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**EFFECT OF AGING ON THE COLORS OF INKS WRITTEN  
ON UNCOVERED AND COVERED PAPERS  
WITH PLASTIC SHEET**

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Photocopy paper and paperboard were written with two types of inks: blue roller ink and black ink jet, and then covered with hot melt adhesive plastic sheet namely, ethylene vinyl acetate copolymer. Uncovered and covered samples were subjected to thermally accelerated aging at 100 °C for different time intervals. Each sample was exposed to ultraviolet radiation at 25°C for 72 hours. The effect of accelerated thermal and photo-oxidative aging at different time intervals on the stability of colors of inks on uncovered and covered paper with plastic sheet was examined in day light and under ultraviolet lamp. The results were explained on the basis of FTIR spectra and elemental analysis of the plastic and ink samples.

### **I. Introduction**

Several comprehensive studies <sup>(1)</sup> have addressed the area of natural and artificial (accelerated) aging of documents in an effort to determine the conditions and period of time under which a writing ink will fade on a document. The light-fading stability, included digital output from thermal dye transfer printers, medium and high resolution ink jet printers, was studied <sup>(2)</sup>. Ink jet print quality depends highly on properties of papers and inks, and their mutual interactions <sup>(3)</sup>.

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On the other hand, some polymers can be used as hot-melt adhesives or thermoplastic powder coating in the temperature range of about 100 to 200 °C <sup>(4)</sup>. Hot-melt adhesion and wettability between polyethylene and poly (vinyl acetate) or other polymers in the vicinity of the adherent melting point was investigated <sup>(5)</sup>. A previous study <sup>(6)</sup> was conducted to obtain information about the change in the IR spectrum of plastic cover sheet of ethylene vinyl acetate copolymer of some documents during thermal treatment.

However, no work seems to have been carried out on the effect of thermal and photo-oxidation treatments on the properties of paper documents written with inks and covered with plastic sheets. In the present work, photocopy paper and paperboard were used, and each type of paper was written on it with two types of ink: blue roller ink and black ink jet, and then covered with hot melt adhesive plastic sheets, and subjected to thermal and photo-oxidation aging. The objective of this work was to study the effect of accelerated aging on the stability of colors of inks on uncovered and covered papers with plastic sheets during examination in daylight and under ultraviolet lamp. This study was intended to bring more light on the correlation between the effect of accelerated aging on the types of papers used, the types of inks, the presence of adhesive plastic sheet on the papers and the duration time of accelerated aging. The results were explained on the basis of FTIR spectra and elemental analysis of plastic and ink samples.

## **II. Materials And Methods**

### **I- Materials**

Two Types of Papers Were Used in this Work Namely:

- Photocopy paper made from imported Kraft soft wood pulp.
- Paperboard made from soft wood pulp blended with rice straw pulp produced locally at Rakta mill-Alexandria.

These Types of Papers were Written with Two Types of Inks Namely:

- Blue Roller ball ink (model um-100(07), Japan)
- Black ink jet for computer (model BCL-21, Japan).

Each paper was adhesive by one type plastic sheet (ethylene- vinyl acetate copolymer) coating machine for all samples.

## **2- Methods**

Paper sheet and paper covered with sheet were thermally accelerated aging in thermostatically controlled oven at 100 °C for different time intervals (20, 30, 40, and 50 hr.) by suitably hanging them by hooks. Then the samples were exposed to UV lamp at 245 nm wavelength at 25 °C for 72 hours.

## **3- Analysis of samples**

### **- Elemental analysis**

Elemental analysis (C, H, Cl, N, and S) of the initial samples of plastic and inks were determined. The measurements were done at the Micro-analytical Center, Cairo University.

### **- FTIR analysis**

FTIR spectra of all samples were measured using Fourier Transform Infrared Spectrophotometer (FTIR) model 1050, Perkin Elmer.

### **- Identification of the type of polymer of plastic sheet**

FTIR spectra of plastic cover sheet was identified by matching with FTIR spectra of different types of polymers, taking into consideration the results of elemental analysis of the plastic sheet. The plasticizer was separated from the plastic sample by ether extract method, and its FTIR spectra were compared with known spectra for identification purpose.

### **- Measurements of the change of ink colors**

The change of color of exposed and unexposed inks written on uncovered and covered papers with plastic sheet was determined after 24 hours in atmospheric air at 25 °C with naked eye in day light and under ultraviolet light.

### III. Results And Discussion

The corresponding change in colors of inks, written on uncovered and covered papers with plastic sheet were examined in day light and under ultraviolet lamp at 254 nm, are represented in (Table 1).

It is clear from (Table 1) that the black ink was more resistance to fading or changes its color during time intervals of aging comparing with blue roller ballpoint ink, either an-uncovered or covered papers with plastic sheet. Moreover, the long exposure time of aging for 40 and 50 hours to uncovered and covered paper samples with blue roller ink showed no significant difference of the colors of ink between them when examined in day light.

The results clearly showed that the major fading occurred on the roller ball ink comparing with ink jet on uncovered papers when exposed to thermal treatment for duration time from 30-50 hours, and ultraviolet radiation for 72 hours at room temperature. The color of the blue roller ball ink changed from dark blue to faint blue on the photocopy paper and to greenish blue on paperboard when examined under ultraviolet lamp. In case of ink jet, the fading was less dramatic on the uncovered papers resulting dark brown color up to 40 hours exposure and then become brown color with prolonged the exposure time on photocopy paper when examined in day light, while all treated samples showed dark brown color on paperboard. The color of ink jet on uncovered paper under ultraviolet lamp turned from dark black to brownish black when exposed to long exposure time. It was observed also from the results of (Table 1) that the two types of inks were generally more stable to fading on paper board than on photocopy paper.

The color change of inks is greatly affected by various factors; the chemical composition of the dye of inks, the properties of organic ink solvent, the chemical and physical properties of cellulosic paper fibers, the nature of bond between ink dye and papers, the aggregation

of ink through the fibers, oxidative destruction and other transformations of ink dye, resins and polymers, the chemical structure of plastic sheet, the temperature, the relative humidity, and the duration of thermal and photo treatments.

The stability of black ink jet on the papers to fading comparing with blue roller ball ink can be explained on the basis of the black ink jet solvent may contain a material of hydroxyl functionality, like ethylene glycol, which act as free radical quenchers leading to increase its stability against thermal and photo-oxidation. However, the hydroxyl groups have ability to create hydrogen bonding between ink and cellulosic fibers of the paper and reduce the fading of ink. Black ink jet may contain carbon black to give surface modified carbon black blended with hydroxyl compound and water, used as ultraviolet absorber to give ink of light resistance. On the other hand, ink contains amino groups can also be able to form intermolecular hydrogen bonds with cellulosic fibers of the paper to be favorable for stabilization towards thermal and photo-oxidation. This was confirmed experimentally from the results of FTIR spectra of black ink jet (Figure 1), since it shows the presence of a broad band at  $3353\text{ cm}^{-1}$  corresponding to (OH) and (N-H) groups. Further, two absorption bands appeared at  $2927\text{ cm}^{-1}$  and  $2877\text{ cm}^{-1}$  which corresponded to acid dimer (-COOH). A strong intensive bands at  $1664\text{ cm}^{-1}$  corresponded to (C=N) stretch and at  $1215\text{ cm}^{-1}$  for (C-N) stretch were observed. On the other hand, the results of elemental analysis of this type of ink (Table 2) showed the presence of nitrogen and higher percent age of carbon.

The blue roller ball ink used in this work is water based and pigment and gel ink as recorded information on the ball. This type of pen contains organic liquids such as glycols and formamide to retard the drying of the ink. The light fastness of the dyes of this ink ranges from good for the metalized acid dyes to poor for some of the basic dye salts. <sup>(7)</sup>

It is clear from the FTIR spectrum of blue roller ball ink (Fig. 2), the presence of broad band at  $3366\text{ cm}^{-1}$  which is assigned to (N-H) region, while a strong absorption band appeared at  $2924\text{ cm}^{-1}$  corresponded to (C-H) stretching. The band at  $1288\text{ cm}^{-1}$  for (C-N) stretch and a while the series of bands from  $1117 - 1044\text{ cm}^{-1}$  corresponded to (C-N) stretch due to -NHR group. Moreover, the elemental analysis of this type of ink reveals the presence of nitrogen (Table 2).

Although, the dipole-dipole interaction of the amide group (-CONH<sub>2</sub>) causing -OCN<sup>+</sup> dipole to align, rather than the inherently weak hydrogen bonding, controls the packing of the molecular chains<sup>(8)</sup>. The thermal and photo-treatment of the ink may cause by the partial decomposition of the amide group into CO and NH<sub>3</sub> leading to fading.

The two types of inks showed more stability to fading on paperboard than on photocopy paper during aging. This can reasonably be understood by assuming that the paperboard contained a higher amount of hydrophilic fraction more than photocopy paper,<sup>(9)</sup> and to some extent to association of the dye inside the fibers and consequently its stability to fading, in spite of the presence of very thin layer of wax as a surface sizing, since this do not prevent the movement of the liquid inside the fibers during aging.

The results in Table 3 indicated that the covered papers with plastic sheet showed a higher resistance to fading of both types of inks comparing with uncovered papers during aging due to additives incorporated in the plastic sheet.

FTIR spectra of plastic cover sheet (Fig. 3) was identified by matching with FTIR spectra of different types of polymers, taking into consideration that the results of elemental analysis of plastic sheet (Table 3). The spectra of the used (or investigated) plastic cover sheet were exactly identical to the FTIR spectra of ethylene vinyl acetate



copolymer  $\{-(\text{CH}_2)_2-\text{CH}_2-\text{CH}(\text{OCOCH}_3)-\text{CH}_2-\}_n$ . However, the plastic sample included some additives such as plasticizer, antioxidant and ultraviolet absorber. The plasticizer was separated from the plastic sample by ether extraction method, and its FTIR spectra was exactly identical to the FTIR spectra of secondary amides (RCONHR) (Fig. 4).

The additives incorporated in the plastic sheet resisted the oxidation to some extent and capable of capturing and dissipating a large amount of harmful radiation. That is why the covered papers with plastic sheet had a protective effect to some extent on the fading of inks comparing with uncovered one during aging.

Table (1): Effect of aging on color of inks written on uncovered and covered papers with plastic sheet

Samples	Time (hrs.)	Color in day light		Color under UV light	
		Uncovered	Covered	Uncovered	Covered
Black ink jet on photocopy paper	--	Dark Black	Dark Black	Dark Black	Dark Black
	20	Dark Black	Dark Black	Blackish brown	Dark Black
	30	Dark Black	Brownish Black	Blackish brown	Brownish Black
	40	Brown	Brownish Black	Blackish brown	Brownish Black
	50	Brown	Blackish brown	Blackish brown	Brownish Black
Black ink jet on paperboard	--	Dark Black	Dark Black	Dark Black	Dark Black
	20	Dark brown	Dark Black	Blackish brown	Dark Black
	30	Dark brown	Dark Black	Blackish brown	Dark Black
	40	Dark brown	Dark Black	Blackish brown	Brownish Black
	50	Dark brown	Dark Black	Blackish brown	Brownish Black
Blue roller ball ink on photocopy paper	--	Dark Blue	Dark Blue	Dark Blue	Dark Blue
	20	Greenish blue	Dark Blue	Greenish blue	Greenish blue
	30	Faint Blue	Greenish blue	Greenish blue	Greenish blue
	40	Faint Blue	Faint Greenish blue	Faint bluish green	Greenish blue
	50	Faint Blue	Faint Greenish blue	Faint bluish green	Greenish blue
Blue roller ball ink on paperboard	--	Dark Blue	Dark Blue	Dark Blue	Dark Blue
	20	Greenish blue	Dark Blue	Greenish blue	Greenish blue
	30	Greenish blue	Dark Blue	Bluish green	Greenish blue
	40	Greenish blue	Greenish blue	Bluish green	Greenish blue
	50	Greenish blue	Greenish blue	Bluish green	Greenish blue

**Table 2 : Elemental analysis of inks**

Types of inks	C%	H%	N%	Cl%	S%
Blue roller ball ink	70.6	7.4	4.82	Nil	Nil
Black ink jet	86.4	9.8	3.65	Nil	Nil

**Table 3 : Elemental analysis of plastic sheet**

C%	H%	N%	Cl%	S%
86.4	7.1	3.1	Nil	3.6

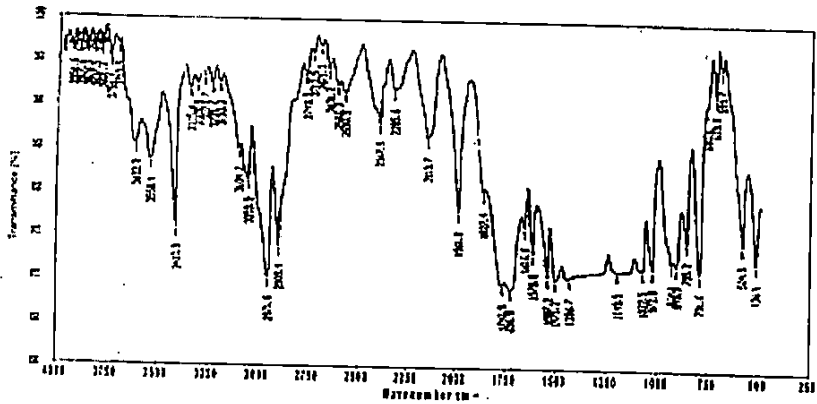


Fig. (3): FTIR Spectra of Plastic Cover Sheet

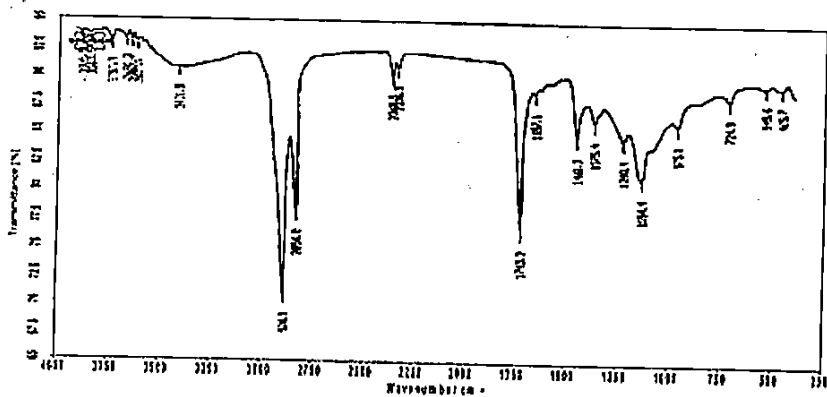


Fig. (4): FTIR Spectra of Extracted Plasticizer from Plastic Cover Sheet

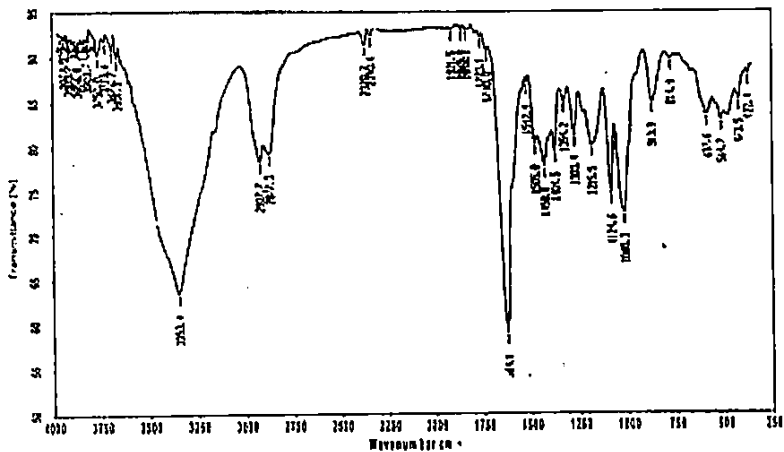
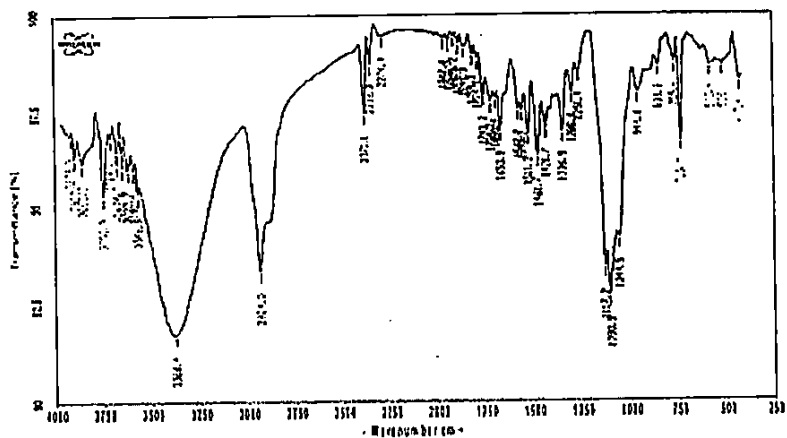


Fig. (1): FTIR Spectra of Black Ink Jet



## REFERENCES

- 1- Arney, J.S. and Chapdelaine, A. H., A Kinetic Study of Influence of Acidity on the Accelerated Aging of Paper, in Preservation of Paper and Textiles of Historic and Artistic Value 11, Williams, J.C. Ed., Advances in Chemistry Series No. 193, *American Chemical Society*, 1981, Chapter 14, pp. 189-204.

### And Also:

Robertson, D.D., Permanence/Durability and Preservation Research at Barrow Laboratory, in Preservation of Paper and Textiles of Historic and Artistic Value 11, Williams, J.C. Ed., Advances in Chemistry Series No. 193, *American Chemical Society*, 1981, Chapter 5, pp. 45-55.

Hilton, O., *Scientific Examination of Questioned Documents*, CRC Press, 1982, pp. 273-278.

Santokh, S. and Amar, S., Anachronistic Features in Limiting the Age of Documents, *Journal of Forensic Sciences*, Vol. 30, No. 4, 1991, pp. 377-382.

Safy El-Din, N. M. and Fahmy, A. M., Effect of Accelerated Aging on the Properties of some Writing Paper Sheets, *Polymer International*, Vol. 34, No. 1, 1994, pp. 15-18.

Stewart, L. F., Artificial Aging of Documents, *Journal of Forensic Science*, Vol. 27, No. 2, 1982, pp. 450-453.

Sen, N. K. and Ghosh, P. C., Dating Iron-Base Ink Writing on Documents, *Journal of Forensic Science*, Vol. 16, No. 4, 1985, pp. 511-520.

Hamed, H. R.; Safy El-Din, N.; El-Laithy, S. A.; Mansour, O. Y. and Sabaa, M. W., Effect of Accelerated Fading on the Stability of Inks Marked on Different Types of Paper, *Journal of Forensic Science*, Vol. 3, No. 3, 1997, pp. 229-236.

- 2- Henry, w., *Proceeding of the IS and T's international Conference on Digital Printing Technologies*, 505, 1995.
- 3- Lavery, A.; Provost, J.; Sherwin, A.; and Watkinson, J., The Influence of Media on the Light Fastness of Ink Jet Prints, *Proceeding of the IS and T's international Conference on Digital Printing Technologies*, Toronto, Canada, Oct. 18-23, USA, 1998, pp. 123-128.

### And Also:

Lee, H., Progress and Trends in Ink Jet Printing Technology, *Journal of Image Science Technology*, 42, 1998, pp. 49-62.

- 4- Zimmermann, H. and Schaaf, E., *IUPAC congress*, Budapest, Aug. 17-22, 1991.
- 5- Imachi, M., *Journal of Applied Polymer Science*, 34, 1987, pp. 2485-2491.
- 6- Safy El-Din, N., IR spectroscopic Study on the Thermal Degrading of the Plastic Security Cover Sheets of some Documents, *Journal of Applied Polymer Science*, 47, 1993, pp 911-916.

- 7- Richard, L. and Robert, W., *Forensic Examination of Ink and Paper*, Library of Congress Catalog, Card no. 83-18039,20, USA. 1984.
- 8- Cannon, C., *Journal of Chemistry and Physics*, 24, 1986, pp. 491-504.
- 9- Safy El-Din, N.; Matawie, M., Youssif, S. and Soliman, M., Effect of Accelerated Aging on the Properties of Photocopy Papers and Paperboard, *Egyptian Journal Applied Science*, 20, 2005, pp. 419-429.

## تأثير التقادم على ألوان أحبار الكتابة على الورق المغطى

### وغير المغطى بأغلفة البلاستيك

نبيل صفى الدين هشام رضا

محمد سليمان

تم فى هذه الدراسة الكتابة على ورق التصوير والورق المقوى بنوعين من الأحبار هما : الحبر الأزرق الجاف ، والحبر الأسود السائل ، وتم تغطيتهما بأغلفة من البلاستيك اللاصق من نوع كوبوليمر الإيثيلين فينايل أسيتات .  
تم تعريض العينات المغطاة وغير المغطاة للتقادم باستخدام معجل حرارى عند ١٠٠ ° مئوية ، لفترات زمنية مختلفة . كما تم تعريض كل عينة للأشعة فوق البنفسجية عند درجة ٢٥ مئوية ، لمدة ٧٢ ساعة .  
تم اختبار تأثير التقادم بالتعجيل الحرارى والأكسدة الضوئية - لفترات زمنية مختلفة - على ثبات ألوان الأحبار المكتوب بها على الورق المغطى وغير المغطى ، وذلك فى ضوء النهار ، وبالأشعة فوق البنفسجية .  
تم تفسير النتائج من خلال التحليل الطيفى بالأشعة تحت الحمراء ، وتحليل العناصر فى عينات الأحبار والأغلفة البلاستيك .  
وتفيد هذه الدراسة فى الكشف عن التزوير فى المحررات الرسمية من خلال قياس ثبات ألوان أحبار الكتابة .