3. Results and Discussion

Disappearing inks may be abused in forgery or counterfeiting crimes and in this case, the handwriting surface is paper so we applied it on different paper. In this part, the results obtained in case of paper handwriting surfaces are set out in Section 3.1 to Section 3.6, disappearing inks can be used in dressmaking crafts so we applied it on different textile fabrics and the results obtained in case of fabric handwriting surfaces are set out in Section 3.7 to Section 3.12.

There are many "one-color" indicators, only one form of which (usually the alkaline species) absorbs light in the visible region of the spectrum. The same equations hold for one colour and two colour indicators **[22]**. Some of commonly one-color indicators are shown in Table 3

Table 3: lists of a number of commonly one-color indicators and their pH ranges [22]

Indicator Name	Acid Color	Transition Range, pH	Alkaline Color
Picric acid	Colorless	0.0 – 1.3	Yellow
Quinaldine red	Colorless	1.4 – 3.2	Red
2,6 - Dinitrophenol	Colorless	1.7 – 4.4	Yellow
2,4 - Dinitrophenol	Colorless	2.4 – 4.7	Yellow
2,5 - Dinitrophenol	Colorless	4.0– 5.8	Yellow
***p*-Nitrophenol**	Colorless	5.3 – 7.6	Yellow
***m*-Nitrophenol**	Colorless	6.4 – 8.8	Yellow
Quinoline blue	Colorless	7.0 – 8.0	Violet
Ethyl bis (2,4-dinitrophenyl) acetate	Colorless	7.5 – 9.1	Blue
Phenolphthalein	Colorless	8.2 – 9.8	Red
Thymolphthalein	Colorless	9.3 – 10.5	Blue
2,4,6-Trinitrotoluene	Colorless	11.7 – 12.8	Orange
1,3,5-Tinitrobenzene	Colorless	12.0 – 14.0	Orange

Let us imagine a compound whose acid (HIn) form is distinctly different in color than its conjugate base (In^-) form. In solution, the following equilibrium is established [**22**]:

$HIn = H^+ + In^-$

The equilibrium constant is:

$K_{In} = [H^+] [In^-] / [HIn]$

Rearrange this equation gives

$[H^+] = K_{In} [HIn] / [In^-]$

Taking the negative logarithm of the equation, we get

$-\log [H^+] = -\log K_{In} - \log [HIn] / [In^-]$

$pH = p K_{In} + \log [In^-] / [HIn]$

For most indicators

$[In^-] / [HIn] \leq 0.1$ in case of acid color

and $[In^-] / [HIn] \geq 10$ in case of base color

Therefore, the pH range over which the indicator changes color is

$pH = p K_{In} \pm 1$

Many acid base indicators can be used as disappearing inks. But the indicator range must be suitable for the used handwriting surface. The colorless pH of the used acid- base indicator should be greater than pH of the used handwriting surface.

Thymolphthalein and phenolphthalein can be used as disappearing ink because their pH transition range is suitable for most handwriting surfaces.

3.1 Effect of Different Concentrations of NaOH with Different Concentrations of Thymolphthalein on the Fading Time Using Paper Surfaces.

When NaOH solution was added to T_1, T_2, T_3, T_4 and T_5 (thymolphthalein 0.1, 0.2, 0.4, 0.8 & 1.2% wt/v respectively), blue inks were produced and used for handwriting, then the writing will be disappeared with time this is may be due to the decreased pH of the ink.

NaOH reacted with CO_2 (in the air) in the presence of H_2O to form colorless sodium bicarbonate. The reaction of alcoholic thymolphthalein with alkaline solution (NaOH) caused the mixture to become rapidly colored. The blue ink turned colorless when NaOH reacted with the carbon dioxide (acid) in the air.

$$2\,NaOH + CO_2 \xrightarrow{H_2O} Na_2CO_3 + 2\,H_2O$$

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$

1. Sodium hydroxide reacted with carbon dioxide in the air to form sodium bicarbonate, which was less basic than sodium hydroxide.
2. Sodium bicarbonate caused the indicator to change from blue to colorless. Thymolphthalein transition range is at pH 9.3-10.5. Below this pH, it is colorless and it is blue above the range.
3. The alcohol evaporates and left only the colorless residue.

It is clear from Table 4 and Figures (21-25) that, when the concentration of thymolphthalein increased the stability of the handwriting increased.

Each Figure shows the effect of different concentration of 0.5 ml NaOH with different concentration of thymolphthalein on the same surface. In case of using 0.01 N NaOH it gave ink with pHs less than 10 and so the inks gave colorless writing **(CLW)**. But in case of using 0.1 N NaOH it gave short handwriting stability, also in case of using 0.5 N NaOH gave more handwriting and in case of 1 N NaOH gave the greater handwriting stability.

The fading time following this order 1N NaOH > 0.5 N NaOH> 0.1 N NaOH > 0.01N NaOH. This means that increasing the concentration of sodium hydroxide leads to increasing pH of the ink and hence the pH of the handwriting strokes. The high pH of writing strokes leads to a low decrease in pH of the ink and so gives more stable writing (more fading time). Also increasing the concentration of thymolphthalein leads to increasing the fading time.

Table 4 and Figure 21 show the fading time of Azhar paper. In case of using 0.01 N NaOH, Azhar paper gave colorless writing **(CLW)** and in case of using 0.1 N NaOH, it gave short handwriting stability from 4 mins to 30 mins. In case of using 0.5 N NaOH, it gave more writing stability from 6 hrs to 18 hrs but in case of using 1 N NaOH, it gave the best handwriting stability from 2 days to 4 days.

Furthermore, Table 4 and Figure 22 show the fading time of Xerox paper. In case of 0.01 N NaOH, Xerox paper gave colorless writing and in case of using 0.1 N NaOH, it gave short handwriting stability from 2 mins to 15 mins. In case of using 0.5 N NaOH, it gave more handwriting stability from 3 hrs to 6 hrs but in case of using 1 N NaOH, it gave the best handwriting stability from 18 hrs to 54 hrs.

Table 4: Effect of different concentrations of NaOH with different concentrations of thymolphthalein on the fading time

NaOH	Thymolphthalein Concentration	pH of the ink	Abs. of the ink at 600 nmº	Fading Time*				
				Paper				
				Azhar	Xerox	Quena	Edfo	Rakta
0.5 ml 0.01 N	4ml of T_1	9.45	1.42	CLW**	CLW	CLW	CLW	CLW
	4ml of T_2	9.40	1.42	CLW	CLW	CLW	CLW	CLW
	4ml of T_3	9.30	1.43	CLW	CLW	CLW	CLW	CLW
	4ml of T_4	9.10	1.26	CLW	CLW	CLW	CLW	CLW
	4ml of T_5	8.70	0.64	CLW	CLW	CLW	CLW	CLW
0.5 ml 0.1 N	4ml of T_1	11.45	4.2	4 mins	2 mins	30 secs	TC***	TC
	4ml of T_2	11.31	4.2	5 mins	3 mins	1min	TC	TC
	4ml of T_3	11.23	4.1	10 mins	6 mins	3 mins	TC	TC
	4ml of T_4	11.11	4.1	18 mins	12 mins	5 mins	TC	TC
	4ml of T_5	11.02	4.1	30 mins	15 mins	10 mins	TC	TC
0.5 ml 0.5 N	4ml of T_1	11.65	4.2	6 hrs	3 hrs	1 hr	30 mins	8 mins
	4ml of T_2	11.6	4.25	6 hrs	3.5 hrs	1.5 hrs	45 mins	10 mins
	4ml of T_3	11.55	4.28	12 hrs	4 hrs	2 hrs	1 hr	15 mins
	4ml of T_4	11.52	4.3	18 hrs	5 hrs	2.5 hrs	1.5 hrs	20 mins
	4ml of T_5	11.5	4.3	18 hrs	6 hrs	3 hrs	2 hrs	25 mins
0.5 ml 1 N	4ml of T_1	11.95	4.34	2 days	18 hrs	6 hrs	2 hrs	30 mins then TY****
	4ml of T_2	11.89	4.3	2.5 days	1 day	6 hrs	6 hrs	45 mins h then TY
	4ml of T_3	11.81	4.38	3 days	1.5 days	12 hrs	6 hrs	1 hrs then TY
	4ml of T_4	11.75	4.4	3.5 days	2 days	18 hrs	12 hrs	1.25 hrs then TY
	4ml of T_5	11.70	4.4	4 days	2.25 days	24 hrs	18 hrs	1.5 hrs then TY

T_1, T_2, T_3, T_4 and T_5 (0.1, 0.2, 0.4, 0.8 and 1.2% thymolphthalein wt/v respectively)

***Fading time** of writing is the time from writing to its color disappearance (complete fading), this means when the fading time is short, the handwriting is non stable (short handwriting stability), and vice versa

****CLW** : the ink itself is blue but the writing was colorless.

*****TC** : the handwriting turned colorless rapidly.

******TY** : the handwriting turned yellow.

The color of the writing was blue and then faded. The fading time is shown in Table 4. In some cases, when the ink was light blue in color and had pHs less than 10, colorless writing **(CLW)** was resulted. In other cases, when the ink was dark blue and produced blue writing, the writing turned colorless **(TC)** rapidly.

But when writing on Rakta paper with the ink which contain 1 N NaOH the handwriting turned yellow **(TY)** rapidly, this yellow color result from the reaction of NaOH with Rakta paper components this conclusion was certified by writing with 1N solution of NaOH on Rakta paper it gave yellow writing this may de due to the presence of lignin.

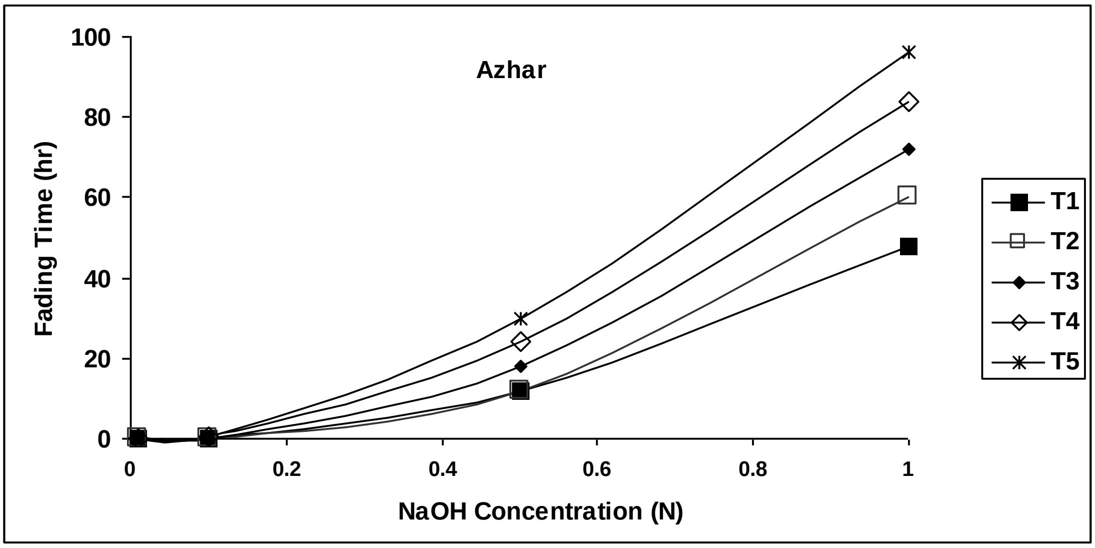

Figure 21: Effect of different concentrations of NaOH with different concentrations of thymolphthalein on the fading time using Azhar paper

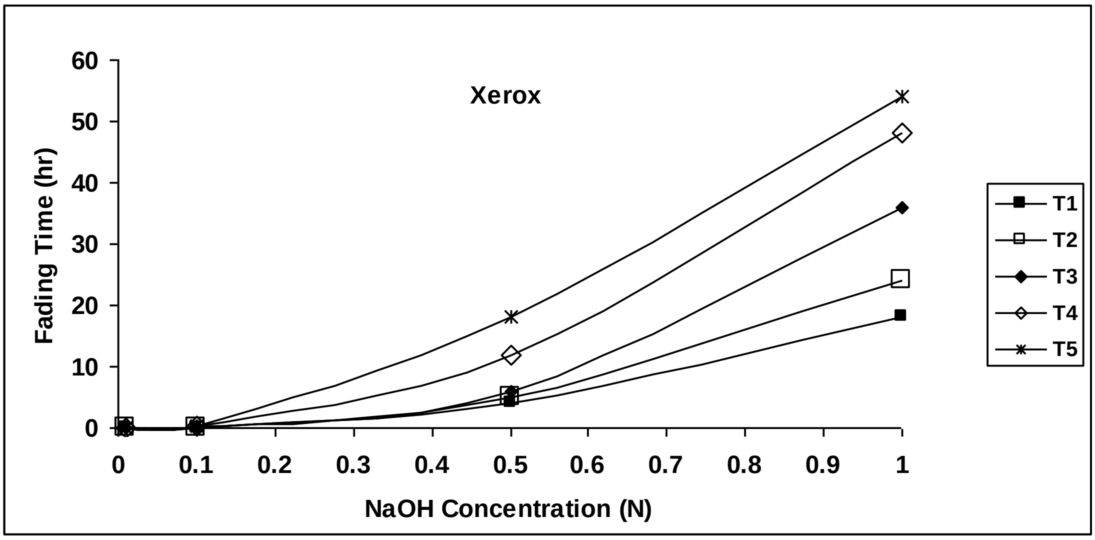

Figure 22: Effect of different concentrations of NaOH with different concentrations of thymolphthalein on the fading time using Xerox paper

Results of Table 4 and Figure 23 disclose the fading time of Quena paper. In case of using 0.01 N NaOH, Quena paper gave colorless writing and in case of using 0.1 N NaOH, it gave short handwriting stability from 30 secs to 10 mins. In case of using 0.5 N NaOH, it gave more handwriting stability from 1 hr to 3 hrs but in case of using 1N NaOH, it gave the best handwriting stability from 2 hrs to 18 hrs.

The results of Table 4 and Figure 24 show the fading time of Edfo paper. In case of using 0.01 N NaOH, Edfo paper gave colorless and in case of using 0.1 N NaOH, it gave very short handwriting stability, the writing turned colorless **(TC)** rapidly. In case using of 0.5 N NaOH, it gave more handwriting stability from 30 mins to 2 hrs but in case of using 1 N NaOH, it gave the best handwriting stability from 2 hrs to 18hrs.

Results of Table 4 and Figure 25 show the fading time of Rakta paper. In case of using 0.01 N NaOH, Rakta paper gave colorless writing **(CLW)** and in case of using 0.1 N NaOH, it gave very short handwriting stability, the writing turned colorless **(TC)** rapidly. In case using of 0.5 N NaOH, it gave more writing stability from 8 mins to 25 mins but in case of 1 N NaOH, it gave the best handwriting stability from 30 mins to 1.5 hrs. In this case (using 1 N NaOH) the blue handwriting turned yellow color **(TY)** this yellow color result from the reaction of NaOH with Rakta paper components this conclusion was certified by writing with 1N solution of NaOH on Rakta paper it gave yellow writing.

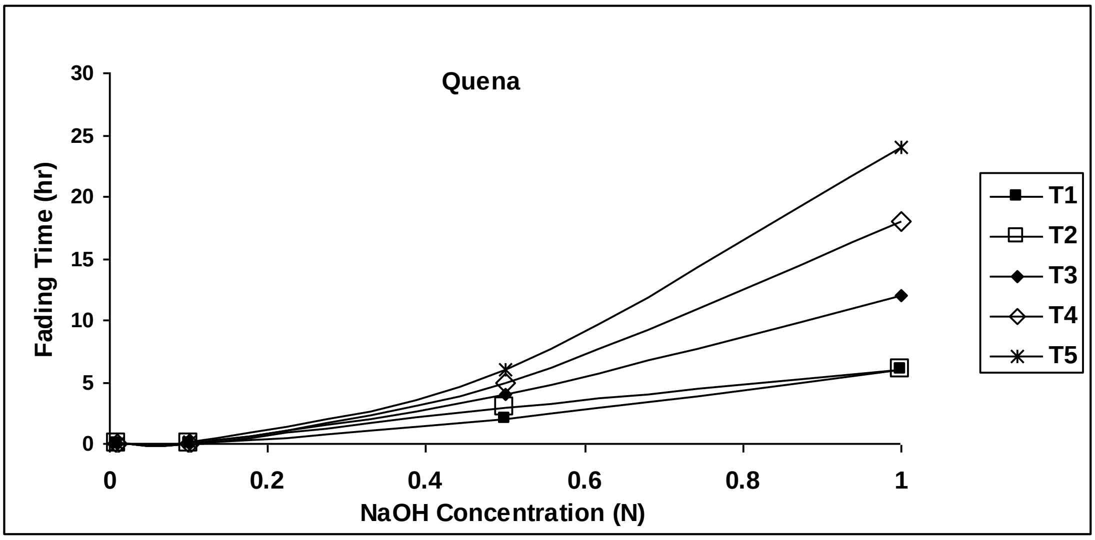

Figure 23: Effect of different concentrations of NaOH with different concentrations of thymolphthalein on the fading time using Quena paper

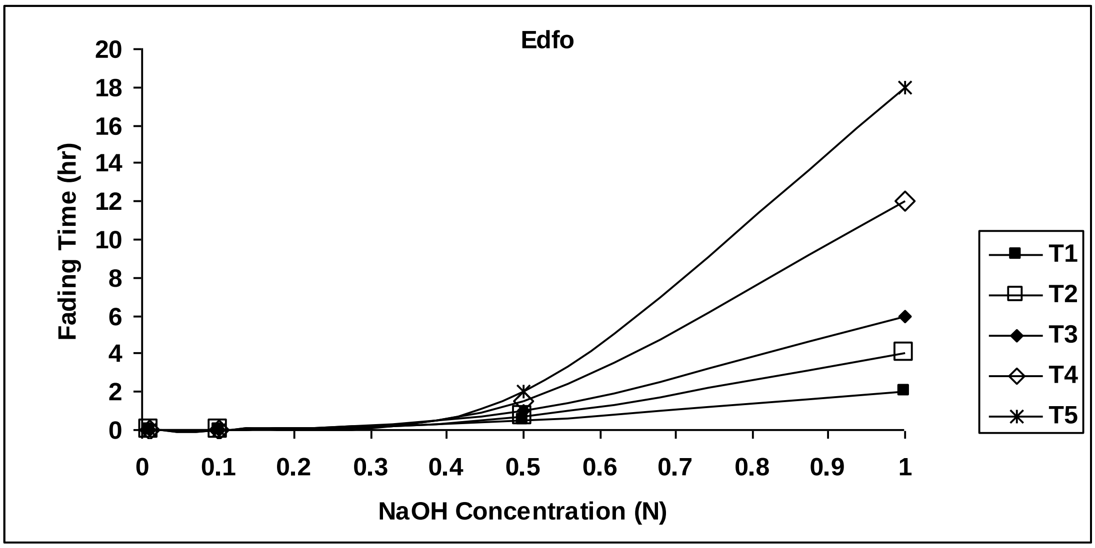

Figure 24: Effect of different concentrations of NaOH with different concentrations of thymolphthalein on the fading time using Edfo Paper

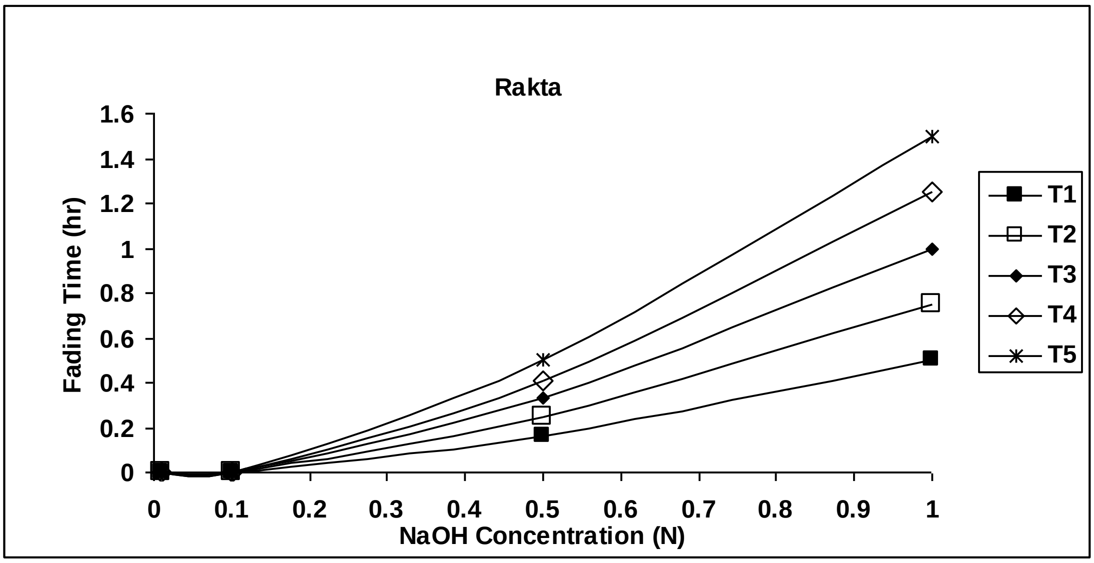

Figure 25: Effect of different concentrations of NaOH with different concentrations of thymolphthalein on the fading time using Rakta paper

It is clear from Table 4 that, at the same conditions (i.e. the same concentration of NaOH and the same concentration of thymolphthalein) Azhar paper gave more writing stability than Xerox than Quena than Edfo than Rakta this due to difference in the properties of these papers.

From the results of the surface scanning and pH measurement the differences in fading time can be explained. The fading time (writing stability) of the paper following this order :-

Azhar > Xerox > Quena > Edfo > Rakta paper.

The increased writing stability may be caused by increased pHs of the paper surface (Table 5). But Rakta paper gave writing stability less than Edfo although its pH is more than Edfo pH, this is because the physical properties of this type of Rakta paper (highly absorption paper for stencil printing), Rakta Microscopy Scanning shows that the size of pits obviously large which may lead to high absorption of ink ad hence accelerate pH decreasing (Figure 26).

Figure 26: Photomicrograph of Rakta paper 1000 x

Figure 26 shows the surface of paper make from rice straw pulp by Rakta company. The paper sheet is less dense and of fewer number of fibers per unit area than that of Quena or Edfo companies. This means that there are a lot of voids on the surface of the paper that could result in easier absorption of the ink or other applied coatings also the size of pits obviously large which may lead to high absorption of ink and hence accelerate a decrease in the pH.

Table 5: pHs of the used paper

Paper type	pH
Azhar	8.4
Xerox	8.2
Quena	7.8
Edfo	6.9
Rakta	7.4

Table 5shows that pH of the used paper following this order

Azhar >Xerox > Quena > Rakta >Edfo

Figure 27: Photomicrograph of Azhar paper 1000 x

Figure 27 shows a lot of filler & sizing materials which lead to reducing of ink absorption and hence inhibits a decrease in of pH.

Figure 28: Photomicrograph of Xerox paper 1000x

Figure 28 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 reduces ink absorption and hence the surface inhibits a decrease in the pH.

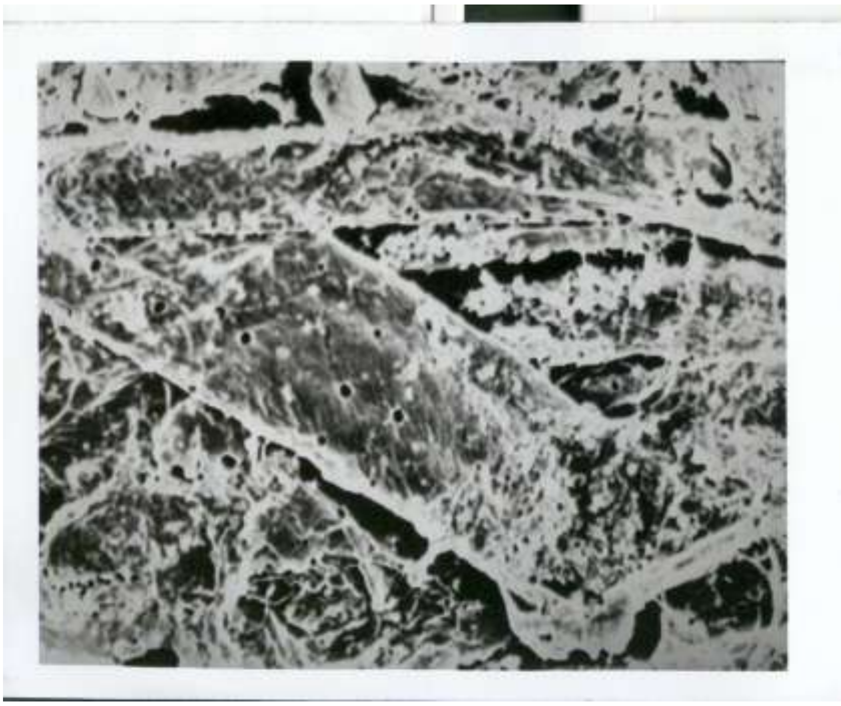

Figure 29: Photomicrograph of Quena paper 1000 x

Figure 29 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 denser with a lot of fibers per unit area and a few voids exist between the fibers.

Figure 30: Photomicrograph of Edfo paper 1000 x

Figure 30 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.

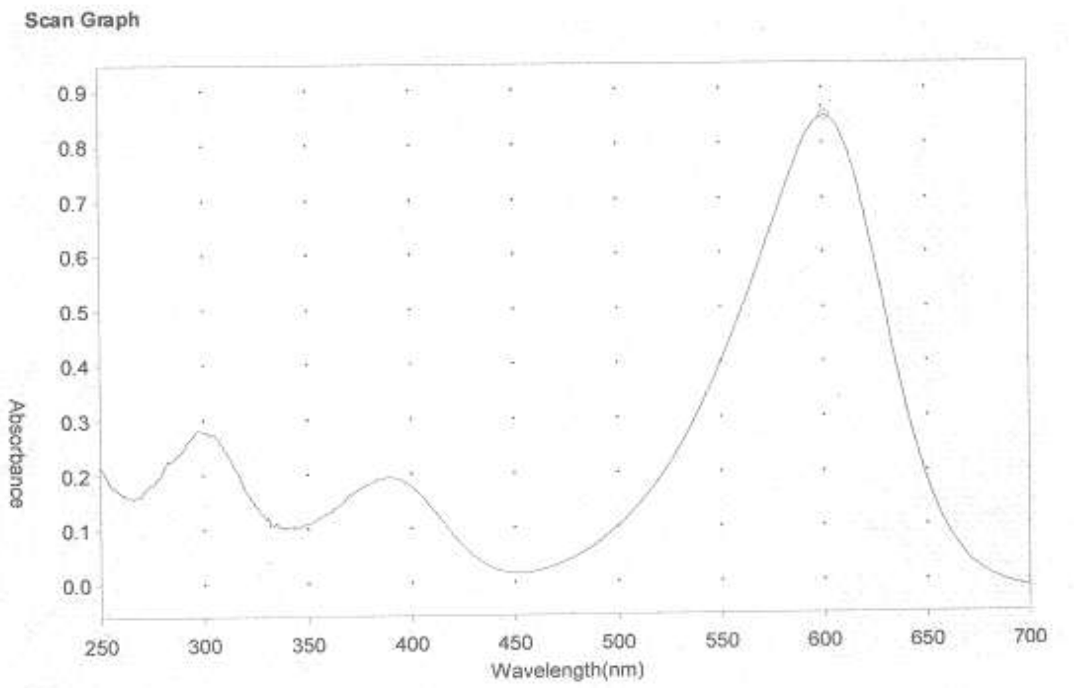

Figure 31: Spectrophotometric scan for thymolphthalein.

Absorbance of the ink at 600 nm°: it is clear from Figure 31 that, the Spectrophotometric scan for diluted solution of thymolphthalein ink (5 ml of T_1 thymolphthalein 0.1% wt/ v and 0.1 ml 0.01 N NaOH) gave the maximum absorbance at 600 nm.

3.2 Effect of Large Volume of 1 N NaOH with Different Concentrations of Thymolphthalein on the Fading Time Using Paper Surfaces

From the pervious Table (Table 4), 1 N NaOH gave more handwriting stability. So increasing the volume of 1N NaOH affects the fading time. Equal volume of 1 N NaOH and thymolphthalein were used and the results obtained are set out in Table 6.

It is clear from Table 6 and Figure 32 that, the handwriting stability in this case (using equal volume of 1 N NaOH) is best than using 0.5 ml of 1 N NaOH (Table 4).

Results of Table 6 and Figure 32 show that, Azhar paper gave writing stability from 15 days to 23 days, Xerox paper gave writing stability from 11days to 18 days, Quena paper gave writing stability from 2.5days to 5 days, Edfo paper gave writing stability from1.5 days to 4 days and Rakta paper gave writing stability from 12 hrs to 1.5 days. Also it is clear from results of Table 6 and Figure 32 that for the same handwriting surface, the stability of handwriting increased with increasing thymolphthalein concentration. The fading time (writing stability) of the paper following this order:-

Azhar > Xerox > Quena > Edfo > Rakta paper.

From the above results we noticed that the best conditions for preparing more stable thymolphthalein disappearing ink (for using it on paper surface) are using thymolphthalein concentration 1.2% thymolphthalein wt/v with equal volum of 1 N NaOH. Also Azhar handwriting surface gave the more handwriting stability.

Table 6: Effect of large volume of 1 N NaOH with different concentrations of thymolphthalein on the fading time

NaOH	Thymolphthalein Concentration	pH of the ink	Abs. of the ink at 600 nm	Fading Time*				
				Paper				
				Azhar	Xerox	Quena	Edfo	Rakta
4 ml 1 N	4ml of T_1	13.6	4.49	15 days	11 days	2.5 days	1.5 days	12 hrs then TY****
	4ml of T_2	13.41	4.57	16 days	12 days	3 days	2 days	18 hrs then TY
	4ml of T_3	13.22	4.62	18 days	14 days	3.5 days	2.5 days	1day then TY
	4ml of T_4	13.00	4.9	21 days	16 days	4 days	3 days	1.25 days then TY
	4ml of T_5	12.9	5.2	23 days	18 days	5 days	4 days	1.5 days then TY

T_1, T_2, T_3, T_4 and T_5 (0.1, 0.2, 0.4, 0.8 and 1.2% thymolphthalein wt/v respectively).

*__Fading time__ of writing is the time from writing to its color disappearance (complete fading).

****__TY__ : the handwriting was blue then turned yellow

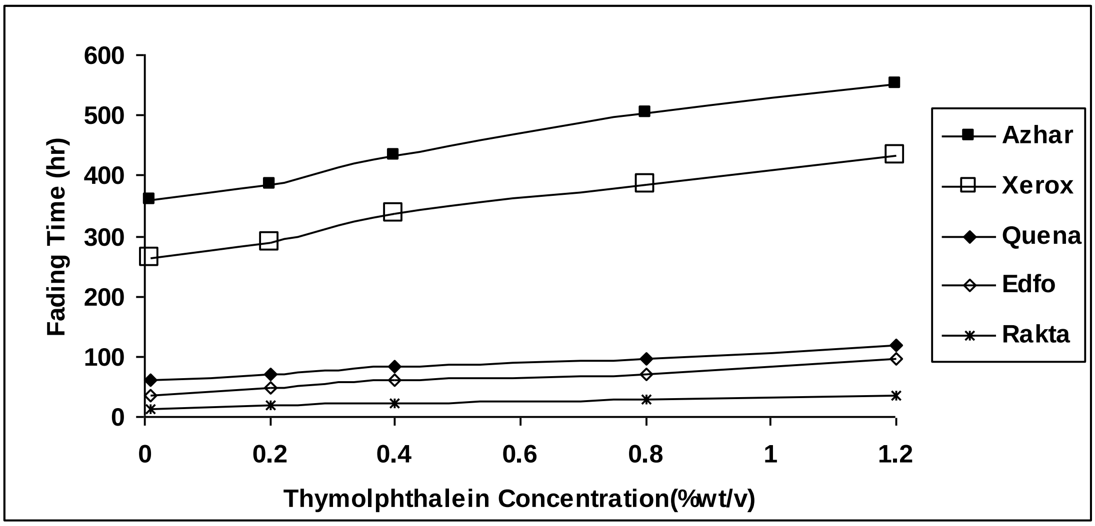

Figure 32: Effect of large volume of 1 N NaOH with different concentrations of thymolphthalein on the fading time using different paper surfaces

3.3 Effect of Different Concentrations of NaOH with Different Concentrations of Phenolphthalein on the Fading Time Using Paper Surfaces

Different concentrations of NaOH were added to the prepared phenolphthalein and red inks were produced.These inks were used in handwriting on paper surfaces by filling a dry 1 mm-point felt-tip pen, the writing with these inks was red.

The color of the writing was red and faded. The results of the fading time of writing are set out in Table 7. In case of using 0.01 N NaOH, the red inks were a light red and had pHs less than 10, so these inks gave colorless writing **(CLW)**. In case of using 0.1 N NaOH the ink has a dark red color and produced red writing but this writing turned rapidly to colorless (**TC**) so the handwriting gave short handwriting stability, in case of 0.5 N NaOH gave more handwriting and in case of using 1 N NaOH, it gave the greater handwriting stability. The fading time following this order:-

1N NaOH > 0.5 N NaOH > 0.1 N NaOH > 0.01N NaOH.

This means that, increasing the concentration of sodium hydroxide leads to increasing the pH of the ink and hence the pH of the handwriting strokes. The high pH of writing strokes leads to a low decrease in pH of the ink and so it gives more stable writing. Also increasing the concentration of phenolphthalein leads to increasing the fading time.

Results of Table 7 and Figure 33 show the fading time of Azhar paper. In case of using 0.01 N NaOH, Azhar paper gave colorless writing **(CLW)**. In case of using 0.1 N NaOH, it gave short handwriting stability from 1 hrs to 2.5 hrs. In case of using 0.5 N NaOH, it gave more writing stability from 18 hrs to 2 days but in case of 1 N NaOH, it gave the best handwriting stability from 4 days to 6 days.

Table 7: Effect of different concentrations of NaOH with different concentration of phenolphthalein on the fading time

NaOH	Phenolphthalein Concentration	pH of the ink	Abs. of the ink at 560 nm°	Fading Time*				
				Paper				
				Azhar	Xerox	Quena	Edfo	Rakta
0.5 ml 0.01 N	4ml of P_1	9.25	2.05	CLW**	CLW	CLW	CLW	CLW
	4ml of P_2	9.22	1.0	CLW	CLW	CLW	CLW	CLW
	4ml of P_3	8.95	0.5	CLW	CLW	CLW	CLW	CLW
	4ml of P_4	8.76	0.19	CLW	CLW	CLW	CLW	CLW
	4ml of P_5	8.60	0.11	CLW	CLW	CLW	CLW	CLW
0.5 ml 0.1 N	4ml of P_1	10.95	4.9	1 hr	10 mins	1 min	TC***	TC
	4ml of P_2	10.90	4.9	1 hr	20 mins	2 mins	TC	TC
	4ml of P_3	10.25	5.3	1.5 hrs	30 mins	3 mins	1 min	TC
	4ml of P_4	9.75	5.3	2 hrs	45 mins	6 mins	2 mins	TC
	4ml of P_5	9.55	5.3	2.5 hrs	1 hr	15 mins	3 mins	TC
0.5 ml 0.5 N	4ml of P_1	11.35	5.45	18 hrs	12 hrs	3 hrs	1.25 hrs	5 mins
	4ml of P_2	11.3	5.4	1 day	12 hrs	4 hrs	1.5 hrs	10 mins
	4ml of P_3	11.25	5.3	1.25 days	18 hrs	4.5 hrs	2 hrs	15 mins
	4ml of P_4	11.15	5.2	1.5 days	1 day	5 hrs	2.5 hrs	20 mins
	4ml of P_5	11.08	5.1	2 days	1.25 days	6 hrs	3 hrs	25 mins
0.5 ml 1 N	4ml of P_1	11.57	5.0	4 days	2 days	12 hrs	6 hrs	1 hr then TY****
	4ml of P_2	11.51	5.3	4.5 days	2.25 days	18 hrs	12 hrs	1.25 hrs then TY
	4ml of P_3	11.42	6.0	5 days	2.5 days	1 day	18 hrs	1.5 hrs then TY
	4ml of P_4	11.35	6.0	5.5 days	3 days	1.5 days	18 hrs	2 hr then TY
	4ml of P_5	11.30	6.0	6 days	4 days	2 days	1 day	2.25 hr then TY

P_1, P_2, P_3, P_4 and P_5 (0.1, 0.2, 0.4, 0.8 and 1.2% phenolphthalein wt/v respectively)

***Fading time** of writing is the time from writing to its color disappearance (complete fading).

****CLW** : the ink itself in this case (phenolphthalein) is red but the writing was colorless.

*****TC** : the handwriting turned colorless rapidly.

******TY** : the handwriting turned yellow.

Absorbance of the ink at 560 nmº: the Spectrophotometric scan for diluted solution of phenolphthalein ink (5 ml of P_1 thymolphthalein 0.1% wt/ v and 0.1 ml 0.01 N NaOH) gave the maximum absorbance at 560 nm.

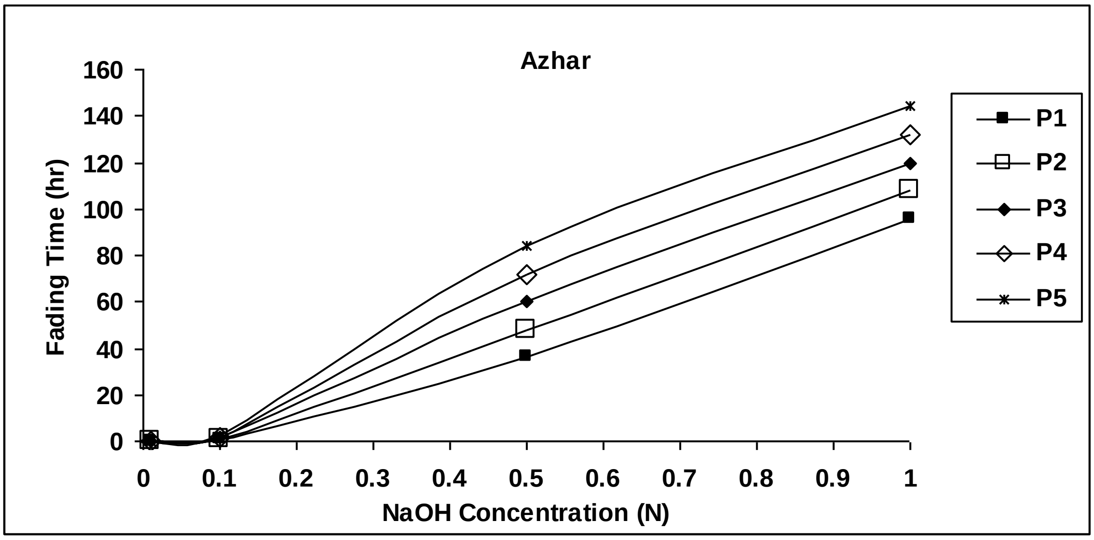

Figure 33: Effect of different concentrations of NaOH with ifferent concentrations of phenolphthalein on the fading time using Azhar paper

Table 7 and Figure 34 show the fading time of Xerox paper. In case of using 0.01 N NaOH, Xerox paper gave colorless writing **(CLW)** and in case of 0.1 N NaOH, it gave short handwriting stability from 10 mins to 1 hr. In case of 0.5 N NaOH, it gave more writing stability from 12 hrs to 1.25days but in case of using 1 N NaOH, it gave the best handwriting stability from 2 days to 4 days.

Table 7 and Figure 35 show the fading time of Quena paper. In case of using 0.01 N NaOH, Quena paper gave colorless writing **(CLW)** and in case of using 0.1 N NaOH, it gave short handwriting stability from 1 min to 15 mins. In case of using 0.5 N NaOH, it gave writing stability from 3 hrs to 6 hrs but in case of 1 N NaOH, it gave the best handwriting stability from 12 hrs to 2 days.

Results of Table 7 and Figure 36 show the fading time of Edfo paper. In case of using 0.01 N NaOH, Edfo paper gave colorless writing **(CLW)** and in case of using 0.1 N NaOH, it gave short handwriting stability from (**TC)** to 3 mins. In case of using 0.5 N NaOH, it gave more writing stability from 1.25 hrs to 3 hrs but in case of using 1 N NaOH, it gave the best handwriting stability from 6 hrs to 1 day.

Table 7 and Figure 37 show the fading time of Rakra paper. In case of using 0.01 N NaOH, Rakra paper gave colorless writing **(CLW)** and in case of using 0.1 N NaOH, it gave short handwriting stability **(TC)**. In case of using 0.5 N NaOH, it gave more writing stability from 5 mins to 25 mins but in case of using 1 N NaOH, it gave the best handwriting stability from 1 hr to 2.25 hrs. In this case (1 N NaOH), we noticed that, the blue handwriting turned to yellow color **(TY)** this yellow color may be due to the reaction of NaOH with Rakta paper components as explained in Section 3.1.

Furthermore, Table 7 shows that a similar pattern of results is obtained. When the concentration of NaOH increased, the stability of the writing increased and when the concentration of phenolphthalein increased, the stability of the writing increased.

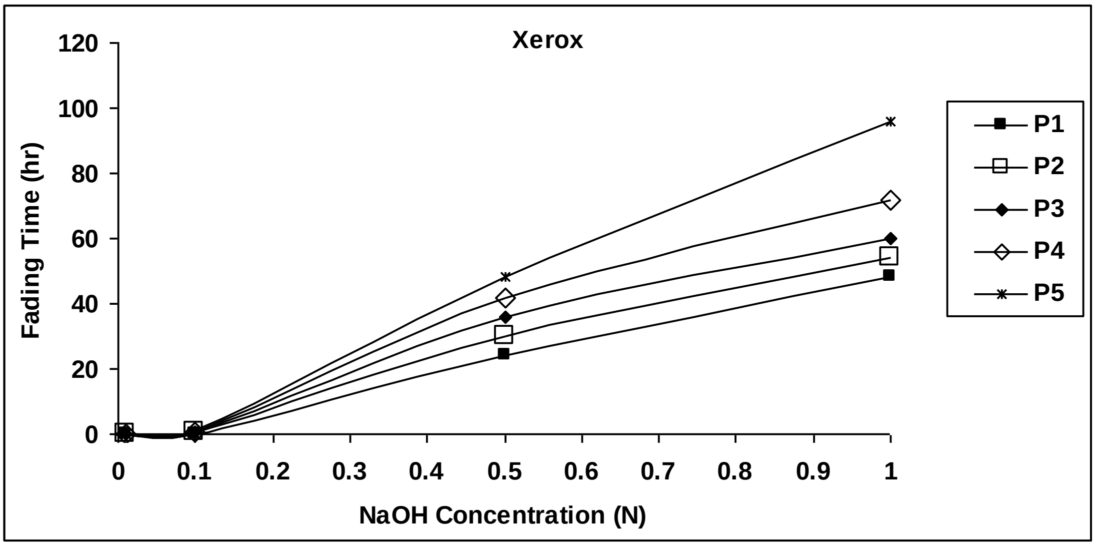

Figure 34: Effect of different concentrations of NaOH with different concentrations of phenolphthalein on the fading time using Xerox paper

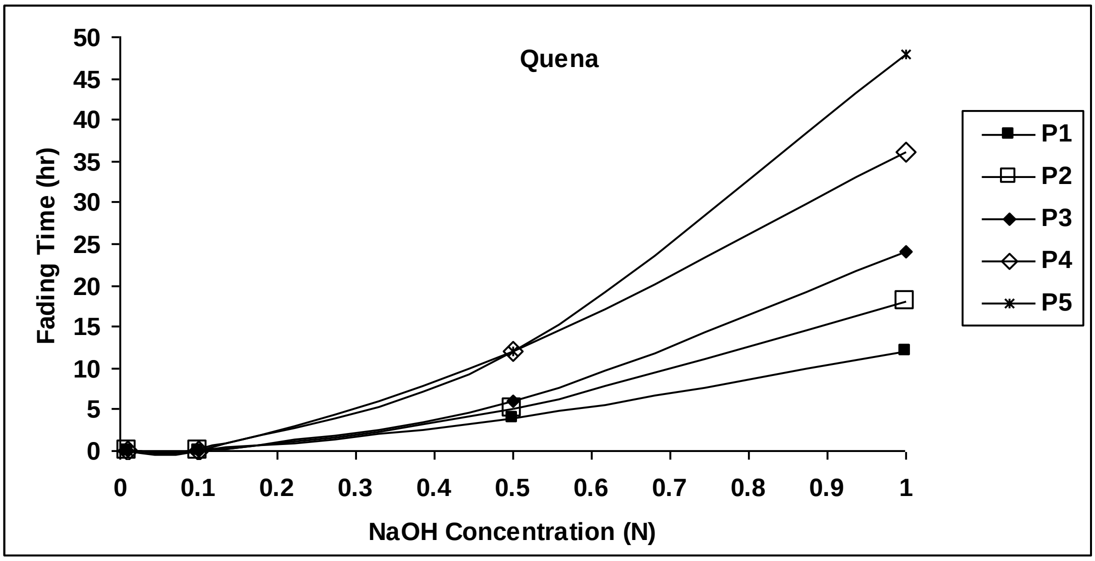

Figure 35: Effect of different concentrations of NaOH with different concentrations of phenolphthalein on the fading time using Quena paper

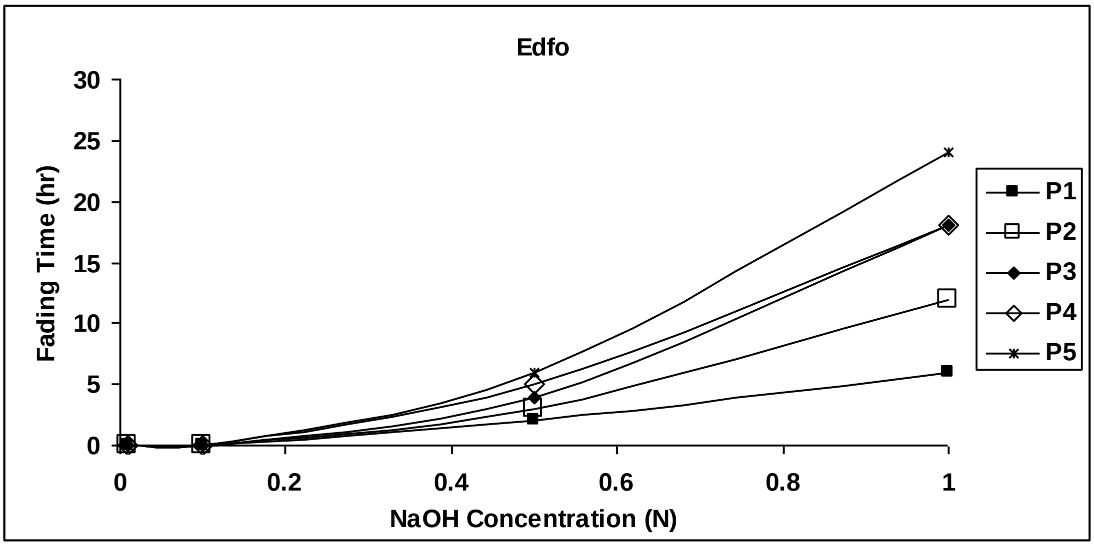

Figure 36: Effect of different concentrations of NaOH with different concentrations of phenolphthalein on the fading time using Edfo paper

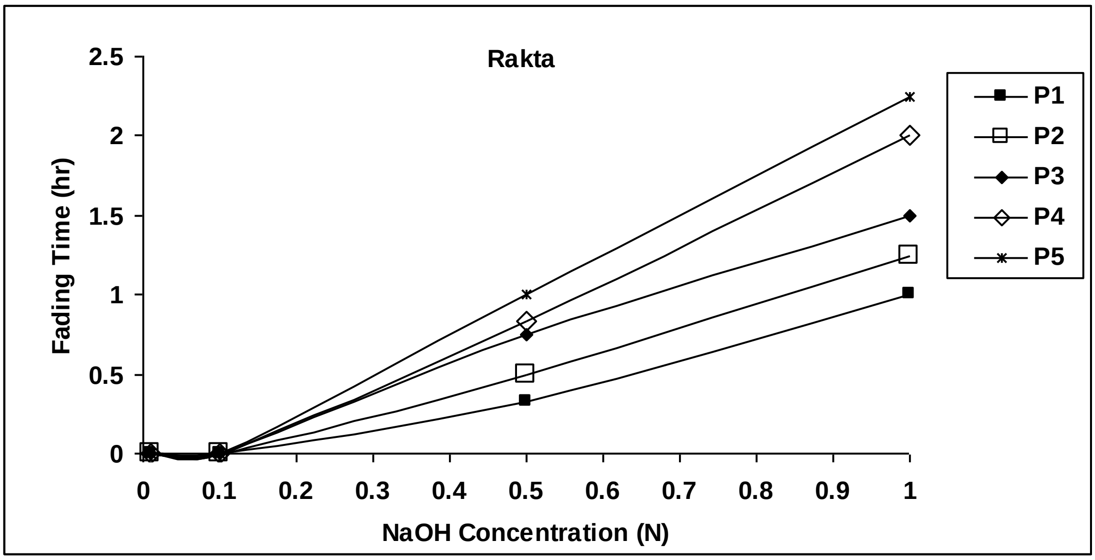

Figure 37: Effect of different concentrations of NaOH with different concentrations of phenolphthalein on the fading time using Rakta paper

It is clear from Table 7 with the same conditions (the same concentration of NaOH and the same concentration of phelphethalein) Azhar paper gave more writing stability than Xerox than Quena than Edfo than Rakta this may be due to the difference in the properties of the used papers.

From the results of the surface scanning and pH measurement the differences in fading time can be explained (Section 3.1). The fading time (writing stability) of the paper following this order :-

Azhar > Xerox > Quena > Edfo > Rakta paper.

The increased writing stability may be caused by increased pHs of the paper surface (Table 5). But Rakta paper gave writing stability less than Edfo although its pH is more than Edfo pH, this is because the physical properties of this type of Rakta paper (highly absorption paper for stencil printing), Rakta Microscopy Scanning shows that the size of pits obviously large which may lead to high absorption of ink ad hence accelerate pH decreasing (Figure 26).

3.4 Effect of Large Volume of 1 N NaOH with Different Concentrations of Phenolphthalein on the Fading Time Using Paper Surfaces

From Table 7, it is clear that, using 1 N NaOH gave more handwriting stability. Increasing the volume of 1 N NaOH affects the fading time. Equal volume of 1 N NaOH and phenolphthalein were used and the results obtained are set out in Table 8.

It can be seen in Table 8, that with large volume of 1N NaOH (4ml of P + 4 ml 1N NaOH), the handwriting stability decreased because the reaction of alcoholic phenolphthalein added to alkaline solution (NaOH) causes the mixture to become a colored quinoid form of phenolphthalein rapidly. This negative ion is flat and the pi system is conjugated with time. The phenolphthalein color intensity decreased probably because the quinoid form reacts with hydroxide ions at a high concentration to produce the colorless (non-resonant) carbinol form **[78, 79]**

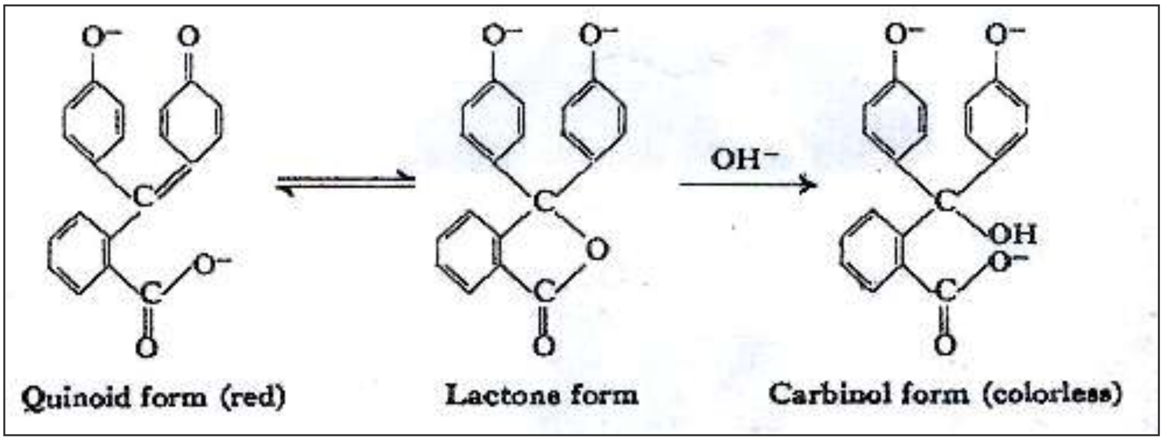

Figure 38: Phenolphthalein forms in alkaline solution[79]

H_2Phenolphthalein acidic no color	↔	$Phenolphthalein^{2-}$ basic red (quinoid form) dibasic form	→	$Phenolphthalein(OH)^{3-}$ strong alkaline no color (carbinol form) tribasic form

Table 8: Effect of large volume of 1 N NaOH with different concentrations of phenolphthalein on the fading time

NaOH	Phenolphthalein Concentration	pH of the ink	Abs. of the ink at 560 nm	Fading Time				
				Paper				
				Azhar	Xerox	Quena	Edfo	Rakta
4 ml 1 N	4ml of P_1	12.60	4.7	***TC	TC	TC	TC	TY****
	4ml of P_2	12.55	5.0	TC	TC	TC	TC	TY
	4ml of P_3	12.52	5.3	TC	TC	TC	TC	TY
	4ml of P_4	12.50	5.3	TC	TC	TC	TC	TY
	4ml of P_5	12.47	5.3	TC	TC	TC	TC	TY

P_1, P_2, P_3, P_4 and P_5 (0.1, 0.2, 0.4,0.8 and 1.2% phenolphthalein wt/v respectively)

***__TC__ : the handwriting turned colorless rapidly.

****__TY__ : the handwriting turned yellow this yellow color result from the reaction of NaOH with Rakta paper components as explained in Section 3.1.

It is clear from the results of Tables 7 & 8 that the best conditions for preparing more stable phenolphthalein disappearing ink (for using it on paper surface) are using phenolphthalein concentration (1.2% phenolphthalein wt/v) with 1 N NaOH with volume ratio (8/1) .

3.5 Effect of Different Concentrations of NaOH with Different Concentrations of the Mixture (Thymolphthalein and Phenolphthalein) on the Fading Time Using Paper Surfaces

By mixing equal volume of the prepared T_1 (0.1%) and P_1 (0.1%), the mixture of $T_1$and P_1 (0.05% thymolphthalein and 0.05% phenolphthalein wt/v) was produced. Different concentrations of NaOH were added to the prepared mixtures, violet inks were produced.

When adding 0.5 ml of 0.01 N NaOH to the prepared mixture (thymolphthalein and phenolphthalein), the handwriting color became light red because of the low pH of the ink, which was slightly lower than thymolphthalein transition range. When adding 0.5 ml of 0.1, 0.5 or 1 N NaOH, the ink gave violet handwriting turned red rapidly, this means that the ink was more affected by phenolphthalein.

It is clear from Table 9 that, either the concentration of NaOH or the concentration of the mixture (thymolphthalein and phenolphthalein) increased, the stability of the handwriting increased.

Table 9 and Figure 39 show the fading time of Azhar paper. In case of using 0.01 N NaOH, Azhar paper gave short handwriting stability from colorless writing **(CLW)** to 15 mins and in case of using 0.1 N NaOH, it gave short handwriting stability from 20 secs to 25 mins. In case of using 0.5 N NaOH, it gave more handwriting stability from 30 mins to 1.5 hrs but n case of 1 N NaOH, it gave the best handwriting stability from 2 hrs to 12 hrs.

Also Table 9 and Figure 40 show the fading time of Xerox paper. In case of using 0.01 N NaOH, Xerox paper gave short colorless writing **(CLW)** to 5 mins and in case of using 0.1 N NaOH, it gave short handwriting stability from 10 secs to 10 mins. In case of using 0.5 N NaOH, it gave more handwriting stability from 10 mins to 40 mins but in case of 1 N NaOH, it gave the best handwriting stability from 50 mins to 4 hrs.

Table 9: Effect of different concentrations of NaOH with different concentration of the mixture (thymolphthalein and phenolphthalein) on the fading time

NaOH	The mixture concentration	pH of the ink	Abs. of the ink		Fading Time				
					Paper				
			At 560 n m	At 600 n m	Azhar	Xerox	Quena	Edfo	Rakta
0.5 ml 0.01 N	4ml of (T_1+P_1)	9.5	0.95	0.65	CLW	CLW	CLW	CLW	CLW
	4ml of (T_2+P_2)	9.15	0.45	0.3	CLW	CLW	CLW	CLW	CLW
	4ml of (T_3+P_3)	8.65	0.35	0.22	3 mins	1 min	CLW	CLW	CLW
	4ml of (T_4+P_4)	8.4	0.25	0.2	10 mins	2mins	CLW	CLW	CLW
	4ml of (T_5+P_5)	8.11	0.2	0.1	15 mins	5 mins	CLW	CLW	CLW
0.5 ml 0.1 N	4ml of (T_1+P_1)	11.2	5.5	4.2	20 secs	10 secs	TC	TC	TC
	4ml of(T_2+P_2)	11.0	5.2	4.3	40 secs	10 secs	TC	TC	TC
	4ml of (T_3+P_3)	10.5	6.0	4.3	7 mins	3 mins	TC	TC	TC
	4ml of (T_4+P_4)	9.8	5.2	1.8	20 mins	5 mins	TC	TC	TC
	4ml of (T_5+P_5)	9.4	5.1	0.9	25 mins	10 mins	TC	TC	TC
0.5 ml 0.5 N	4ml of(T_1+P_1)	11.5	4.5	4.3	30 mins	10 mins	1 mins	TC	TC
	4ml of(T_2+P_2)	11.45	5.0	4.3	50 mins	20 mins	2 mins	TC	TC
	4ml of(T_3+P_3)	11.38	5.2	4.3	1hr	25 mins	3 mins	2 secs	TC
	4ml of T_4+P_4)	11.3	5.3	4.38	1.25 hrs	35 mins	3 mins	3 secs	TC
	4ml of (T_5+P_5)	11.25	5.3	4.4	1.5 hrs	40 mins	4 mins	4 secs	TC
0.5 ml 1 N	4ml of(T_1+P_1)	11.98	4.3	4.4	2 hrs	50 mins	5 mins	3 secs	TY
	4ml of (T_2+P_2)	11.92	5.0	4.4	3 hrs	2.5 hrs	8 mins	6 secs	TY
	4ml of (T_3+P_3)	11.92	6.0	4.4	4.5 hrs	3 hrs	10 mins	10 secs	TY
	4ml of (T_4+P_4)	11.85	6.0	4.4	6 hrs	3.5 hrs	25 mins	30 secs	TY
	4ml of(T_5+P_5)	11.8	5.5	4.4	12 hrs	4 hrs	30 mins	1 min	TY

T_1+P_1 (0.05% thymolphthalein and 0.05% phenolphthalein wt/v)

T_2+P_2 (0.1% thymolphthalein and 0.1% phenolphthalein wt/v)

T_3+P_3 (0.2% thymolphthalein and 0.2% phenolphthalein wt/v)

T_4+P_4 (0.4% thymolphthalein and 0.4% phenolphthalein wt/v)

T_5+P_5 (0.6% thymolphthalein and 0.6% phenolphthalein wt/v)

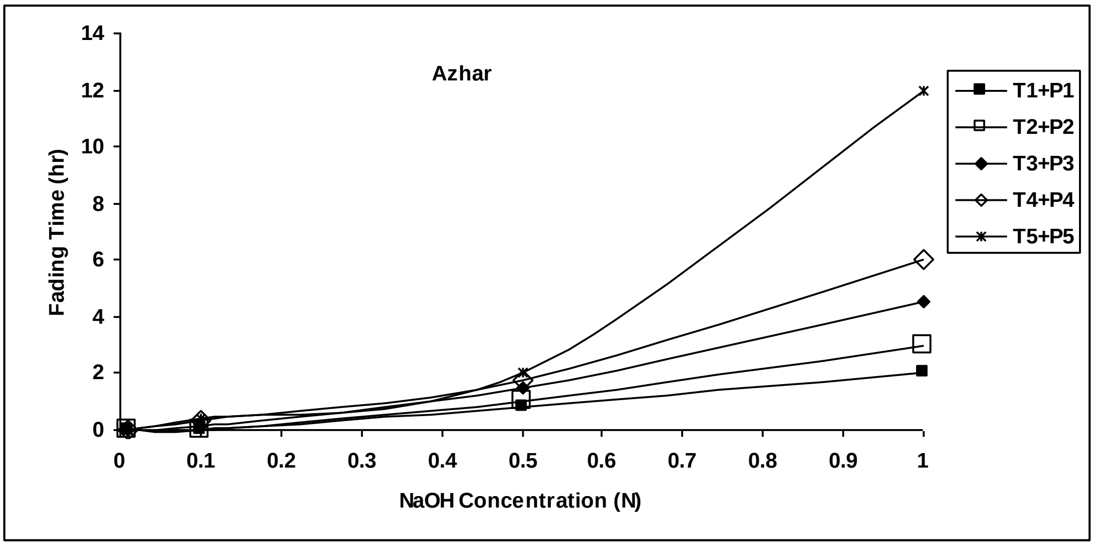

Figure 39: Effect of different concentrations of NaOH with different concentrations of the mixture (thymolphthalein and phenolphthalein) on the fading time using Azhar paper

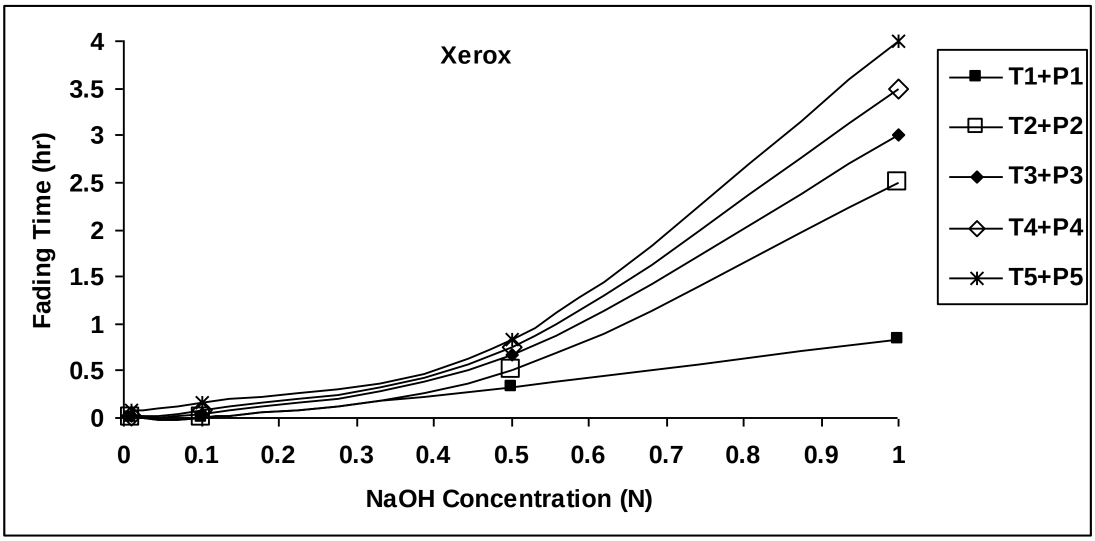

Figure 40: Effect of different concentrations of NaOH with different concentrations of the mixture (thymolphthalein and phenolphthalein) on the fading time using Xerox paper

Furthermore, the results obtained from Table 9 and Figure 41 show the fading time of Quena paper. In case of using 0.01 N NaOH, Quena paper gave colorless writing **(CLW)** and in case of 0.1 using N NaOH, it gave short handwriting stability, the writing turned colorless **(TC)** rapidly. In case of using 0.5 N NaOH, it gave handwriting stability from 1 min to 4 mins but in case of using 1 N NaOH, it gave handwriting stability from 5 mins to 30 mins.

Also Table 9 and Figure 42 show the fading time of Edfo paper. In case of using 0.01 N NaOH, Edfo paper gave colorless writing **(CLW)**, and in case of using 0.1 N NaOH, it gave short handwriting stability, the writing turned colorless **(TC)** rapidly. In case of using 0.5 N NaOH, it gave handwriting stability from **(TC)** to 4 secs but in case of using 1 N NaOH, it gave handwriting stability from 3 Secs to 1 mins.

It is clear from results of Table 9 that the fading time of Rakta paper with all concentrations of NaOH and all concentration of the mixture (mixture of thymolphthalein and phenolphthalein) it gave short handwriting stability. In case of using 0.01 N NaOH it gave colorless writing, in case of using 0.1 and 0.5 N NaOH it gave colorless writing and in case of using 1 N NaOH the handwriting turner rapidly to yellow.

Also Table 9 shows that Azhar paper gave writing stability than Xerox than Quena than Edfo than Rakta.

The fading time (stability) results of the mixture (mixture of thymolphthalein and phenolphthalein) are generally less than the results of individual thymolphthalein and phenolphthalein in Tables 4 & 7, For example, the maximum fading time in Azhar paper in Table 4 (thymolphthalein ink) is 4 days and in Table 7 is 6 days. This means that, addition the two inks together leads to the dilution of each one. Also this also indicates that each one of them produce individual color.

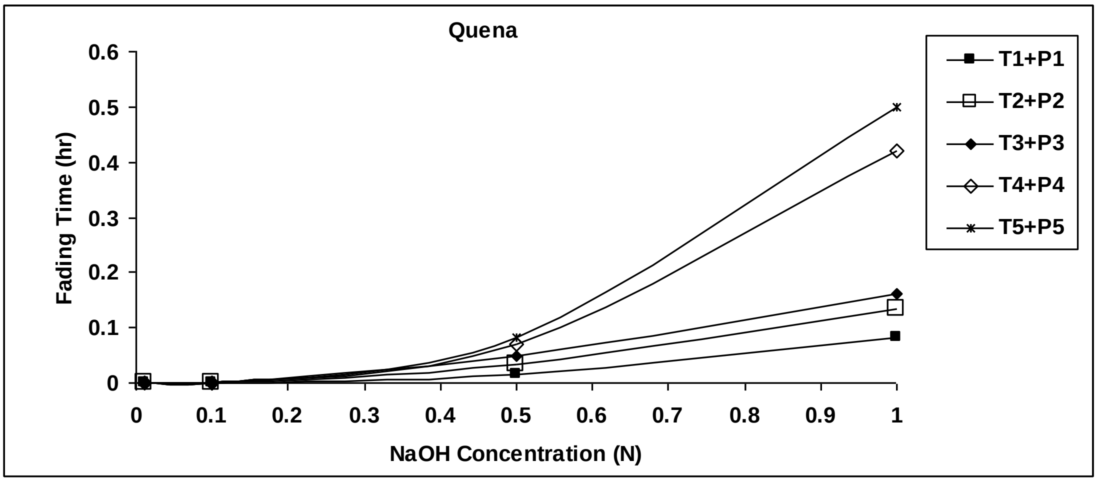

Figure 41: Effect of different concentrations of NaOH with different concentrations of the mixture (thymolphthalein and phenolphthalein) on the fading time using Quena paper

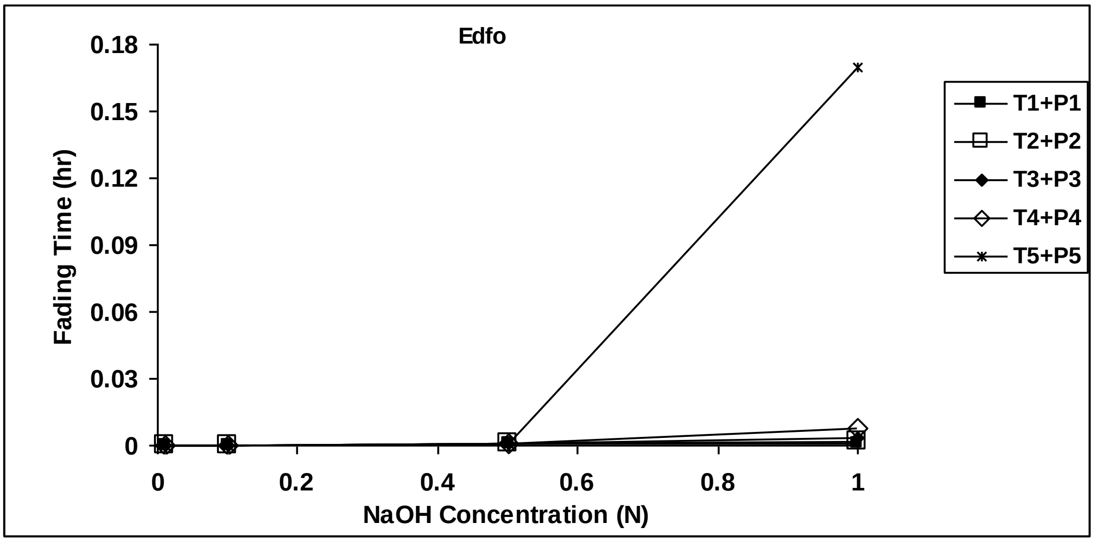

Figure 42: Effect of different concentrations of NaOH with different concentrations of the mixture (thymolphthalein and phenolphthalein) on the fading time using Edfo paper

3.6 Effect of Large Volume of 1 N NaOH with Different Concentrations of the Mixture (Thymolphthalein and Phenolphthalein) on the Fading Time Using Paper Surfaces

From the pervious Table (Table 9) 1 N NaOH gave more handwriting stability. Increasing the volume of 1 N NaOH affects the fading time. Equal volume of 1 N NaOH and the mixture (thymolphthalein and phenolphthalein) were used and the results obtained are set out in Table 10 and Figure 43. It is clear from the result that, adding equal volume of 1 N NaOH and the mixture (thymolphthalein and phenolphthalein) gave blue ink, although the ink gave absorbance at 560, the ink mixture gave blue writing color , this blue color faded to colorless without passing through red color. This means that phenolphthalein has no effect in this mixture. As explained in Section 3.4, the colorless of phenolphthalein in high concentration of alkali, may be due to the reaction of alcoholic phenolphthalein with the alkaline solution (NaOH) caused the mixture to become a colored quinoid form of phenolphthalein rapidly, this negative ion is flat and the pi system is conjugated. With time, the phenolphthalein color intensity decreases because the quinoid form reacted slowly with hydroxide ions at high concentration to produce the colorless (non-resonant) carbinol form **[78, 79]**.

It is clear from Table 10 and Figure 43 that, the handwriting stability in this case (using equal volume of 1 N NaOH) is best than using 0.5 ml of 1 N NaOH (Table 9).

Table 10 and Figure 43 show that, Azhar paper gave writing stability from 8 days to 12 days, Xerox paper gave writing stability from 6 days to 8 days, Quena paper gave writing stability from 1.5 days to 3 days and Rakta paper gave writing stability from 6 hrs to 1 day.

The stability of the mixture ink handwriting in this case less than individual thymolphthalein ink and individual phenolphthalein ink because the color in this mixture case depends only on thymolphthalein, which diluted after mixing with phenolphthalein ink.

Table 10: Effect of large volume of 1 N NaOH with different concentrations of the mixture (thymolphthalein and phenolphthalein) on the fading time using Paper Surfaces

NaOH	The mixture concentration	pH of the ink	Abs. of the ink		Fading Time				
					Paper				
			At 560 n m	At 600 n m	Azhar	Xerox	Quena	Edfo	Rakta
4 ml 1 N	4ml of (T_1+P_1)	12.25	5.8	5.5	8 day	6 days	1.5 days	1 day	6 hrs then TY
	4ml of (T_2+P_2)	12.15	5.8	5.0	9 day	6.5 days	1.75 days	1.25 days	12 hrs then TY
	4ml of (T_3+P_3)	12.05	5.3	5.2	10 days	7 days	2 days	1.5 days	18 hrs then TY
	4ml of (T_4+P_4)	12.0	5.9	5.3	11 days	7.5 days	2.5 days	1.75 days	18 hrs then TY
	4ml of (T_5+P_5)	11.98	6.0	5.4	12 days	8 days	3 days	2 days	1 day then TY

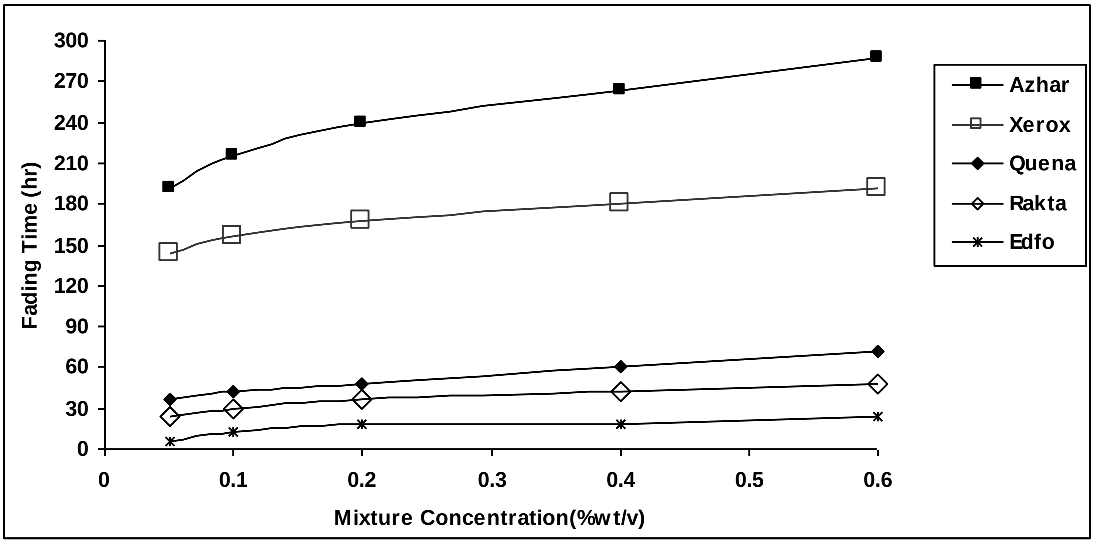

Figure 43: Effect of large volume of 1 N NaOH with different concentrations of the mixture (thymolphthalein and phenolphthalein) on the fading time using paper surfaces

3.7 Effect of Different Concentrations of NaOH with Different Concentrations of Thymolphthalein on the Fading Time Using Textile Surfaces

When NaOH solution was added to T_1, T_2, T_3, T_4 and T_5 (thymolphthalein 0.1, 0.2, 0.4, 0.8 & 1.2% wt/v respectively), blue inks were produced and used for handwriting on textile surfaces (polyamide, polyester and cotton fabrics) by filling a dry 1 mm point felt tip pen. The writing will be disappeared with time this is because of the decreased pH of the ink. It is clear from Table 11 that when the concentration of thymolphthalein increased, the stability of the handwriting increased. Each Figure shows the effect of different concentration of 0.5 ml NaOH with different concentration of thymolphthalein on the same surface. In case of 0.01 N NaOH gave ink pHs less than 10 and so the inks gave colorless writing **(CLW)**. In case of 0.1 N NaOH gave short handwriting stability, in case of 0.5 N NaOH gave more handwriting and in case of 1 N NaOH gave the greater handwriting stability. The fading time following this order

1N NaOH > 0.5 N NaOH > 0.1 N NaOH > 0.01N NaOH.

This means that, increasing the concentration of sodium hydroxide leads to increasing the pH of the ink and hence the pH of the handwriting strokes. The high pH of writing strokes leads to a low decrease in pH of the ink and so gives more stable writing (more fading time). Also increasing the concentration of thymolphthalein leads to increasing the fading time.

Table 11 and Figure 44 show the fading time of polyamide fabric. In case of using 0.01 N NaOH, polyamide fabric gave colorless writing **(CLW)** and in case using of 0.1 N NaOH, it gave short handwriting stability from 10 secs to 4 mins. In case of using 0.5 N NaOH, it gave more writing stability from 30 mins to 1.5 hrs but in case of using 1 N NaOH, it gave the best handwriting stability from 1.5 hrs to 3 hrs.

Table 11: Effect of different concentrations of NaOH with different concentration of thymolphthalein on the fading time

NaOH	Thymolphthalein Concentration	pH of the ink	Abs. of the ink at 600 nm	Fading Time* — Textile Fabric: Polyamide	Polyester	Cotton
0.5 ml 0.01 N	4ml of T_1	9.45	1.42	CLW**	CLW	CLW
	4ml of T_2	9.40	1.42	CLW	CLW	CLW
	4ml of T_3	9.30	1.43	CLW	CLW	CLW
	4ml of T_4	9.10	1.26	CLW	CLW	CLW
	4ml of T_5	8.70	0.64	CLW	CLW	CLW
0.5 ml 0.1 N	4ml of T_1	11.45	4.2	10 secs	15 secs	TC***
	4ml of T_2	11.31	4.2	30 secs	20 secs	TC
	4ml of T_3	11.23	4.1	40 secs	30 secs	TC
	4ml of T_4	11.11	4.1	3 mins	2 mins	TC
	4ml of T_5	11.02	4.1	4 mins	3 mins	TC
0.5 ml 0.5 N	4ml of T_1	11.65	4.2	30 mins	20 mins	2 min
	4ml of T_2	11.6	4.25	45 mins	30 mins	3 mins
	4ml of T_3	11.55	4.28	1 hr	40 mins	4 mins
	4ml of T_4	11.52	4.3	1.25 hr	50 mins	5 mins
	4ml of T_5	11.5	4.3	1.5 hr	1 hr	6 mins
0.5 ml 1 N	4ml of T_1	11.95	4.34	1.5 hrs	1.25 hrs	5 mins
	4ml of T_2	11.89	4.3	2 hrs	1.5 hrs	5 mins
	4ml of T_3	11.81	4.38	2.25 hrs	2 hrs	10 mins
	4ml of T_4	11.75	4.4	2.5 hrs	2.25 hrs	15 mins
	4ml of T_5	11.70	4.4	3 hrs	2.5 hrs	20 mins

T_1, T_2, T_3, T_4 and T_5 (0.1, 0.2, 0.4, 0.8 and 1.2% thymolphthalein wt/v respectively)

*__Fading time__ of writing is the time from writing to its color disappearance (complete fading), this means when the fading time is short, the handwriting is non stable (short handwriting stability), and vice versa

**__CLW__ : the ink itself is blue but the writing was colorless.

***__TC__ : the handwriting turned colorless rapidly.

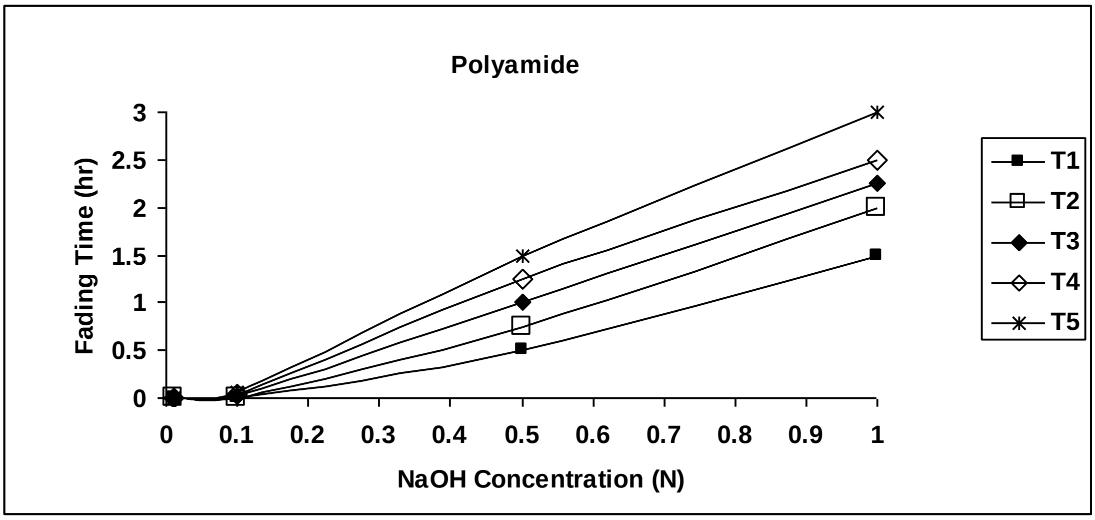

Figure 44: Effect of different concentrations of NaOH with different concentrations of thymolphthalein on the fading time using polyamide fabric

Results of Table 11 and Figure 45 show the fading time of polyester fabric. In case of using 0.01 N NaOH, polyester fabric gave colorless writing **(CLW)** and in case of using 0.1 N NaOH, it gave short handwriting stability from 15 secs to 3 mins. In case of using 0.5 N NaOH, it gave more writing stability from 20 mins to 1 hr but in case of using 1 N NaOH, it gave the best handwriting stability from 1.25 hrs to 2.5 hrs.

Results of Table 11and Figure 46 show the fading time of cotton fabric. In case of 0.01 using N NaOH, cotton fabric gave colorless writing **(CLW)** and in case of using 0.1 N NaOH, it gave short handwriting stability, the writing turned colorless rapidly. In case of using 0.5 N NaOH, it gave writing stability from 2 mins to 6 mins but in case of using 1 N NaOH, it gave more handwriting stability from 5 mins to 20 mins.

It is clear from results of Table 11 that, the fading time (writing stability) of the used textile fabric following also this order:-

Polyamide> Polyester> Cotton

From the results of the surface scanning & pH measurement, the differences in fading time can be explained. The polyamide surface gave more writing stability than polyester and cotton. The increased writing stability may be caused by the increased pH of the surface.

Table 12: pHs of the used fabrics

Textile fabric type	pH
Polyamide	7.65
Polyester	6.96
Cotton	6.61

Table 12 shows that the pH of the used fabric following this order

Polyamide > Polyester > Cotton

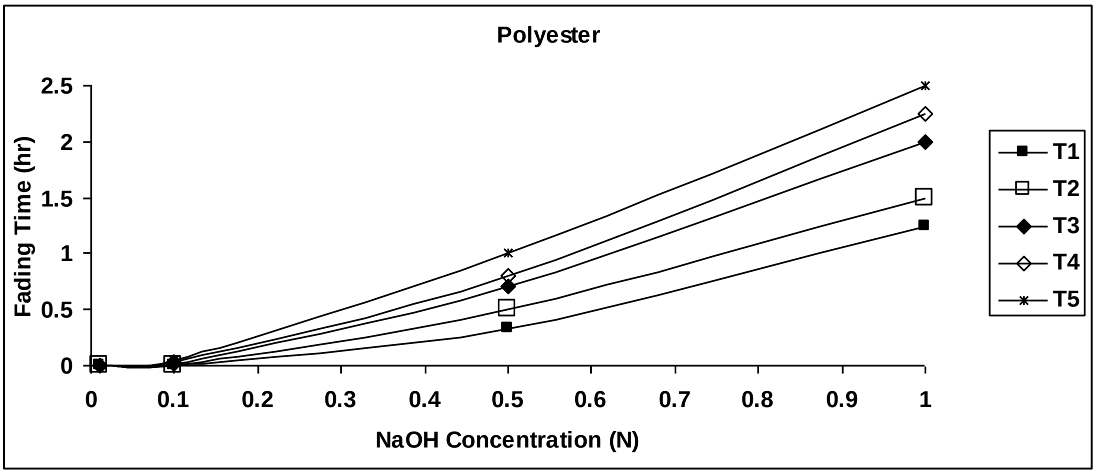

Figure 45: Effect of different concentrations of NaOH with different concentrations of thymolphthalein on the fading time using polyester fabric

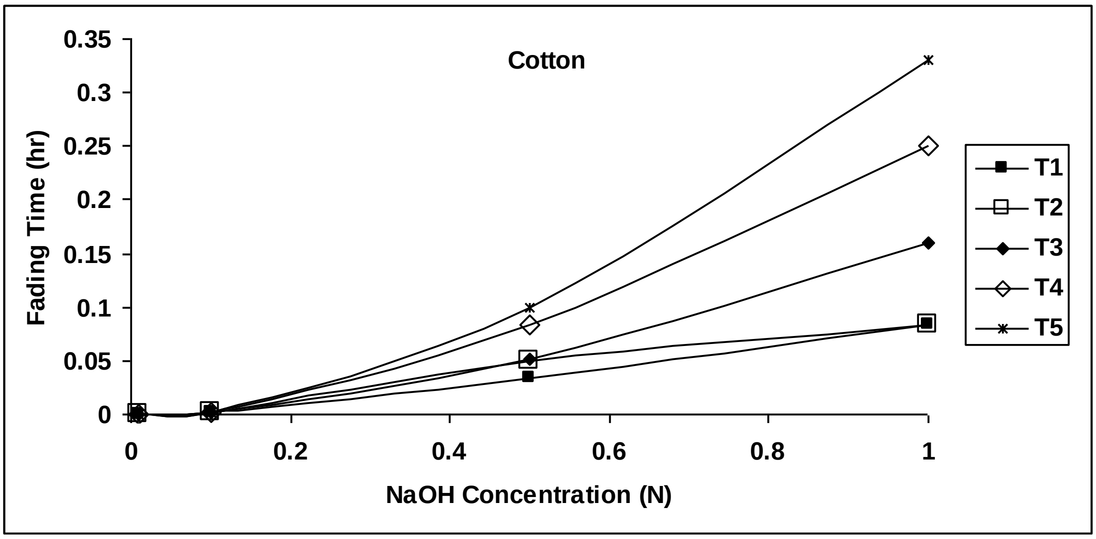

Figure 46: Effect of different concentrations of NaOH with different concentrations of thymolphthalein on the fading time using cotton fabric

The higher handwriting stability is given by polyamide may be caused by its higher pH than that of polyester and/or cotton. Photomicrograph of polyamide showed creases in fibers as showed in Figure 47, which shows, creases in the surface of the fibers, these creases lead to ink trapping and inhibition of the reaction with the atmospheric air and hence the surface inhibits a decrease in pH.

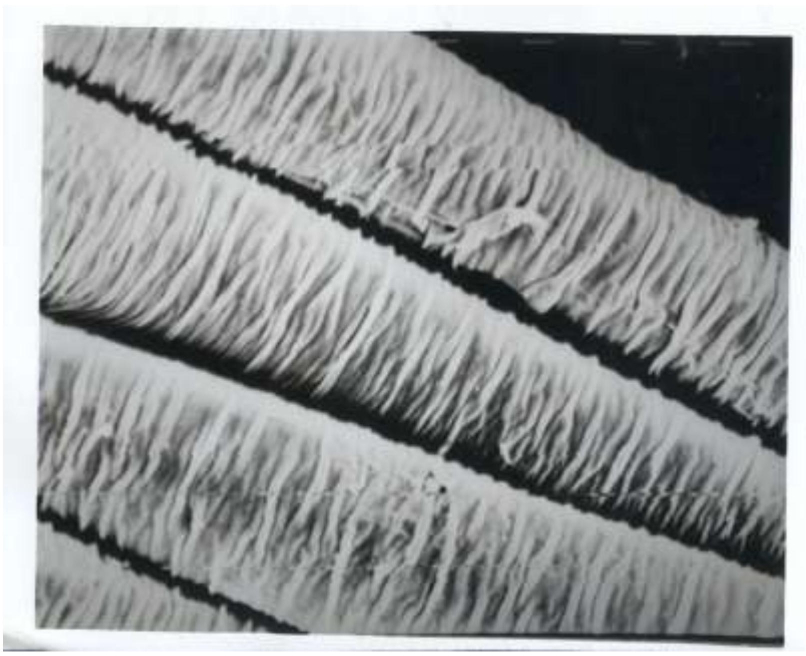

Figure 47: Photomicrograph of polyamide 1500x

Polyester fabric gave handwriting stability less than polyamide fabric this is may be due to the smooth surface of polyester fabric as shown in Figure 48, which shows a highly crystalline form, which produces a smooth surface making it easier for the handwriting to react with air.

Figure 48: Photomicrograph of polyester 1500x

Furthermore, the cotton fiber contains –OH groups so some of the alkali absorb by these groups, and hence pH of the ink decreases. The hydroxyl groups of cellulose have a weak acidic character **[80]**, therefore the handwriting faded quickly, this may be also due to the absorption of the ink on the cotton surface as show in Figure 49 which shows, the highly amorphous parts produce a high degree of random disorder and hence the high absorption of ink on the surface**.**

Figure 49: Photomicrograph of cotton 1500x

3.8 Effect of Large Volume of 1 N NaOH with Different Concentrations of Thymolphthalein on the Fading Time Using Textile Surfaces

From the pervious Table (Table 11), using 1 N NaOH gave more handwriting stability. Therefore, we studied effect increasing the volume of 1N NaOH, in this section, we used equal volume of 1 N NaOH and thymolphthalein and the result obtained are set out in Table 13.

It is clear from Table 13 and Figure 50 that, the handwriting stability in this case (using equal volume of 1 N NaOH) is best than that of using 0.5 ml of 1 N NaOH (Table 11).

Results of Table 13 and Figure 50 show that, polyamide fabric gave writing stability from 2.5 days to 8 days, polyester fabric gave writing stability from 2days to 4.5 days and cotton fabric gave writing stability from 5 days to 11 days.

Also it is clear from results of Table 13 and Figure 50 that, at the same handwriting surface, the stability of handwriting increased with increasing thymolphthalein concentration. The fading time (writing stability) of the used textile fabrics in case of using equal volume of 1 N NaOH following this order:-

Cotton > Polyamide > Polyester.

On the other hand the fading time of the used textile fabric in case of using 0.5 ml of 1 N NaOH (Table 11) following this order:-

Polyamide> Polyester> Cotton

The higher writing stability given by cotton than other used fabrics in case of using equal volume of 1 N NaOH may be due to a high concentration of alkali which leads to the penetration of alkali and dyeing in the deep the microfibre of cotton (mercerization idea) **[81]**. This leads to the inhibition of the reaction of the alkali with the air on the surface.

Polyamide gave more writing stablity than polyester may be due to the creases which were found in polyamide fibers which led to ink trapping and inhibition of the reaction with the atmospheric air and hence a low decrease in pH (Figure 47).

Disappearing inks have several using textile industry, from the results of table 11 and 13, we note that the best conditions for preparing more stable thymolphthalein disappearing inks (to use it in textile industries) are using thymolphthalein concentration 1.2% thymolphthalein wt/v with equal volum of 1 N NaOH.

Table 13: Effect of large volume of 1 N NaOH with different concentrations of thymolphthalein on the fading time using different textile fabric

NaOH	Thymolphthalein Concentration	pH of the ink	Abs. of the ink at 600 nm	Fading Time – Textile Fabric		
				Polyamide	Polyester	Cotton
4 ml 1 N	4ml of T_1	13.6	4.49	2.5 days	2 days	5 days
	4ml of T_2	13.41	4.57	3 days	2.5 days	6 days
	4ml of T_3	13.22	4.62	6 days	3 days	7 days
	4ml of T_4	13.00	4.9	8 days	4 days	10 days
	4ml of T_5	12.9	5.2	8 days	4.5 days	11 days

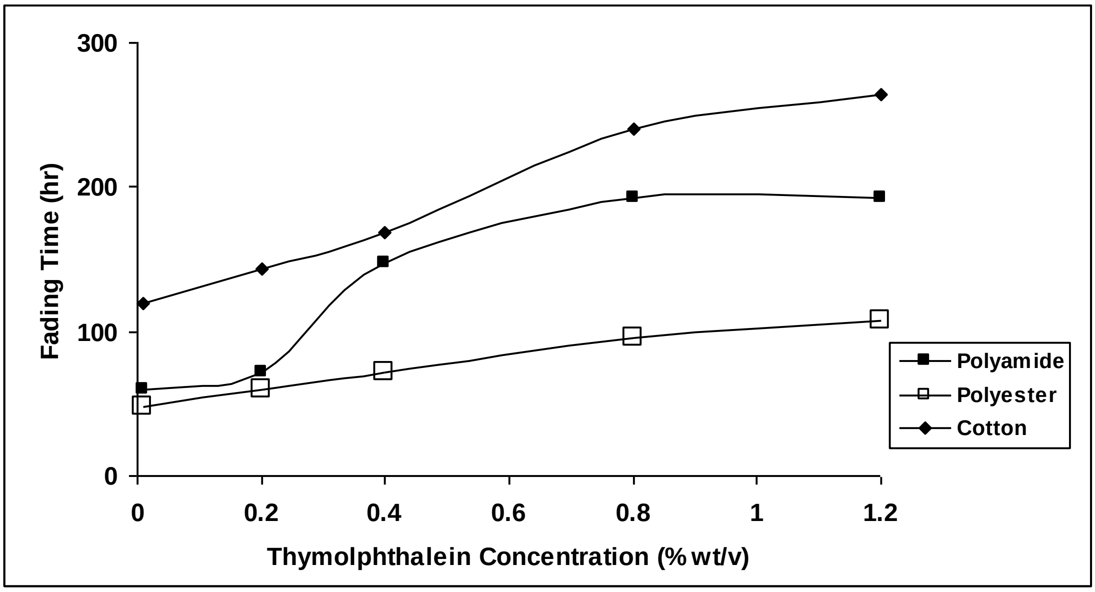

Figure 50: Effect of large volume of 1 N NaOH with different concentrations of thymolphthalein on the fading time using different fabric surfaces

3.9 Effect of Different Concentrations of NaOH with Different Concentrations of Phenolphthalein on the Fading Time Using Textile Surfaces

Different concentrations of NaOH were added to the prepared phenolphthalein and red inks were produced, these inks were used in handwriting on textile fabrics surfaces by filling a dry 1 mm-point felt-tip pen. The writing with these inks was red, the writing will be then disappeared, the results of the fading time of writing on are set out in Table 14.

In case of using 0.01 N NaOH, the red inks were a light red and had pHs less than 10 and so these inks gave colorless writing **(CLW)** and in case of using 0.1 N NaOH the ink short fading time. In case of using 0.5 N NaOH gave more handwriting but in case using of 1 N NaOH gave the greater handwriting stability.

This means, increasing the concentration of sodium hydroxide leads to increasing the pH of the ink and hence the pH of the handwriting strokes. The high pH of writing strokes leads to a low decrease in pH of the ink and so gives more stable writing. Also increasing the concentration of phenolphthalein leads to increasing the fading time.

Results of Table 14 and Figure 51 show the fading time of polyamide fabric. In case of 0.01 N NaOH, polyamide fabric gave colorless writing **(CLW)** and in case of 0.1 N NaOH, it gave short handwriting stability from 30 mins to 1.5 hrs. In case of 0.5 N NaOH, it gave more writing stability from 12 hrs to 1.5 days but in case of 1 N NaOH, it gave the best handwriting stability from 1.5 days to 4.5 days.

Table 14: Effect of different concentrations of NaOH with different concentration of phenolphthalein on the fading time using the fading time using different textile fabric

NaOH	Phenolphthalein Concentration	pH of the ink	Abs. of the ink at 560 nm	Fading Time		
				Textile Fabric		
				Polyamide	Polyester	Cotton
0.5 ml 0.01 N	4ml of P_1	9.25	2.05	CLW	CLW	CLW
	4ml of P_2	9.22	1.0	CLW	CLW	CLW
	4ml of P_3	8.95	0.5	CLW	CLW	CLW
	4ml of P_4	8.76	0.19	CLW	CLW	CLW
	4ml of P_5	8.60	0.11	CLW	CLW	CLW
0.5 ml 0.1 N	4ml of P_1	10.95	4.9	30 mins	20 mins	TC
	4ml of P_2	10.90	4.9	45 mins	25 mins	TC
	4ml of P_3	10.25	5.3	1 hr	30 mins	TTC
	4ml of P_4	9.75	5.3	1.25 hrs	45 mins	TC
	4ml of P_5	9.55	5.3	1.5 hrs	1 hr	TC
0.5 ml 0.5 N	4ml of P_1	11.35	5.45	12 hrs	6 hrs	4 hrs
	4ml of P_2	11.3	5.4	12 hrs	6 hrs	5 hrs
	4ml of P_3	11.25	5.3	18 hrs	12 hrs	6 hrs
	4ml of P_4	11.15	5.2	1 day	18 hrs	12 hrs
	4ml of P_5	11.08	5.1	1.5 day	1 day	18 hrs
0.5 ml 1 N	4ml of P_1	11.57	5.0	1.5 days	1 day	18 hrs
	4ml of P_2	11.51	5.3	3 days	2.5 days	1 day
	4ml of P_3	11.42	6.0	3.5 days	3 days	2 days
	4ml of P_4	11.35	6.0	4 days	3.5 days	3 days
	4ml of P_5	11.30	6.0	4.5 days	4 days	3.5 days

P_1, P_2, P_3, P_4 and P_5 (0.1, 0.2, 0.4, 0.8 and 1.2% phenolphthalein wt/v respectively)

*__Fading time__ of writing is the time from writing to its color disappearance (complete fading).

**__CLW__ : the ink itself in this case (phenolphthalein) is red but the writing was colorless.

***__TC__ : the handwriting turned colorless rapidly.

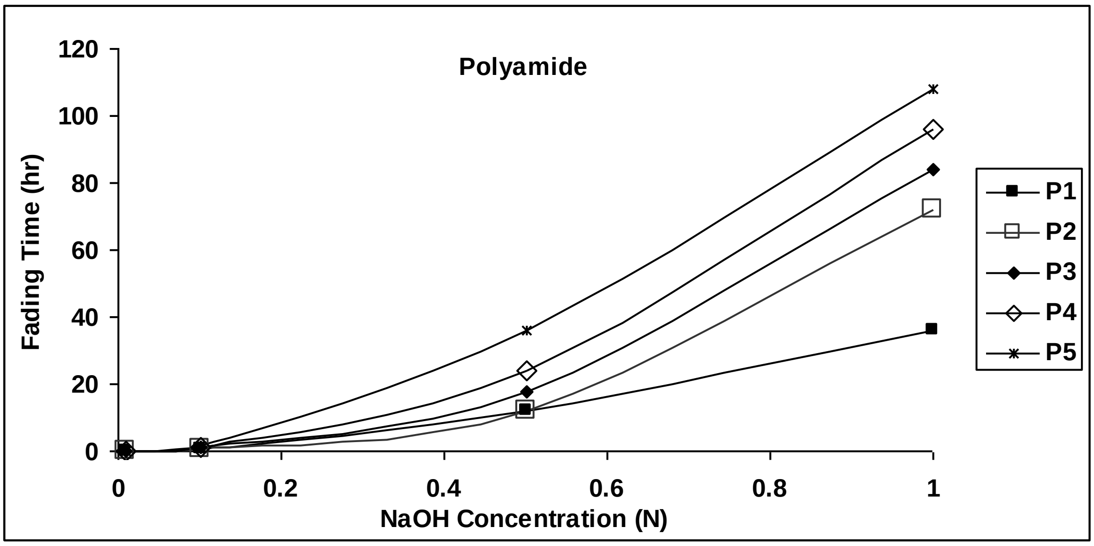

Figure 51: Effect of different concentrations of NaOH with different concentrations of phenolphthalein on the fading time using polyamide fabric

Results of Table 14 and Figure 52 show the fading time of polyester fabric. In case of 0.01 N NaOH, polester fabric gave colorless writing **(CLW)** and in case of 0.1 N NaOH, it gave short handwriting stability from 20 mins to 1 hrs. In case of 0.5 N NaOH, it gave more writing stability from 6 hrs to 1 day but in case of 1 N NaOH, it gave the best handwriting stability from 1 day to 4 days.

Results of Table 14 and Figure 53 show the fading time of cotton fabric. In case of 0.01 N NaOH, cotton fabric gave colorless writing **(CLW)** and in case of 0.1 N NaOH, it gave short handwriting stability, the handwriting turned colorless rapidly. In case of 0.5 N NaOH, it gave more writing stability from 4 hrs to 18 hrs but in case of 1 N NaOH, it gave the best handwriting stability from 18 hrs to 3.5 days.

It is clear from Table 14 that, at the same conditions (the same concentration of NaOH and the same concentration of phelphethalein), polyamide surface gave more writing stability than polyester and polyester gave more handwriting stability than cotton , the fading time of fabrics surfaces following this order:- Polyamide> Polyester> Cotton.

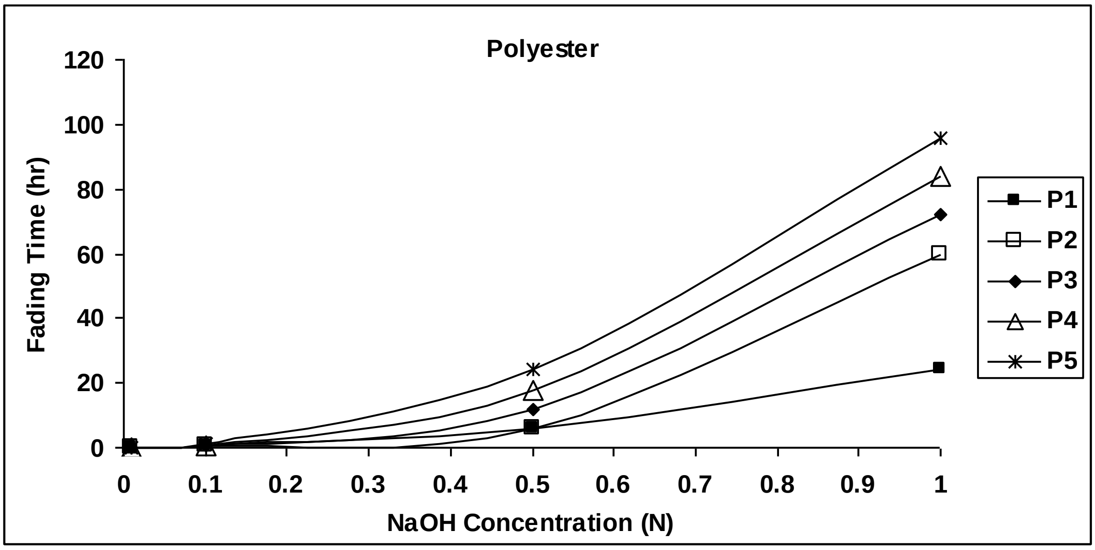

Figure 52: Effect of different concentrations of NaOH with different concentrations of phenolphthalein on the fading time using polyester fabric

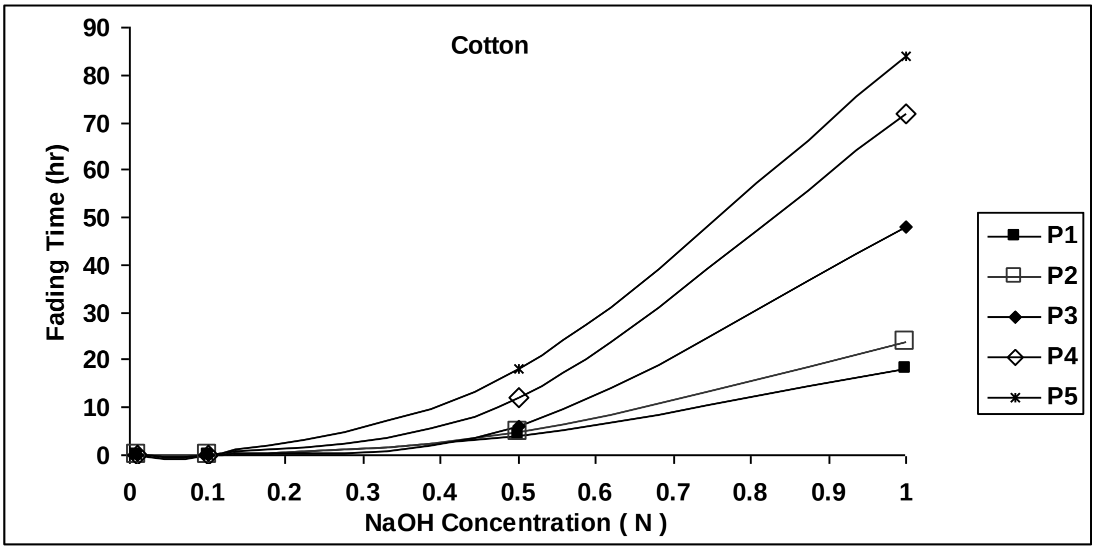

Figure 53: Effect of different concentrations of NaOH with different concentrations of phenolphthalein on the fading time using cotton fabric

3.10 Effect of Large Volume of 1 N NaOH with Different Concentrations of Phenolphthalein on the Fading Time Using Textile Surfaces

From the pervious Table (Table 14) 1 N NaOH gave more handwriting stability, so we studied the increasing the volume of 1 N NaOH, in this section equal volume of 1 N NaOH and phenolphthalein were used and the results obtained are set out in Table 15.

It can be seen that, from Table 15 using large volume of 1N NaOH (4ml of P + 4 ml 1N NaOH), the handwriting stability decreased. As mentioned in Section 3.4 this quickly faded handwriting because of the reaction of alcoholic phenolphthalein added to alkaline solution (NaOH) causes the mixture to become a colored quinoid form of phenolphthalein rapidly. This negative ion is flat and the pi system is conjugated with time. The phenolphthalein color intensity decreased probably because the quinoid form reacts with hydroxide ions at a high concentration to produce the colorless (non-resonant) carbinol form **[78, 79]**.

It is clear from the results of Tables 14 and 15 that the best conditions for preparing more stable phenolphthalein disappearing ink (for using it on fabric surface) are using phenolphthalein concentration (1.2% phenolphthalein wt/v) with 1 N NaOH with volume ratio (8/1) .

Table 15: Effect of large volume of 1 N NaOH with different concentrations of phenolphthalein on the fading time

NaOH	Phenolphthalein Concentration	pH of the ink	Abs. of the ink at 560 nm	Fading Time*		
				Textile Fabric		
				Polyamide	Polyester	Cotton
4 ml 1 N	4ml of P_1	12.60	4.7	CLW**	CLW	CLW
	4ml of P_2	12.55	5.0	CLW	CLW	CLW
	4ml of P_3	12.52	5.3	CLW	CLW	CLW
	4ml of P_4	12.50	5.3	TC***	TC	TC
	4ml of P_5	12.47	5.3	TC	TC	TC

P_1, P_2, P_3, P_4 and P_5 (0.1, 0.2, 0.4,0.8 and 1.2% phenolphthalein wt/v respectively)

***Fading time** of writing is the time from writing to its color disappearance (complete fading).

CLW**: the ink itself is red but the handwriting was colorless.

TC***: the handwriting turned colorless rapidly.

3.11 Effect of Different Concentrations of NaOH with Different Concentrations of the Mixture (Thymolphthalein and Phenolphthalein) on the Fading Time Using Textile Surfaces

By mixing equal volume of the prepared T_1 (0.1%) and P_1 (0.1%), the mixture of $T_1$and P_1 (0.05% thymolphthalein and 0.05% phenolphthalein wt/v) was produced, different concentrations of NaOH were added to the prepared mixtures and violet inks were produced.

Adding 0.5 ml 0.01 N NaOH to the prepared mixture (thymolphthalein and phenolphthalein), the handwriting color became light red because of the low pH of the ink, which was slightly lower than thymolphthalein transition range so the produced color depends only on phenolphthalein. But , upon using 0.5 ml of 0.1, 0.5 or 1 N NaOH, the ink gave violet handwriting turned red rapidly, this means that the ink was more affected by phenolphthalein than thymolphthalein. The red writing then disappeared. The fading time is set out in Table 16.

It is clear from Table 16 that either the concentration of NaOH or the concentration of the mixture (thymolphthalein and phenolphthalein) increased, the stability of the writing increased.

Results of Table 16 and Figure 54 show the fading time of polyamide fabric. In case of using 0.01 N NaOH, polyamide gave colorless writing **(CLW)** and in case of using 0.1 N NaOH, it gave short handwriting stability from 25 mins to 1.5 hrs. In case of 0.5 N NaOH, it gave more handwriting stability from 35 mins to 2 hrs but in case of 1 N NaOH, it gave the best handwriting stability from 45 mins to 1.5 days.

Table 16: Effect of different concentrations of NaOH with different concentration of the mixture (thymolphthalein and phenolphthalein) on the fading time using different textile fabrics

NaOH	The mixture concentration	pH of the ink	Abs. of the ink		Fading Time Textile Fabric		
			At 560 n m	At 600 n m	Polyamide	Polyester	Cotton
0.5 ml 0.01 N	4ml of (T_1+P_1)	9.5	0.95	0.65	CLW	CLW	CLW
	4ml of (T_2+P_2)	9.15	0.45	0.3	CLW	CLW	CLW
	4ml of (T_3+P_3)	8.65	0.35	0.22	CLW	CLW	CLW
	4ml of (T_4+P_4)	8.4	0.25	0.2	CLW	CLW	CLW
	4ml of (T_5+P_5)	8.11	0.2	0.1	CLW	CLW	CLW
0.5 ml 0.1 N	4ml of (T_1+P_1)	11.2	5.5	4.2	25 mins	10 mins	TC
	4ml of(T_2+P_2)	11.0	5.2	4.3	30 mins	14 mins	TC
	4ml of (T_3+P_3)	10.5	6.0	4.3	35 mins	30 mins	TC
	4ml of (T_4+P_4)	9.8	5.2	1.8	1 h	45 mins	TC
	4ml of (T_5+P_5)	9.4	5.1	0.9	1.5 hrs	1 hr	TC
0.5 ml 0.5 N	4ml of(T_1+P_1)	11.5	4.5	4.3	35 mins	25 mins	10 mins
	4ml of(T_2+P_2)	11.45	5.0	4.3	1 hr	45 mins	15 mins
	4ml of(T_3+P_3)	11.38	5.2	4.3	1.25 hr	1 hr	20 mins
	4ml of T_4+P_4)	11.3	5.3	4.38	1.5 hr	1.25 hr	25 mins
	4ml of (T_5+P_5)	11.25	5.3	4.4	2 hr	1.5 hr	30 mins
0.5 ml 1 N	4ml of(T_1+P_1)	11.98	4.3	4.4	45 mins	40 mins	30 mins
	4ml of (T_2+P_2)	11.92	5.0	4.4	2 hrs	1.75 hrs	1.5 hrs
	4ml of (T_3+P_3)	11.92	6.0	4.4	2.5 hrs	2 hrs	1.75 hrs
	4ml of (T_4+P_4)	11.85	6.0	4.4	1 days	12 hrs	4.5 hrs
	4ml of(T_5+P_5)	11.8	5.5	4.4	1.5 days	1 days	12 hrs

T_1+P_1 (0.05% thymolphthalein and 0.05% phenolphthalein wt/v)

T_2+P_2 (0.1% thymolphthalein and 0.1% phenolphthalein wt/v)

T_3+P_3 (0.2% thymolphthalein and 0.2% phenolphthalein wt/v)

T_4+P_4 (0.4% thymolphthalein and 0.4% phenolphthalein wt/v)

T_5+P_5 (0.6% thymolphthalein and 0.6% phenolphthalein wt/v)

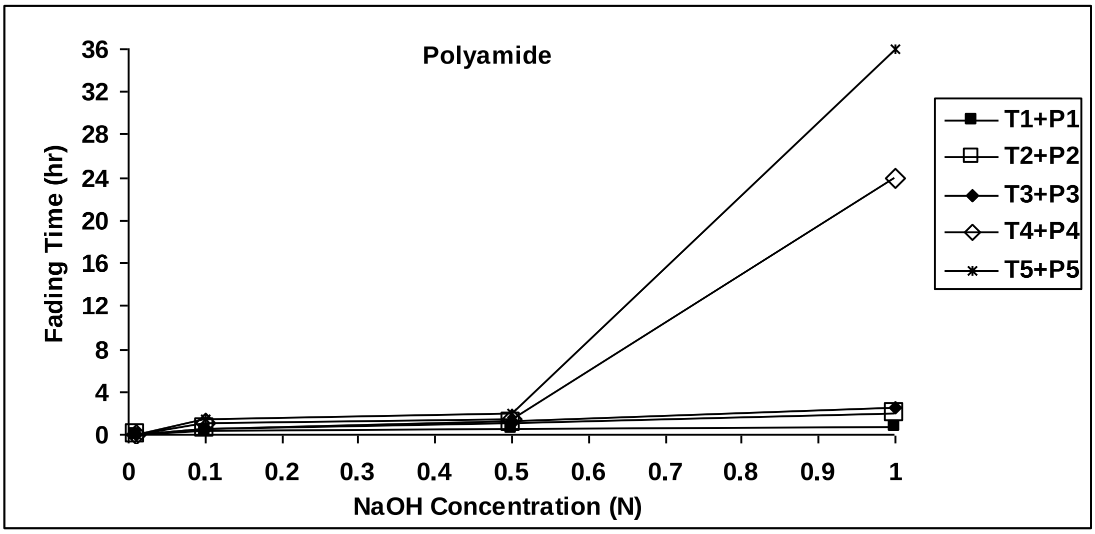

Figure 54: Effect of different concentrations of NaOH with different concentrations of the mixture (thymolphthalein and phenolphthalein) on the fading time using polyamide fabric

Results of Table 16 and Figure 55 show the fading time of polyester fabric. In case of using 0.01 N NaOH, polyester fabric gave colorless writing **(CLW)** and in case of using 0.1 N NaOH, it gave short handwriting stability from 10 mins to 1 hr. In case of using 0.5 N NaOH, it gave more writing stability from 25 mins to 1.5 hr but n case of 1 N NaOH, it gave the best handwriting stability from 40 mins to 1 days.

Results of Table 16 and Figure 56 show the fading time of cotton fabric. In case of 0.01 using N NaOH, cotton fabric gave colorless writing **(CLW)** and in case of using 0.1 N NaOH, it gave short handwriting stability, the writing turned colorless rapidly. In case of 0.5 N NaOH, it gave writing stability from 10 mins to 30 mins but in case of using 1 N NaOH, it gave more handwriting stability from 30 mins to 12 hrs.

It is clear from Table 16 that, at the same conditions (the same concentration of NaOH and the same concentration of the mixture (thymolphthalein and phenolphthalein), polyamide surface gave more writing stability than polyester and polyester gave more writing stability than cotton did. The fading time of fabrics surfaces following this order:-

Polyamide> Polyester> Cotton

The higher writing stability given by polyamide may be caused by its higher pH than that of polyester and/or cotton. Also, polyamide photomicrograph (Figure 47) showed creases in fibers which led to ink trapping and inhibition of the reaction with the atmospheric air and hence a low decrease in pH, but the cotton fabric gave the least fading time because of it contains –OH and have weak acidic character **[80]**. Therefore the handwriting faded quickly, also may be due to the absorption of NaOH on the cotton surface.

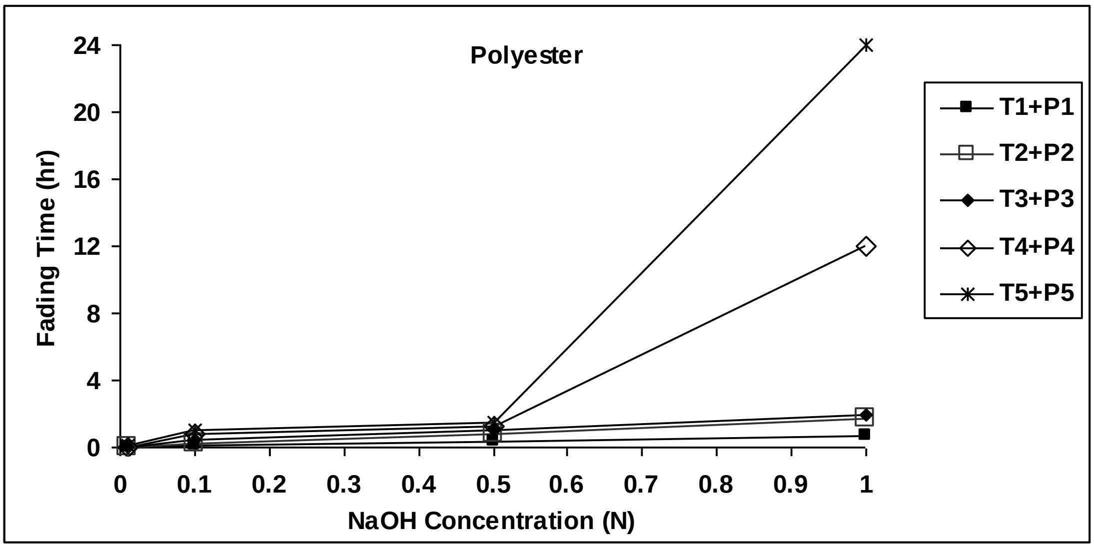

Figure 55: Effect of different concentrations of NaOH with different concentrations of the mixture (thymolphthalein and phenolphthalein) on the fading time using polyester fabric

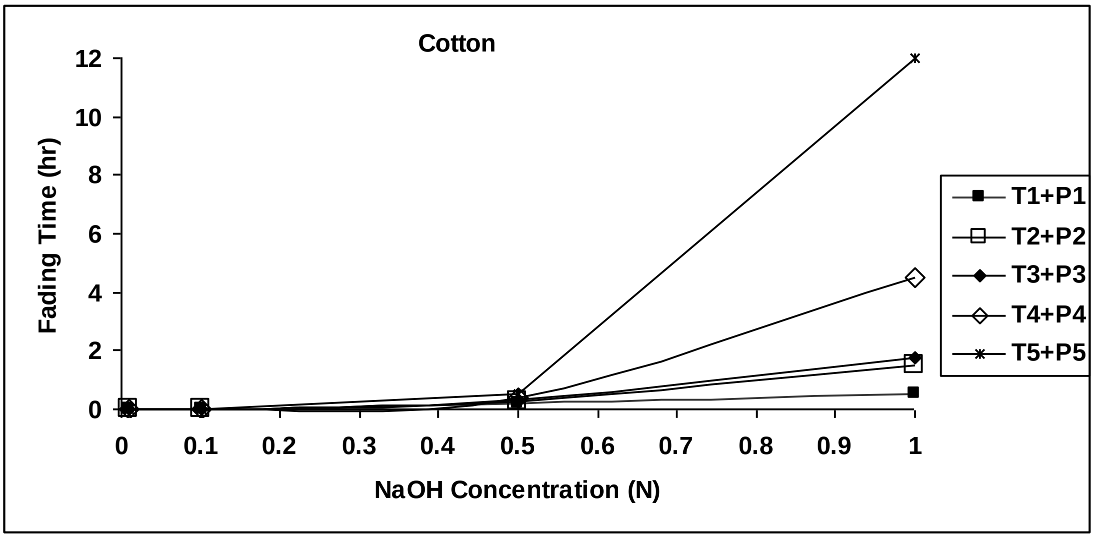

Figure 56: Effect of different concentrations of NaOH with different concentrations of the mixture (thymolphthalein and phenolphthalein) on the fading time using cotton fabric

3.12 Effect of Large Volume of 1 N NaOH With Different Concentrations of the Mixture (Thymolphthalein and Phenolphthalein) on the Fading Time Using Textile Surfaces

From the pervious Table (Table 16), 1 N NaOH gave more handwriting stability. Therefore, we studied effect of increasing the volume of 1N NaOH, in this section, we used equal volume of 1 N NaOH and thymolphthalein and the result obtained are set out in Table 17.

Adding equal volume of 1 N NaOH and the mixture (thymolphthalein and phenolphthalein) gave blue ink, although the ink gave absorbance at 560, the ink mixture gave blue writing color , this blue color faded to colorless without passing through red color. This means that phenolphthalein has no effect in this mixture. As explained in section 3.4, the colorless of phenolphthalein in high concentration of alkali, the reaction of alcoholic phenolphthalein with the alkaline solution (NaOH) caused the mixture to become a colored quinoid form of phenolphthalein rapidly. This negative ion is flat and the pi system is conjugated. With time, the phenolphthalein color intensity decreases because the quinoid form reacted slowly with hydroxide ions at high concentration to produce the colorless (non-resonant) carbinol form **[78, 79]**, so the color in case of using large volume of 1 NaOH with (thymolphthalein and phenolphthalein mixture) depends only on thymolphthalein.

Also it is clear from results of Table 17 and Figure 57 that for the same handwriting surface, the stability of handwriting increased with increasing thymolphthalein concentration. The fading time (writing stability) of the used textile fabrics following this order:-

Cotton > Polyamide > Polyester.

On the other hand the fading time of the used textile fabric in Table 16 (0.5 ml NaOH) following this order

Polyamide> Polyester> Cotton

The higher handwriting stability given by cotton than other used fabrics in case of using equal volume of 1 N NaOH may be caused by a high concentration of alkali which leads to the penetration of alkali and dyeing in the deep the microfibre of cotton (mercerization idea) **[81]**. This leads to the inhibition of the reaction of the alkali with the air on cotton surface so it gave more writing stability.

Table 17: Effect of large volume of 1 N NaOH with different concentrations of the mixture (thymolphthalein and phenolphthalein) on the fading time

NaOH	The mixture concentration	pH of the ink	Abs. of the ink		Fading Time Textile Fabric		
			At 560 n m	At 600 n m	Polyamide	Polyester	Cotton
4 ml 1 N	4ml of(T_1+P_1)	12.25	5.8	5.5	4 mins	3 mins	3 hrs
	4ml of (T_2+P_2)	12.15	5.8	5.0	5 mins	4 mins	5 hrs
	4ml of (T_3+P_3)	12.05	5.3	5.2	6 mins	5 mins	5.5 hrs
	4ml of (T_4+P_4)	12.0	5.9	5.3	10 mins	8 mins	15 days
	4ml of(T_5+P_5)	11.98	6.0	5.4	15 mins	12 mins	15 days

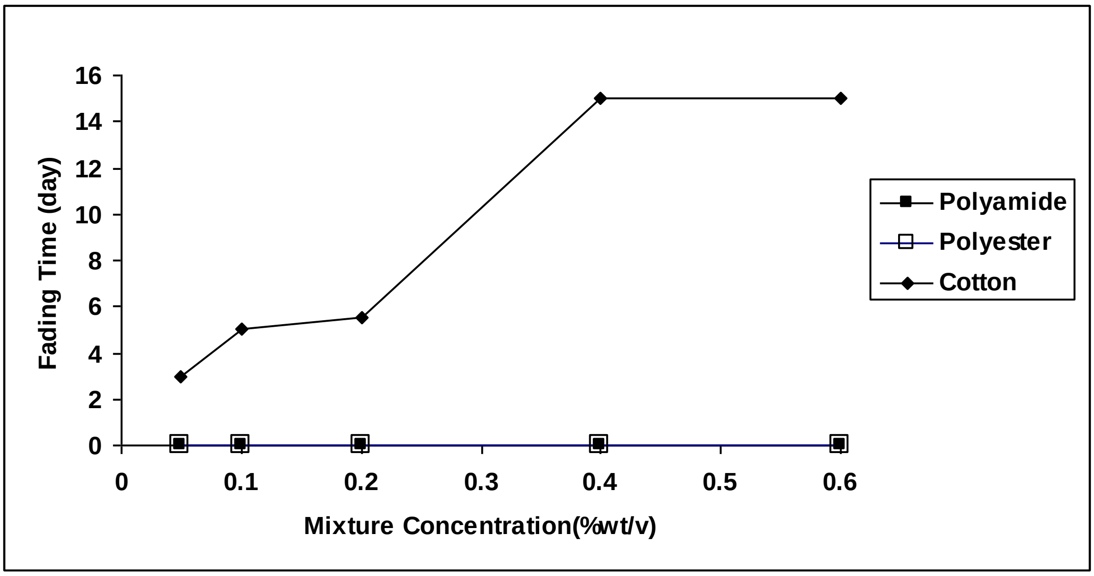

Figure 57: Effect of large volume of 1 N NaOH with different concentrations of the mixture (thymolphthalein and phenolphthalein) on the fading time using different fabric surfaces

3.13 Deciphering of the Faded Handwriting

Deciphering of the faded handwriting was carried out with several techniques.

3.13.1Optical Examination

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

3.13.2 Heat Deciphering

The faded handwriting surfaces were subject to the thermal effect in a thermostatically controlled oven at 100 ºC for 10 minutes by hanging them with suitable hooks, There was no change in all the faded handwriting surfaces.

The faded handwriting surfaces were subjected to 150° C for 20 minute this result was obtained:

In case of phenolphthalein inks only the faded phenolphthalein inks which contain 0.5 ml 1N NaOH handwriting was found to become visible and gave red writing in case of Azhar and Xerox paper, but there is no change in the faded Quena, Edfo and Rakta paper handwriting surface even with more heating time. Also the faded polyamide and polyester was found to become visible and red but there was no change on the faded cotton handwriting surface even with longer heating time. This may be because phenolphthalein transition range is at pH 8.2- 9.8 the thermal effect decreased the moisture on the surface and caused a slight increase in pH value (alkalinity increasing) of the handwriting strokes. This slight increase is effective in cases of Azhar and Xerox paper and in case of polyester and polyamide with phenolphthalein inks with 0.5 ml 1 N

NaOH but not effective in case of Quena, Edfo , Rakta paper and cotton textile fabric because of its low pH (7.8, 6.9 , 7.4and 6.61).

In case of the thymolphthalein ink, there was no change in the faded handwriting. This may be attributed to the high transition range of thymolphthalein at pH 9.3-10.5. The handwriting was colorless when the pH of thymolphthalein was below the range and it was Blue when the pH of thymolphthalein was above the range.

In case of the mixture ink of thymolphthalein and phenolphthalein only the faded mixture inks which contained 0.5 ml of 1N NaOH handwriting was found to become visible and gave red color in cases of Azhar, Xerox paper, probably because of the presence of phenolphthalein. But there was no change in the faded Quena, Edfo and Rakta handwriting surface even with longer heating time. . Also the faded polyamide and polyester was found to become visible and red but there was no change on the faded cotton handwriting surface even with longer heating time.

3.13.3 Chemical Deciphering

The faded handwriting was visible when treated with the alkaline solution. The solution was sprayed over the writing using an atomizer to release a spray over the textile surface. Sodium hydroxide and ammonium hydroxide were used, also the handwritimg was visible when subjected to ammonia vapor. A camera was employed to take pictures before the writing was fading. The fading speed depended on the concentration of the alkali used.

3.14 Effect of Adding Optical Brightener

The faded handwriting did not respond to the different light, this means the forensic investigation of the faded disappearing ink under different light sources is useless (Section 3.13.1); therefore, we studied effect of adding optical brightener to the prepared thymolphthalein, phenolphthalein and their mixture.

The prepared disappearing inks are colored in alkaline solution, so the used optical brightener should be stable at alkaline medium and general stable with disappearing ink components.

Uvitex RSB liquid 150 % (Stilbene disulfonic acid triazine derivative) were added to the prepared disappearing inks with ratio 2% volume per volume, the prepared inks were applied on the used paper and fabrics surfaces. After complete fading, the handwriting surfaces were investigated under different light illumination with different wavelengths.

Examination of all the faded paper and textile surfaces gave fluorescence under short and long UV. However, do not give response to the other light (IR and Visible).

In case of using, disappearing inks in forgery and counterfeiting crimes, the optical brightener make forensic examination of the suspected documents and following up the handwriting strokes easy with non-destructive method.

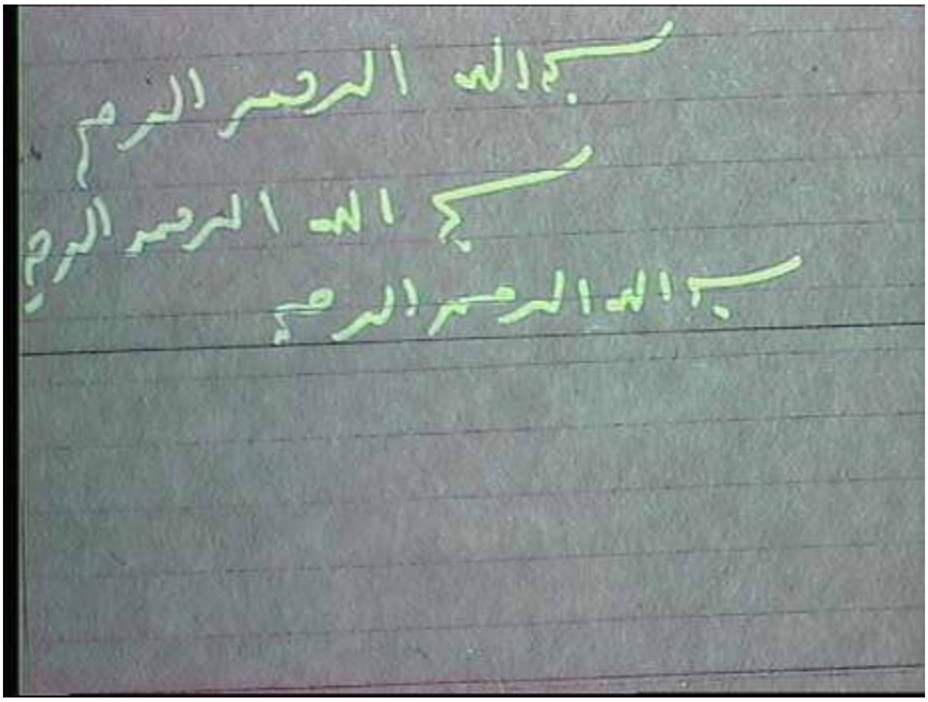

Figure 58: Fluorescence of the faded writing under long UV 356 nm

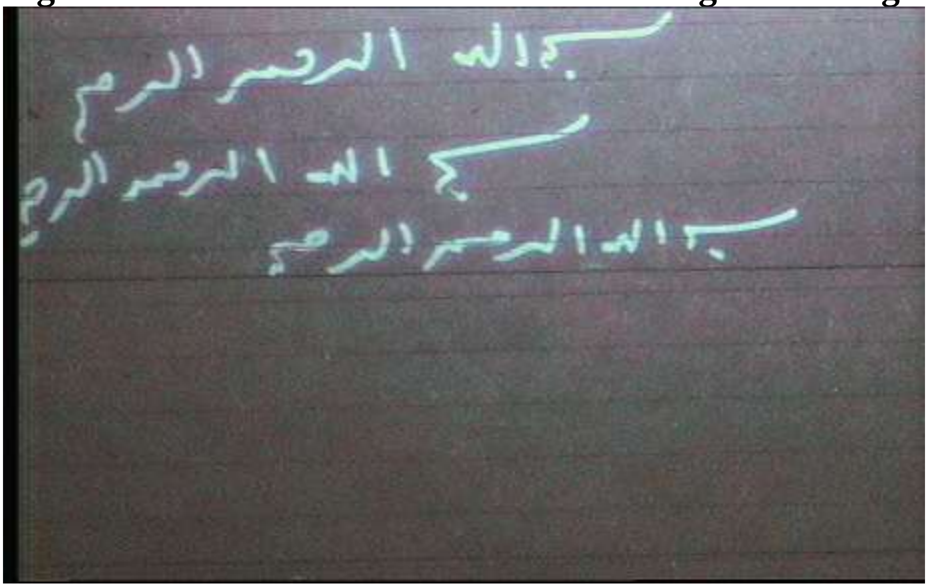

Figure 59: Fluorescence of the faded writing under short UV 254