EFFECT OF THERMAL AND COLD TREATMENTS FOLLOWED BY ULTRAVIOLET RADIATION ON THE PROPERTIES AND COLOUR OF PAPER DOCUMENTS

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The effect of thermally accelerated aging and cold treatments followed by exposure to ultraviolet (UV) radiation at wavelength 336 nm on the chemical and physical properties, as well as on the colour of the bill paper, delivery note paper and application paper form used for identity card (ID) in daylight and under UV lamp were investigated. The results obtained revealed that the changes in the properties and colour of the papers depend upon, the type of natural fibers, sizing and coating materials, residual elements in the fibers and the conditions used in the treatments process.

INTRODUCTION

Natural and environmental conditions: heat, sunlight, moisture and dust are the main agents which cause yellowing, recolouration of bleached lignin residues and colouration of sizing agents.[1] Paper exposed to light over periods of time will become yellow and eventually crumble. The ultraviolet portion of the spectrum causes paper deterioration by promoting the oxidation of cellulose by atmospheric oxygen. Several comprehensive studies[2] have addressed the area of natural and artificial (accelerated) aging of documents and have been

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concerned with the effect of the accelerated heat aging on chemical, physical, mechanical and optical properties of the papers. Low temperature however retards the process of aging[(3)].

It was found that artificial aging of papers made form straw, birchwood, pinewood and rag for 72 hours at 100º C is equivalent to 25-28 years of natural aging at room temperature[(4)].

In this work three types of paper documents made from different types of natural fibers were studied. One part of each type was subjected to thermal accelerated aging and another part to cold treatment and then exposed to ultraviolet radiation. The changes in their physical, chemical, and optical properties in daylight and under ultraviolet lamp were studied. The main objective of this work is to study the correlation between the changes in colour of the treated document papers and in their properties under different conditions used to shed light on their effects on aging.

MATERIALS AND METHODS

Materials:

Three types of document papers were used in this work:

1- Bill paper made from rice straw pulp blended with kraft soft wood pulp produced locally at Rakta mill, Alexandria, Egypt.
2- Delivery note paper made from bagasse dissolving pulp, kindly supplied by the Egyptian Sugar and Distilling Company at Edfo.
3- Application paper form used for identity card produced from sulfite wood pulp.

Methods:

1. The treatments of the paper documents:

One part of the document papers were subjected to thermal accelerated aging in thermostatically controlled oven at 100ºC for 36 hours by suitably hanging them from hooks. Another part of papers were exposed to cold treatment at -5ºC for 36 hours. Then each treated sample was exposed to UV lamp giving 336 nm wavelengths at 25ºC for 18 hours using controlled cooling system at constant relative humidity (RH) 65$\pm$ 5%.

2. Analysis of samples:

The untreated and treated document papers were analysed by the following methods:

Chemical analysis:

The pH values of samples were determined by a cold extraction method[5]. While carboxyl content was determined by an indirect iodometric method[6]. Pentosan content[7], hot alkali solubility (HAS)[8] and lignin content[9] of the samples were estimated according to TAPPI standard.

Physical analysis:

The opacity [10], whiteness[11], water retention value (WRV)[12], and thickness [13](um) were measured according to TAPPI standards. Degree of Polymerization (DP) was measured by Jayme and Wellm method[14]. The sizability was measured by the method given by Mansour et al[15]. The crystallinity of the paper was determined by x-ray diffraction[16] using the following equalion.

$$\text{Crystallinity ratio (CR)} = 1 - \frac{I_{min}}{I_{max} - I_{min}}$$

Where I_{max} is the height of the 22.5º (2 ϴ) peak above the base line and I_{min} is the height of the 16º (2 ϴ) minimum above the base line.

3. Colour examination of the document papers:

The colours of the untreated and treated document papers were examined in day light and under ultraviolet lamp (336 nm).

4. Identification of paper additives:

Although paper consists primarily of cellulose fibers, many possible combinations of ingredients are added to give the paper its desired quality, depending on how the paper will be used. The starch, rosin, wax, talc, kaolin, calcium carbonate and calcium sulphate were tested according to Browning's "Analysis of paper".[17]

5. Elemental analysis:

Elemental analysis (Cl, N and S) of the initial samples were determined in the Analytical unit, Faculty of Science, Cairo University.

RESULTS AND DISCUSSION

CHEMICAL ANALYSIS:

Table (1)
Effect of thermal and cold treatments followed by UV radiation used as accelerated aging on the chemical properties of paper document.

Analysis	1	2	3	4	5
Bill paper					
Carboxyl content (m Eq /100g)	14.8	11.7	11.5	13.1	12.4
Pentosan %	12.7	10.9	10.3	11.6	10.6
Alkali solubility %	6.5	5.8	5.2	6.0	5.4
pH	7.97	8.30	8.76	8.04	8.15
Lignin content	1.46	1.03	1.00	1.40	1.30
Delivery note paper					
Carboxyl content (m Eq /100g)	30.2	36.6	38.0	30.7	31.8
Pentosan %	18.5	20.3	22.1	18.6	19.1
Alkali solubility %	10.3	11.6	12.1	10.8	10.4
pH	6.56	6.29	6.17	6.68	6.57
Lignin content	2.83	2.41	2.35	2.72	2.60
Application paper used for I.D					
Carboxyl content (m Eg /100g)	8.6	7.2	6.1	7.8	7.0
Pentosan %	8.1	5.7	6.6	7.4	6.9
Alkali solubility %	4.4	3.7	3.2	4.0	3.8
pH	8.30	8.44	8.51	8.36	8.39
Lignin content	0.04	-	-	-	-

(1) Without treatment, (2) Thermal treatment at 100ºC for 36 hours, (3) Thermal treatment at 100ºC for 36 hours followed by UV exposure (336 nm) for 36 hours. (4) Cold treatment at -5ºC for 36 hours and (5) Cold treatment at -5ºC for 36 hours followed by UV exposure for 18 hours.

It is clear from (Table 1) that the carboxyl content of the bill paper and the paper used for ID decreased with thermal treatment and more decrease was observed when both papers were exposed to UV radiation.

This may be due to oxidation and degradation during thermal and photo treatments which lowered the short-chain hemicellulose fractions. Moreover the oxidative cleavage of acetyl linkage which formed from crosslinking of carbonyl group of the hemicellulose and the neighbouring carbohydrate chain in both types of papers is the reason for the decreased pentosan content. However, the cold treatment was less effective on oxidation process to cleavage the acetyl linkage and consequently the papers treated with lower temperature had carboxyl content more than thermal treated papers. The carboxylic content of the paper used for ID was lower than bill paper. This can be explained by the presence of lignin content residue in the bill paper which characterized by hydroxyl, methoxyl and possibly carbonyl groups attached to aromatic ring which assisted in raising the value of carboxyl content in the bill paper, while the paper used for ID was nearly free from lignin. The hot alkali solubility of the two treated papers, either with higher or lower temperatures, was lower than that of the initial samples due to the decrease of acidic carboxyl groups by treatment and for this reason the hydrogen ion concentration of the treated samples was increased. The effect of thermal and cold treatments and ultraviolet radiation on delivery note paper led to increase the carboxyl content, since this type of paper made from bagasse dissolving pulp contained a higher amount of short-chain hemicellulose as it contains a higher pentosan content comparing with other two papers. Oxidation of higher amount of hemicellulose fractions led to formation of oxidative short chain oxycellulose and some degradation products during thermal treatment which is accompanied by an increase in the acidic carboxyl groups. Thermal treated delivery note paper was deteriorated especially when exposed to ultraviolet radiation by promoting the oxidation of cellulose and short-chain hemicellulose by atmospheric oxygen as well as decomposing most sizing materials leading to more increase in the carboxyl content. The delivery note paper had also higher content of lignin comparing with other used papers which degraded and decomposed by thermal and photo treatment.

PHYSICAL ANALYSIS

Table (2)
Effect of thermal and cold treatments followed by UV radiation used as accelerated aging on the physical properties of paper document.

Analysis	1	2	3	4	5
Bill paper					
Sizability (sec)	110	170	75	115	90
Whiteness	75.0	73.0	70.0	75.0	73.0
Opacity	67.0	64.0	62.0	67.0	63.0
Crystalline (x-ray)	0.61	0.65	0.58	0.61	0.60
W.R.V. %	195	143	220	175	186
D.P.	620	690	597	626	608
Thickness (m)	100	90	85	95	95
Delivery note paper					
Sizability (sec)	55	100	30	60	50
Whiteness	66.0	56.0	52.0	65.0	61.0
Opacity	79.0	77.0	74.0	78.0	77.0
Crystalline (x-ray)	0.52	0.62	0.50	0.54	0.53
W.R.V. %	265	228	252	256	270
D.P.	605	640	480	600	526
Thickness (m)	90	80	80	90	90
Paper used for ID					
Sizability (sec)	165	250	120	170	140
Whiteness	86.0	81.0	78.0	86.0	83.0
Opacity	73.0	70.0	68.0	73.0	70.0
Crystalline (x-ray)	0.68	0.73	0.62	0.69	0.66
W.R.V. %	158	102	127	134	156
D.P.	762	820	700	755	732
Thickness (um)	120	110	110	115	110

(1) Without treatment, (2) Thermal treatment at 100ºC for 36 hours, (3) Thermal treatment at 100ºC for 36 hours followed by UV exposure (336 nm) for 36 hours. (4) Cold treatment at -5ºC for 36 hours and (5) Cold treatment at -5ºC for 36 hours followed by UV exposure for 18 hours.

It is clear from (Table 2) that the elevated temperature improves the degree of sizing i.e. increase the time of liquid penetration probably due to the spreading of sizing materials on the surface of the paper by temperature effect and assists the fiber surface to coverage by the sizing agent to make the sized cellulose surface more hydrophobic. However, the exposure of the thermal treated sampls to UV radiation decomposes most sizing agents in addition to oxidation and degradation of cellulosic fibers, thus reducing the degree of sizing of treated samples. No clear effect of cold treatment on the sizability was observed. The degree of whiteness of all samples was reduced by thermal treatment and the papers tend to yellowing. The treated delivery note paper had more yellowing i.e. lower whiteness than other two document papers due to the presence of high value of the carboxyl groups which are considered as an important factor for yellowing, in addition to increasing the hydrogen bonding and formation of ether linkage between adjacent cellulose molecules. These two factors caused highly reduction in the degree of whiteness.

In spite of the decrease of carboxylic content of the bill paper and paper used for ID with treatment, the whiteness of the thermal treated samples was decreased and not increased due to increase in the hydrogen bonding and formation of chemical bonds between cellulosic fibers which lead to reduction in the degree of whiteness.

The treatment of the document papers with lower temperature has no effect on the degree of whiteness. The opacity of the treated delivery note paper was higher than the other two document papers due to presence of a higher amount of lignin and short-chain carbohydrates which increased the carboxyl content by different treatments used. For this reason the opacity of the delivery note paper increased with treatments. However, the contrary took place in the other two document papers due to decrease in carboxyl content by treatment. The treated paper used for ID possessed a higher opacity comparing with bill paper. Thus it contained kaolin as a coating material (Table 4) which characterized by improving the opacity, having chemical and thermal stability and therefore still remained on the fibers leading to higher opacity more than bill paper. The crystallinity of all thermal treated samples increased and higher increase was observed in case of delivery note paper probably due to the presence of more accessible non-cellulosic fractions which have the ability to moisture less by thermal treatment, consequently decreased the interfibrillar spaces and results in the formation of new crystalline regions and so the affinity of the samples towards water (WRV) decreased. High reduction in crystallinity was observed on exposing the thermal treated samples to UV radiation due to the oxidation, degradation of cellulose itself and formation of new accessible non-cellulosic fractions and decomposition of most sizing materials which raise the water retention values of the photo treated samples comparing with thermal treated samples. The degree of polymerization of all thermal treated samples increased due to formation of contracted chain of hydrogen bonding which resist the depolymerization of the chain length. While, the contrary took place on exposing the thermal or even cold treated samples to UV radiation, since it assists oxidation leading to the breaking of the chain links of the samples especially in the thermal treated samples and consequently depolymerization occurred.

THE COLOUR OF THE TREATED DOCUMENT PAPERS IN DAYLIGHT AND UNDER UV LAMP (336 NM)

Table (3)
Effect of thermal and cold treatments with and without exposure to ultraviolet radiation (336nm) on the colour of some document papers

Samples	Conditions	Colour in day light	Colour under UV
Bill paper	Without treatment	White	Purplish violet (non flu.)
	Thermal treatment	White	Blue (strong flu.)
	Thermal treatment + UV	Faint yellow	Dark violet (non flu.)
	Cold treatment	White	Violet (non flu.)
	Cold treatment + UV	Very faint yellow	Dark violet (non flu.)
Delivery note paper	Without treatment	Very faint yellow	Faint violet (non flu.)
	Thermal treatment	Yellow	Bluish violet (F.flu.)
	Thermal treatment + UV	Yellow	Bluish violet (F.flu.)
	Cold treatment	Very faint yellow	Faint violet (non flu.)
	Cold treatment + UV	Faint yellow	Violet (F.flu.)
Paper used for ID	Without treatment	White	Blue (strong flu.)
	Thermal treatment	Faint yellow	Bluish violet (M.flu.)
	Thermal treatment + UV	Faint yellow	Bluish violet (M.flu.)
	Cold treatment	White	Blue (strong flu.)
	Cold treatment + UV	Very faint yellow	Dark violet (F.flu.)

Flu. = Fluorescence, F = Faint, M = Medium

It is clear from (Table 3) that the colour of bill paper is white for observer's eye in daylight, while it gave purplish violet colour without fluorescence when examined under ultraviolet lamp (336 nm). This can be explained on the basis that the bill paper contained lignin and percent of carboxyl groups which possessed well-defined ultraviolet absorption with no excitation and no reflection, therefore gave purplish violet colour without fluorescence. However, the colour of the thermal treated bill paper did not clearly change when examined in daylight but it turned to blue colour with strong fluorescence when examined under ultraviolet lamp. This is probably because the thermal treatment led to degradation of lignin, decreasing the carboxyl content, giving compounds absorb UV light and emit visible radiation of longer wavelengths above 400 nm and appear as blue colour fluorescence. On examining thermal treated bill paper exposed to UV radiation in daylight it appears faint yellow in daylight, while reversed to dark violet with disappearance of the fluorescence when examined under UV lamp. This may be due to oxidative cleavage of acetyl linkage and decomposition of strarch which used as sizing material leading to absorption of UV light without excitation. The cold treatment had lower effect on oxidation of cellulosic fibers and can not capable to decompose lignin but decomposed starch when exposed to UV radiation and therefore showed dark violet colour without fluorescence under UV lamp.

Delivery note paper is characterized by the presence of higher content of lignin and carboxyl groups. The thermal treatment led to increase the carboxyl content and that is why its colour showed yellow in daylight, and the partial degradation of lignin gave the paper bluish violet colour with faint fluorescence when examined under UV lamp. However, the cold treatment had lower effect on the degradation of lignin and also on increasing the carboxyl content and for this reason it showed very faint yellow colour in daylight. The addition of photo treatment to cold treated paper led to appearance of violet colour with faint fluorescence due to decomposition of some sizing materials (starch) and lignin. Generally this type of paper did not give strong fluorescence under UV lamp at any condition of treatment used due to the increase in carboxyl content and the presence of higher content of lignin.

Table (4)
Additives of paper documents

Additives	Bill paper	Delivery note paper	Application paper for ID
Starch	++	+	+
Rosin	-	-	-
Wax	-	-	-
Talc		-	-
Kaolin	-	-	+
Calcium carbonate	++	+	+
Calcium sulphate	-	-	-

Table (5)
Elemental analysis of paper documents

Type of paper documents	N%	CI%	S%
Bill paper	Nil	Nil	3.75
Delivery note paper	Nil	Nil	0.53
Application paper for ID	Nil	Nil	2.60

The application paper form used for identity card (ID) is characterized by higher whiteness since, it contained kaolin as a coating material in addition to starch as sizing material (Table 4) which gave a white colour for observer's eye in daylight. However it showed blue colour with strong fluorescence under UV lamp. This may by attributed to the presence of sulphur residue (Table 5) which absorb UV light and emit visible radiation of longer wavelengths and appear as blue colour fluorescence. The thermal treated paper showed bluish violet colour with moderate fluorescence when examined under UV lamp. This may be due to the oxidation of sulphur residue and partial decomposition of sizing materials which decreased the fluorescence emition. The exposure of the thermal treated sample to UV radiation did not produce any significant change in colour either in daylight or under UV lamp. Lower temperature treatment of paper has no effect on oxidation of sulphur residue which remains as sulphite compound, and on decomposition of starch so it appears as blue colour with strong fluorescence. However, exposure of the cold treated paper to photo treatment changeds the colour to dark violet with faint fluorescence when examined under UV lamp due to the ability of UV radiation to decompose the starch while it is not capableof oxidizing the sulphur.

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تأثير المعالجات الحرارية والباردة والأشعة فوق البنفسجية على خواص وألوان أوراق الوثائق والمستندات

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تم دراسة تأثير التعجيل بالمعالجات الحرارية والباردة ، ثم تبعها التعريض للأشعة فوق البنفسجية عند طول موجى ٣٣٦ نانوميكرون على الخواص الكيميائية والفيزيائية ودرجة اللون لكل من أوراق الكمبيالات ، وأوراق مستندات الصرف ، وأوراق الاستمارات المستخدمة لاستخراج بطاقات تحقيق الشخصية . وقد اتضح من النتائج أن التغير فى خواص وألوان الأوراق قد اعتمد على نوع الألياف الورقية الطبيعية ، ومواد الصقل والحشو ، والعناصر المتبقية فى ألياف الأوراق أثناء صناعتها ، والظروف التى استخدمت فى عمليات المعالجة .