6 m	20 m	8h 30 m	20 h
C4	2 m	15 m	7h 14 m	16 h
Edfo	10 s	1 m	7 h	12h

TABLE 8. Effect of different documents on O-Cph ink dye stability (time of fading) in presence of KOH.

Type of handwriting paper	0.471x10^{-2} M		1.571X10^{-2} M	
	Time of fading		Time of fading	
	0.5M KOH	1.0MKOH	0.5M KOH	1.0MKOH
C2	2 h 30 m	5 h	2 days	7 days
C1	2 h 2 m	4h 45 m	1 day 20 h	6 day
Azhar	1.5 h	4 h	1 day	4.5 days
Xerox	1 h 15 m	3.5 h	20 h	4 day 5 h
C3	1h 5m	3 h	16 h	2 day 15 h
C4	1h 2m	2h 40 m	11 h	1.5 day
Edfo	1 h	2 h	8 h 54m	15h 24 m

TABLE 9. Effect of different documents on O-Cph ink dye stability (time of fading) in presence of Na_2CO_3.

Type of handwriting paper	0.471x10^{-2} M		1.571X10^{-2} M	
	Time of fading		Time of fading	
	0.5M Na_2CO_3	1.0M Na_2CO_3	0.5M Na_2CO_3	1.0M Na_2CO_3
C2	30 m	2h	18 h	1.5 day
C1	28 m	1h 45m	17h	1 day 7h
Azhar	20 m	1.5h	14h	1day 5h
Xerox	17 m	1h 20m	12h	23 h
C3	14 m	1h 12m	9 h 20m	18 h 35m
C4	4 m	1h	8h	17h
Edfo	50s	50 m	6 h 40 m	14 h 3 m

the type of the used alkali and its concentration. The color of Th-ph and O-Cph inks returns when the colorle (احمد حسن يوسف) is treated with an 1.0 M alkaline solution **Fig. 19** So, it is desirable to facilitate accessibility of such alkaline solutions to forensic document examiners.

Thermal Reconquest

The faded document surfaces are exposed to the thermal effect in thermostatically controlled oven at 100°C then to 150°C for 30 min by hanging them with suitable hooks; there is no change in any of the faded document.

Possible interactions between ink and the writing surface

Elucidation of the mechanism of ink adsorption is a major challenge, as many interactions can occur during the adsorption process on writing paper. There are many factors that may influence the ink sorption behavior, such as ink structure and size, paper surface properties, steric effect and hydrogen bonding, van der Waals forces, etc. The formation of ink film on the paper is substantially influenced by paper-ink interactions. Several processes occur simultaneously when ink applied on writing surface, such as evaporation of solvents in the ambient air, diffusion/absorption and adsorption by the writing surface substrate Volatilization occurs in the ink surface, in the writing surface near the ink and in the writing surface the opposite from the ink. Moreover, the solvent molecules may diffuse into adjacent surfaces (for example in a stack of paper sheets) [16] **Fig. 20.**

Fig. 19: Reconquest of Th-ph ink from C4 paper as an examples of papers under investigations by using 1.0 M KOH at 25°C.

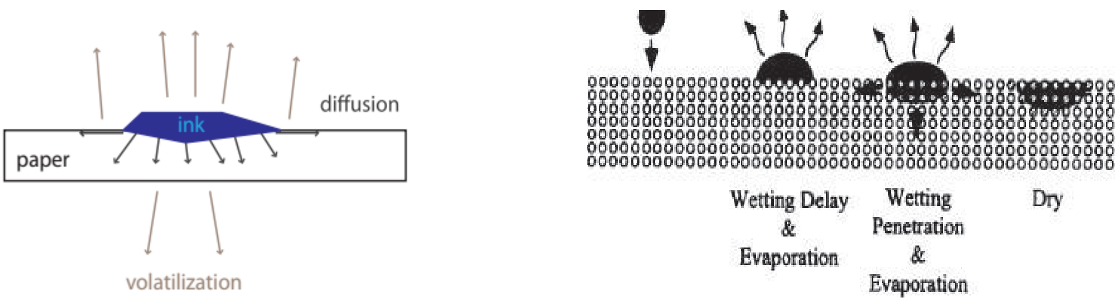

Fig. 20 .Simultaneous ink transferring processes on paper

Papers are complex materials and consist of cellulose which includes polar functional groups such as alcohol and ethers. Paper network is composed from randomly laid fibrous (cellulose) and non-fibrous (fillers) materials, it contains a complicated set of cavity pore channels with a variety of capillary dimensions. The mechanism of ink adsorption on writing paper can be take in four steps: (1) migration of ink molecules from the pen to the surface of the paper; (2) diffusion through the boundary layer to the surface of paper; (3) adsorption at a site; and (4) intraparticle diffusion into the interior of the paper.

Th-ph and O-Cph are an anionic dye that contains a hydroxyls group in its structure (which ionizes in aqueous solution, forming colored anions), together with aromatic rings. The writing paper adsorbents were lignocellulosic materials composed primarily of cellulose, hemicellulose, and lignin. Characterization of the adsorbents revealed heterogeneous surfaces and the presence of hydroxyl and carbonyl groups. Three possible interaction mechanisms [17 -19] can be proposed for the adsorption of O-Cph by the writing paper: (i) hydrogen bonding, (ii) electrostatic attraction, and (iii) π electron resonance **Fig. 21.**

Conclusion

Adding a solution of KOH or Na_2CO_3 to thymolphthalein and O-Cresollphthalein, gave blue and violet inks, respectively. The stability of the handwriting increased with increasing the concentration of alkali with the same surface, and low concentration of alkali resulted in colorless writing. Also, the stability of the handwriting increased with increasing the concentration of ink dye and high alkali concentration. The faded document is examined by Projectina Docucenter 3000 using different light sources and different barrier filters. The faded document did not respond to the different light. When the faded documents surfaces are exposed to the thermal effect in thermostatically controlled oven at 100°C then to 150°C for 30 min there is no change in all the faded documents. Commercial paper C2 (Contract Amana Blue) surfaces gave the more handwriting stability than other paper, the order of stability were C2(Contract Amana Blue) ≥ C1 (Contract Rent Blue) > Azhar >Xerox > C3(White Contract) >C4(Blue Delivery Mzarkh)

> Edfo. But the faded handwriting is visible when sprayed with the alkaline solution.

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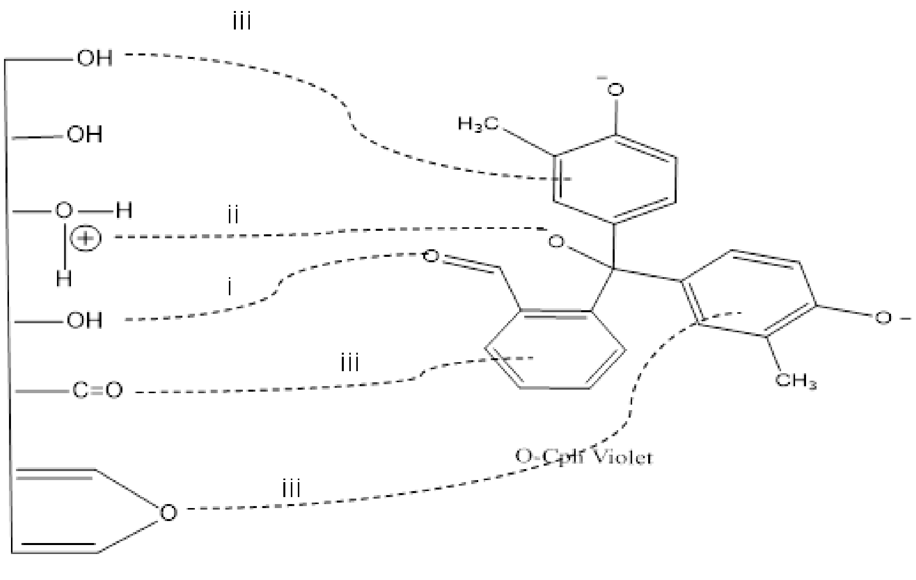

Fig. 21. Possible adsorbent-dye interactions: (i) hydrogen bonds; (ii) electrostatic attraction; (iii) π electron resonance.

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دراسة اختفاء كتابات الحبر على أنواع مختلفة من الوثائق

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تستخدم الأحبار التي تختفي في صناعة الغزل والنسيج، مثل حياكة الملابس وأيضا تستخدم كمواد تعليمية؛ على سبيل المثال، الأسئلة المطبوعة مرئية والمسافات الخاصة بالإجابة تظهر حبر تختفي غير مرئي. الإجابات تصبح مرئية فقط باستخدام مساعد التلوين. أجري هذا البحث على تحضير الأحبار التي تختفي باستخدام تركيزات مختلفة من ثيمول فثالين (Th-ph) والارثو كريزول فيثالين(O-Cph). تم تطبيق الأحبار المعدة على أنواع مختلفة من أوراق الكتابة اليدوية. وقد وجد أن ثبات الكتابة على انواع الورق المختارة زاد بزيادة ثيمول فثالين (Th-ph) والارثو كريزول فيثالين(O-Cph)، كما زاد ثبات الحبر على الورق بزيادة تركيز القلويات. تم تقييم بهتان الحبر على الورق بطرق مختلفة. ومن النتائج تبين ان نوع الورق التجاري المتداول استخدامه في ايصالات الامانة C2)) درجة ثبات الكتابة اليدوية علية أكثر من الأوراق الأخرى، ترتيب الثبات كان كالاتي

$C1 \geq C2 < Azhar < Xerox < C3 < C4 < Edfo$. كما تبين ان جميع انواع أوراق الكتابة المستخدمة المختفية او الباهتة ممكن ان ترى مره أخرى بعد إضافة المحلول القلوي. عندما تتعرض أسطح المستندات الباهتة للتأثير الحراري، لا يوجد أي تغيير في جميع المستندات الباهتة. تم استخدام أحبار تختفي في مجالات مختلفة، لكن يمكن إساءة استخدامها في التزوير والتزييف.