Summary

In this work different variety of written papers were used namely, Japanese writing paper, Brazilian writing paper, yellow writing paper and ruled writing paper which marked with three types of inks namely, iron blue aqueous ink (Vispen), blue ball point ink (Reynolds), Blue ballpoint ink (Bic) . Two types of chemical erasures were chosen, acidic solution of sodium hypochlorite prepared from commercial Clorox solution with oxalic acid till pH_5 . The second erasure is benzyl alcohol followed by wiping with ethyl alcohol. The accelerated aging was used by subjected the samples of inks marked on different types of papers at 100 °C for different time periods from 100 to 400 minutes.

The **first** part of this work was used to study the relative aging of inks using single- solvent extraction technique. The extraction method of Cantu and Prough was applied for measuring the relative age of ink. The change of absorbance of dye of inks in the solvent was measured by spectrophotometer in visible region at 550 nm. The single aging curves of each type of ink placed on different papers, or different formula of inks placed on the same type of paper was determined during a period of accelerating aging from 100 - 400 minutes at 100 °C, it was found that the stability of the inks to aging on the papers, is affected by the type of paper used, as the following order:

Yellow paper > Ruled paper >Brazilian paper >Japanese paper

the stability depended upon the type of fibers of the papers, the conditions of pulping and bleaching used during the manufacture of the papers, type of sizing and loading materials, the nature of the chemical bonds between ink and paper, oxidative destruction and other transformation of ink dye, resins and polymers in ballpoint inks. The different papers causes

different shaped ink aging curves, which means that only inks on the same paper can be compared for age.

In forensic examination of hand written documents, it is very important to ascertain whether a sentence or word of the text was written before or after the signature on a receipt or document if written with the same ink, and also to compare between the suspected and legal words of the text before using the erasure process. Thus by comparing the rate and extent of extraction of absorbance curves (in visible region) one can know which ink is oldest than the other on the same type of paper. The inks on the paper samples must be stored under the same conditions (heat, light, humidity, and so forth). A detailed study of the natural aging of ink is however, beyond the scope of this work and will be investigated in another study.

The **second** part of this work was used to study the examination of disappearance or change the color of inks by naked eye and under ultraviolet light. The changes in colors of samples were depend on the types of inks, chemical erasure, properties of paper used, and time of thermal aging.

It was found that the acidic solution of sodium hypochlorite erasure had a great effect on iron blue aqueous ink placed on all types of papers used in this work, either aged or unaged samples, since it's blue color was completely bleached and disappeared on contact with any type of paper, and the color of erased sites of inks did not also appear under ultraviolet lamp. Time required for bleached the color of ink on the papers increased steadily with increasing time of thermal aging, and this was more pronounced in the case of ruled and yellow papers. However, the erased

sites of papers- and not the ink -showed different colors. Thus, The color of the erased sites of the Japanese and Brazilian papers- and not the color of ink- remained yellow with erasure and did not show any significant changes in color with time of thermal aging when examined by naked eye, while, in case of ruled and yellow papers, the color was changed to white and faint yellow respectively for all thermal aging samples due to degradation of cellulosic fibers instead of short -chain of hemicellulose fraction during thermal aging and consequently the erasure solution penetrated easily through the fibers and caused completely bleach for the impurities and residual lignin in this types of papers.

Scanning electron microscope (SEM) was used to confirm the behavior of paper fibers during thermal aging from the examination of the fracture surface of the fibers. It must be mentioned that the acidic solution of sodium hypochlorite erasure did not remove the dyes of all samples of blue ballpoint inks placed on papers, but the color of inks was changed to different colors.

On the other hand, benzyl alcohol erasure followed by wiping with ethanol, had a lower effect on change the color of unaged and aged iron blue aqueous ink placed on papers and the aging time had not any effect on the change of color of ink by erasure, since the blue color of ink did not change either when examined by naked eye or under ultraviolet lamp, while , the blue ballpoint ink model Reynolds either aged or unaged samples, was easily erased and disappeared on all types of papers, and the aging time had not effect on the erasing process . However, the blue ballpoint ink model Bic is not completely removed by the previous erasure on all types of papers but changed only to faint blue or very faint

blue colors, and gave the same colors when examined under U.V lamp. The presence of additional functional groups in ink model Bic increases It's stability towards environmental conditions and chemical erasing comparing with ink model Reynolds. This is supported from the results of FTIR spectra of the two ballpoint inks and from the results of elemental analysis of the ink.

It should be mentioned that the goodness of erased aged inks applied here, depends upon completely removal or disappearance the unaged or aged inks on the different types of papers with suitable chemical erasure.

A very important factor in connection to this attempt was erasing inks on papers without destruction of the fiber from the surface of the paper. Another important thing should be mentioned in connection, is examination the color of the erased sites of paper itself.

It was found from the examination of completely erased aged iron blue and blue ballpoint ink model Reynolds on papers by acidic hypochlorite erasure and benzyl alcohol erasure respectively that the color of the erased inks for all samples was completely disappeared when examined either by naked eye or under ultraviolet light. The erased sites of papers showed different colors. Examination of completely erased aged iron blue aqueous ink on papers by acidic hypochlorite erasure showed that the glossy of the Japanese and Brazilian papers decreased slightly with erasing. The change of the color of the papers to yellow was obvious especially in unaged and aged papers at 100 and 200 minutes, which clearly appeared under ultraviolet light and gave dark orange color and consequently the erased inks of this samples are clearly detectable and gave bad results for erasing, while erased ruled papers gave clear

white color with aging and yellow color under ultraviolet lamp, in addition to removing the fibers from the surface of the paper during erasing process. Moreover, the printed lines of ruled paper was removed and the erasing can be detected easily giving also bad erased sites. In spite of the color of erased yellow paper changed to very faint yellow when erased the aged paper which difficulty detectable when examined by naked eye and under ultraviolet lamp, a higher amount of fiber disturbance to the paper surface especially at long time aging (300 – 400 minutes) has been done since this type of paper has less sized material (free from starch) and for this reason it gave bad results in erasing. On the other hand, the good erased sites of inks were obtained in the case of using benzyl alcohol followed by or wiping with ethanol as a chemical erasure for unaged and aged blue ballpoint ink model Reynolds on all paper samples. This erased sites either ink or paper did not appear with naked eye and difficulty appeared under ultraviolet lamp since, they gave very faint blue color. The glossy of paper slightly affected by erasure, and consequently the erased sites were difficult to be identified, thus it gives a good erasing. Conductivity, FTIR, and Scanning electron microscope (SEM) were used to identify chemical erasure sites.