Preparation Of Safety Paper Using Fluorescent Thienopyrimidinone Hydrazone Compound and Other Additives

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ABSTRACT

Forensic safety paper from wood pulp blended with 5% polyester fiber, have been prepared embedding fluorescent thienopyrimidinone hydrazone compound (2-ethylacetoacetatehydrazon-3H-cyclohexano[4,5]thieno[2,3-d]pyrimidin-4(4H)-one), titanium dioxide and ferric chloride. The papers produced were characterized with UV light, special tests (for detection of $FeCl_3$), and scanning electron microscopy. The changes occurring in visual observation as well as optical and strength properties have been explained.

Introduction

Security paper must be made so that they are difficult to counterfeit yet easy to verify as authentic. Security paper serves the needs of two primary sectors namely high security and leisure industry. High security end consists of cheque papers, bonds, passports and other government documents. Leisure industry includes, coupons and tickets[1]. Security paper is chemically treated to prevent any forger attempts. Recent advances in the manufacturing of specialty papers and paper additives have extended the options for enhancing the document security[2]. Security paper may be made by using land quart specials in combing and a large number of the long proven and innovative security features. Security paper is provided with visible and invisible pigments and mottling fibers as well as with chemically effective additives and reagents[3]. The watermark is one of the highest security features available for paper. It is an integral part of the paper produced using a special mould. They are true watermarks and artificial watermarks. A true watermark is produced during paper manufacture and is visible from both sides of the paper. Artificial watermarks are applied after the paper manufactured by the paper manufacturer. The multi watermarks are achieved by varying the thickness of the paper[4].

The fiber are invisible under normal viewing condition but a document containing them can be checked for authenticity by viewing the document under ultraviolet light. The invisible fluorescent fibers would be very difficult to replicate[5,6].

Pearle scene is another feature which distinguishes the security paper from commercially available paper. This process involves the manufacture of artificial pearl lustre pigments containing mica particles coated with metal oxides such as titanium dioxide. Light is reflected and scattered by the layers of minute particles and by the super composition of the reflected rays, a changing band of colors is created[7]. The successful use of many security papers, and safety strip made from different materials in different colors and using different processes depend on technology of chemical fastening systems, especially pressure-sensitive adhesives. These adhesives are often required to have optical properties to allow the security materials to have a special appearance. The adhesives system may itself contribute as a carrier for various security materials[8].

In this work, some additives have been embedded during the manufacture of paper to obtain safety paper used for some important documents. The additives were polyester fiber, fluorescent thienopyrimidinone hydrazone compound, titanium dioxide and ferric chloride. The purpose of these additives is to identify and characterize the obtained security paper and at the same time to improve the optical and strength properties.

Results And Discussion

Hand sheets were prepared from wood linter only or blended with 5% polyester fibers with or without certain additives. Hand sheets were evaluated for mechanical and optical properties and the results are listed in **Table 1** . It is clear from **Table 1** that the addition of polyester fibers increases the strength properties of the paper due to more hydrogen bonding which improves fiber to-fiber bonding[9].

It can also be seen from **Table 1** that there is a remarkable decrease in tensile strength and breaking length after the addition of 2-ethylacetoacetatehydrazon-3H-cyclohexano[4,5]thieno[2,3-*d*]pyrimidin-4(4H)-one(retention in fiber 82 %), titanium oxide(retention in fiber 25 %) and ferric chloride. This can be explained by the formation of a weaker filler-fiber bond instead of fiber-fiber bonds[10]. These additives

TABLE--1
STRENGTH and OPTICAL PROPERTIES of DIFFERENT PAPER SHEETS.

Paper sheets prepared from	Strength properties				Optical properties	
	Tensile strength, kg	Breaking length, m	Burst strength, kg/Cm^2	Tear resistance, gm	Brightness % (Tappi)	Opacity %(Tappi)
Wood pulp (a)	3.7	3118.2	2.13	214	72.6	90
Wood pulp containing 5% polyester fiber (b)	4.28	3546.9	2.30	220	76.4	90
Wood pulp containing 5% polyester fiber and 2% fluorescent thienopyrimidinone hydrazone compound (c)	3.68	3016.4	2.20	212	73.0	87
Wood pulp containing 5% polyester fiber , 2% fluorescent thienopyrimidinone hydrazone compound and 10% titanium dioxide (d)	3.70	3226.1	2.20	274	75.7	90
Wood pulp containing 5% polyester fiber , 2% fluorescent thienopyrimidinone hydrazone compound ,10% titanium dioxide and 0.2% ferric chloride (e)	3.42	2910.0	2.10	226	71.0	87

affect the bursting strength and tearing resistance of the prepared paper to some extent . On the other hand, the tearing resistance increased after the addition of titanium dioxide due to the fact that titanium dioxide filling the spaces between the fibers of the paper and the paper became more homogenous. Results in **Table 1** show that the brightness and the opacity decreased after the addition of 2-ethylacetoacetatehydrazon-3H-cyclohexano[4,5]thieno[2,3-*d*]pyrimidin-4(4H)-one (brightness decreases from 76.4 to 73). Also, addition of ferric chloride decreased both brightness and opacity (brightness decreases from 75.6 to 71.2 and the opacity decreases from 90.4 to 86). This occurred as 2-ethylacetoacetatehydrazon-3H-cyclohexano [4,5]thieno[2,3-*d*]pyrimidin-4(4H)-one and ferric chloride are colored and this led to decrease in the brightness of the paper. Decrease in the opacity may be attributed to interaction or reaction between 2-ethylacetoacetatehydrazon-3H-cyclohexano[4,5]thieno[2,3-*d*]pyrimidin-4(4H)-one, titanium dioxide and ferric chloride.

Titanium dioxide increased both brightness (from 73 to 75.6) since it has high refractive index ,whiteness and opacity (increased from 87 to 90) since it fills the spaces between fibers and this make the paper more opaque[11].

Examination of samples under UV lampe

The light fastness of brightened paper is an important quality consideration. The simple measurements of the light fastness of brightened paper is the direct measurement of the fluorescence[12].

In this method, the paper is illuminated with pure near-ultraviolet light, fluorescent agents in the paper are activated and the reflected blue white light is detected. The florescent pigments have the unusual property of absorbing light at particular frequency and emitting this absorbed energy at lower or higher wavelength[8]. The sample which contains fluorescent thienopyrimidinone hydrazone compound gives yellowish green fluorescence spots inside the paper. The paper sample which contains titanium dioxide and fluorescent thienopyrimidinone hydrazone compound seems dark under the UV lamp, since the titanium dioxide absorbs the ultraviolet rays with yellowish green fluorescence spots. The sample of the paper which contains titanium dioxide, fluorescent thienopyrimidinone hydrazone compound and ferric chloride gives yellowish brown fluorescence spots inside the paper under the UV lamp, due to the interaction between these additives as shown in **Table 2.**

Addition of ferric chloride

Although the addition of ferric chloride solution decreases the strength and optical properties of the paper to a certain extent, it is necessary and interesting

TABLE --2
EXAMINATION OF PAPER SHEETS in ULTRAVIOLET LIGHT

Sample	Color of zone in:	
	Daylight	Ultraviolet light 336nm
a	White	Blue
b	White	Blue
c	White	Yellowish green fluorescent spots inside the paper
d	White	The paper more dark with yellowish green fluorescent spots inside the paper
e	White	Yellowish brown fluorescent spots inside the paper

for the manufacture of the security paper. Ferric chloride can be used as a component of the paper and can be detected by a special test.

To recognize the presence of ferric chloride in the paper, ammonium thiocyanate with a concentration of 10 % was used. The addition of one drop of this solution to the paper, a blood color was clearly observed on drying the paper[7].

Scanning electron microscopy:

Figs. **1a-e** show the morphology of the paper before and after additives. Fig. 2a shows the wood pulp alone and in **Fig**. **1b** the fibers appear wider and thicker than that in **Fig. 1a**. due to the blended wood pulp with polyester fibers. In **Fig. 1c**, it is clear that there are many big black spots inside the paper sheet due to addition of organic fluorescencent heterocyclic compound (2-ethylacetoacetate- hydrazon-3H-cyclohexano [4,5]thieno--3H-cyclohexano [4,5]thieno [2,3-*d*] pyrimidin -4(4H)-one).

In **Fig. 1d**, all the spaces between the fibers are filled due to addition of titanium dioxide, and the picture becoming more opaque.

After the addition of ferric chloride, the fibers are more clear in **Fig.1e** than in **Fig. 1d**.
This may be attributed to the interaction between titanium dioxide, fluorescent thienopyrimidinone hydrazone compound and ferric chloride.

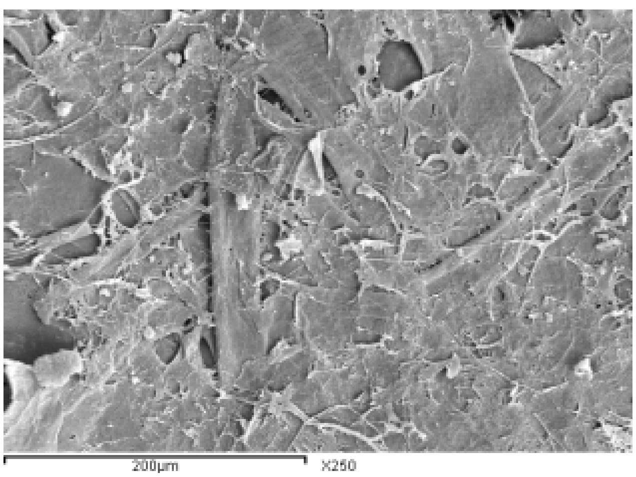

Fig.1a: SEM of sample a.

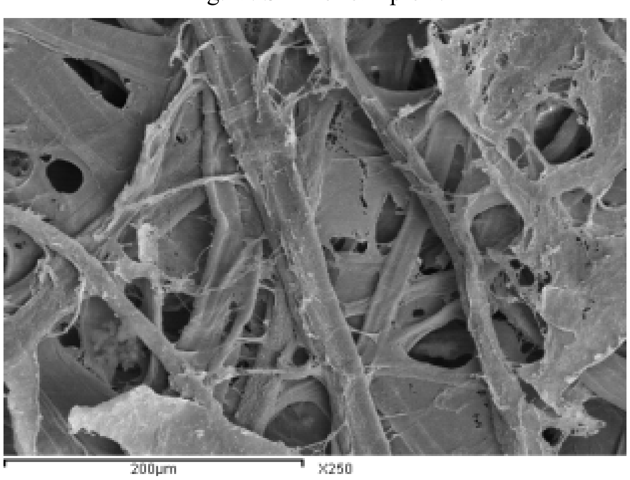

Fig.1b: SEM of sample b.

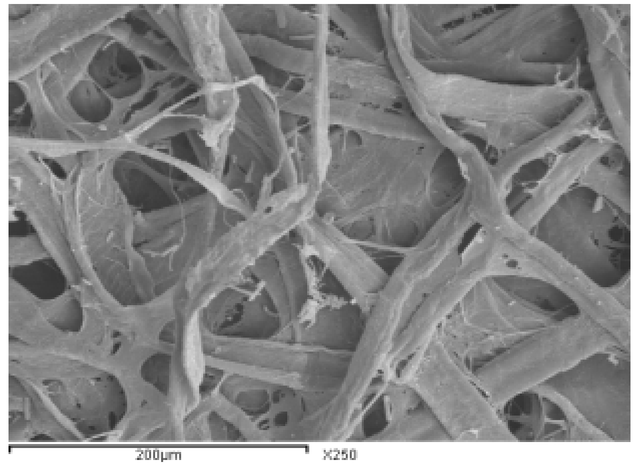

Fig.1c: SEM of sample c

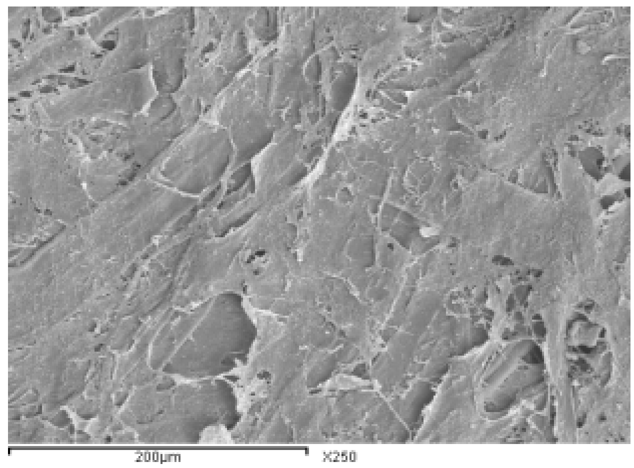

Fig.1d: SEM of sample d.

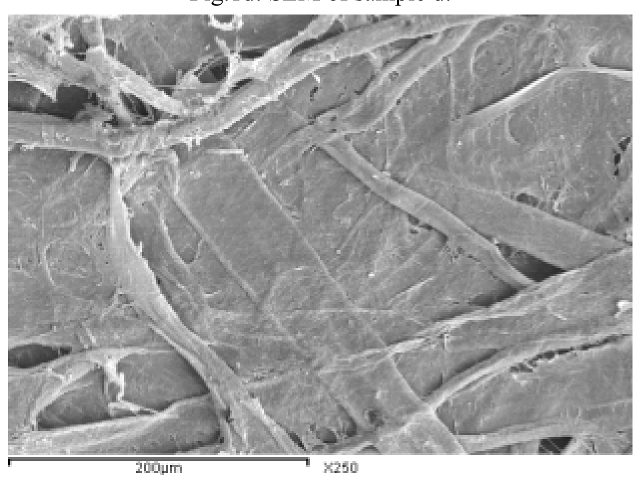

Fig.1e: SEM of sample e .

Conclusions

Use of polyester fiber, fluorescent thienopyrimidinone hydrazone compound, titanium dioxide and ferric chloride solution in certain amount can produce paper that have a proper strength and optical properties and are difficult to counterfeit yet easy to verify as authentic. These papers were identified with UV light, special tests laboratories (for detection of $FeCl_3$) , and scanning electron microscopy .

Experimental

Materials

Bleached wood pulp (84.1 α-cellulose, 7.8 hemi-cellulose and 0.7 lignin) was used as a raw material while 5% polyester fiber (straight, density 210, width 58/60, weight 200 gm)and its source had been provided from Kafre El-Dawar Company(Egypt), 2% (2-ethylacetoacetatehydrazon-3H-cyclohexano[4,5]thieno[2,3-d]pyrimidin-4(4H)-one) compound (had been prepared in the laboratory)[13], 10% titanium dioxide (volatile matter 0.2 % ,water-soluble matters 0.2 %, pH(aqueous slurry) 6.5-8.0, whiteness 96.6 %)and its source had been provided from El-Gomhoria Company in Egypt, and 0.2% ferric chloride (based on weight of dry pulp) were used as additives.

Paper Manufacture

The pulp was soaked in water for 24 hrs. then put in the valley Beater at 2% consistency, with 5% polyester fiber beaten up to 45 °SR (Schopper Riegler). The water was drained from the stock and preserved in refrigerator for further experiments.

Certain weight of the stock was taken containing 8g oven-dry pulp to make 5-sheets. To this mixture, different additives were used under thorough stirring to achieve good homogenization. Sheets for the control samples were prepared from the pulp according to the SCAN-C 26:27 and SCAN-C 5:76 test methods.

The sheets of the paper from each sample were conditioned at 20°C and 50 percent relative humidity for 24 hrs. The conditioned papers were subjected to optical and mechanical properties.

Paper properties

The optical properties (brightness and opacity) and mechanical properties of the paper (tensile strength, breaking length, tearing resistance and bursting strength) have been measured as suggested by Casey[14].

The fluorescent color of the samples was detected by using ultraviolet lamp with wave length 366nm (EMITA VP-60).

Scanning electron microscopy (SEM) of specimens were conducted on JEDL JEM-100 S electron microscope using the gold-sputtering technique for sample preparation to make it conducting .

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