

Preparation of specialized paper

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ABSTRACT: Paper for special applications was produced using transition metals, cellulose derivatives, and fillers in the presence of fluorescent dye. Sheets were prepared from bleached wood pulp after fluorescein sodium was added along with solutions of transition metals as well as methyl cellulose, cellulose sulfate, starch, and kaolin. The papers produced were identified with UV light and/or alkaline and acidic solutions. The appearance of the papers was changed under the UV light when the fluorescein sodium was used at pH 4.0. The solution of the transition metal of Ni^{2+} led to slightly yellow fluorescent spots as a result of the ground-state configuration of the transition metal. Moreover, a fluorescent yellow-green color was observed when methyl cellulose, cellulose sulfate, kaolin, and starch were added as fillers in the presence of sodium fluorescent dye. The color appears because the fiber network is disrupted by the inclusion of the filler particles with the fluorescent dye.

Application: Made with transition metals or cellulose derivatives as additives along with fluorescent dye, security papers show identifiable fluorescent spots under ultraviolet light.

Specialty papers have long served to prevent or discourage counterfeiting and the forgery of banknotes and other security documents. Security printing is often considered a specialized field in the graphic arts. When viewed in visible light, ultraviolet fluorescent inks are invisible or inconspicuous to the human eye, but they fluoresce in bright colors when exposed to UV radiation [1].

Recent advances in the manufacturing of specialty papers and paper additives have extended the options for enhancing document security [2]. Safety or security papers are specially treated to make it difficult for anyone to alter the writing or printing visible on them [3]. Security papers must be made so that they are difficult to counterfeit yet are easy to verify as authentic.

The successful use of many security papers, foils, and films depends on the technology of chemical fastening systems, especially pressure-sensitive adhesives [4]. In addition to their physical properties, these adhesives are often required to have optical properties to allow the security materials to have a special appearance. The adhesive system may itself contribute as a carrier for various security materials [4]. On the other hand, the performance of a brightener can be imparted by the presence of transition metal ions, by competition from other ultraviolet absorbers, and by strong oxidants [5].

In this work, some additives were embedded in the pulp to produce safety papers of the kind used for particularly important documents. The additives were

cuprous chloride, nickel chloride, kaolin, starch, cellulose sulfate, methyl cellulose, and fluorescein sodium dye. The purpose of these additives in safety papers is to identify and characterize the documents in question.

EXPERIMENTAL

Materials

Cuprous chloride (CuCl), nickel (II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), fluorescein sodium, and starch were purchased. Kaolin and wood pulp were obtained from Rakta Co., Alexandria, Egypt. Methyl cellulose and cellulose sulfate were synthesized in our laboratory [6].

Sample preparation

White sheets of paper made from bleached wood pulp were prepared after treatment with sodium fluorescent dye, with and without the addition of transition metals and/or additives. Bleached wood pulp (82.7% α -cellulose, 0.7% lignin) was beaten to reach 40°SR (Schopper-Riegler). Sheets for the control samples were prepared from the pulp according to the SCAN-C 26:27 and SCAN-C 5:76 test methods.

For the fluorescent dyeing samples, we suspended 1.6 g of bleached, oven-dry wood pulp in 200 mL of water and added 3% fluorescein sodium. The suspension was allowed to heat in a water bath at 65°C with constant shaking for 2 h. This mixture was allowed to cool before the sheets were formed.

For experiments on the effects of pH, the dyeing was carried out in exactly the same manner as described except that the pH was adjusted to 4.0 after the fluo-

rescent dye was added. For the experiments on the effects of transition elements, dyeing was carried out in the manner described except that we added 2% fluorescein sodium without adjusting the pH and the transition elements (Cu^+ and Ni^{2+}) were added at 1% (on dry pulp weight).

For experiments on the effects of cellulose derivatives, starch, and kaolin, we added methyl cellulose, cellulose sulfate, starch, and kaolin at 10% based on dry pulp weight before beating. Dyeing was carried out as described except that we added the fluorescein sodium at 2% (on dry weight of the additives) without adjusting the pH.

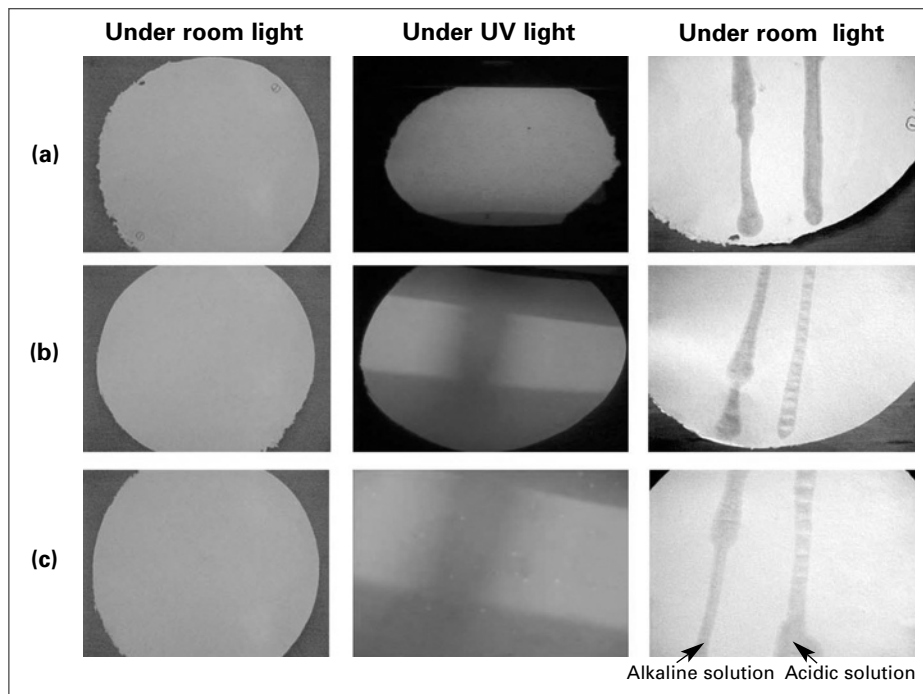
Measurement of fluorescence

We detected the fluorescent color by using a UV light source (EMITA VP-60), as well as by using alkaline and acidic solutions.

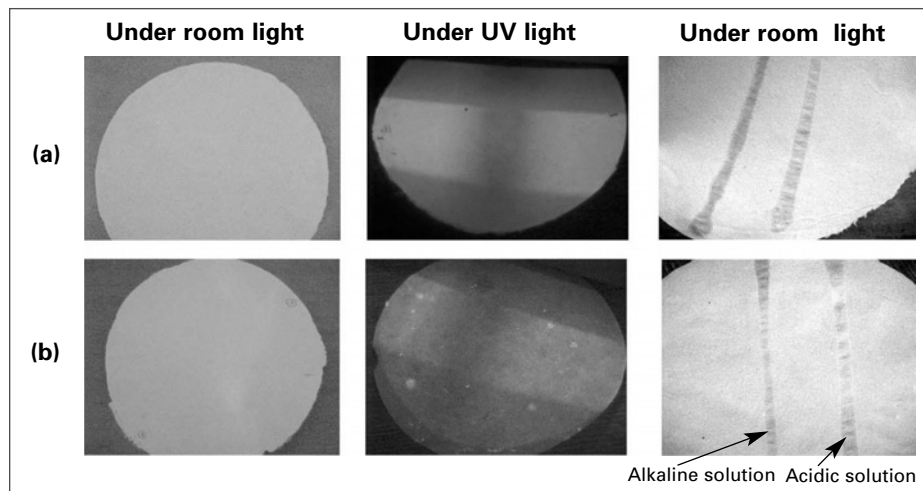
RESULTS AND DISCUSSION

The lightfastness of brightened paper is an important quality consideration. It is normally assessed by exposing the paper to artificial daylight according to ISO Method 105 BO2 [5]. This method was designed for colored papers and is not easy to carry out reproducibly on brightened papers. Another simple measurement is the direct measurement of fluorescence [5]. 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.

Fluorescent pigments have the unusual property of absorbing light at particular



1. Effect of adding sodium fluorescent dye: (a) control sample, (b) control sample with fluorescent dye, and (c) fluorescent dye at pH 4.0.



2. Effect of adding transition metals: (a) CuCl and (b) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.

frequencies and emitting this absorbed energy at lower frequencies (or longer wavelengths) [7]. Many natural products will fluoresce in response to ultraviolet radiation. Special luminescent materials, which can fluoresce in response to excitation by ultraviolet light, have also been developed [7].

pH

Sodium fluorescent dye was added alone or in the presence of transition metal ions or cellulose derivatives or in the presence of starch and kaolin. The appearance of the papers changed under UV light (Figs. 1–3). When sodium fluo-

rescent dye was used alone without the pH being adjusted (Fig. 1b), no fluorescent color appeared under UV light. However, with the pH adjusted to 4.0, a slight fluorescent color appeared (Fig. 1c).

The effect of pH on the fluorescence of a given organic system is often difficult to predict [7]. A change in fluorescent properties that accompanies a change in pH can be indicated either by a change in the wavelength of fluorescence or a change in whether or not fluorescence exists at all. The fluorescence of many less-complicated systems can

also be correlated directly with pH. In all cases, these changes depend on the protonation or dissociation of some group [7]. However, there are no changes in the color when alkaline or acidic solutions are used.

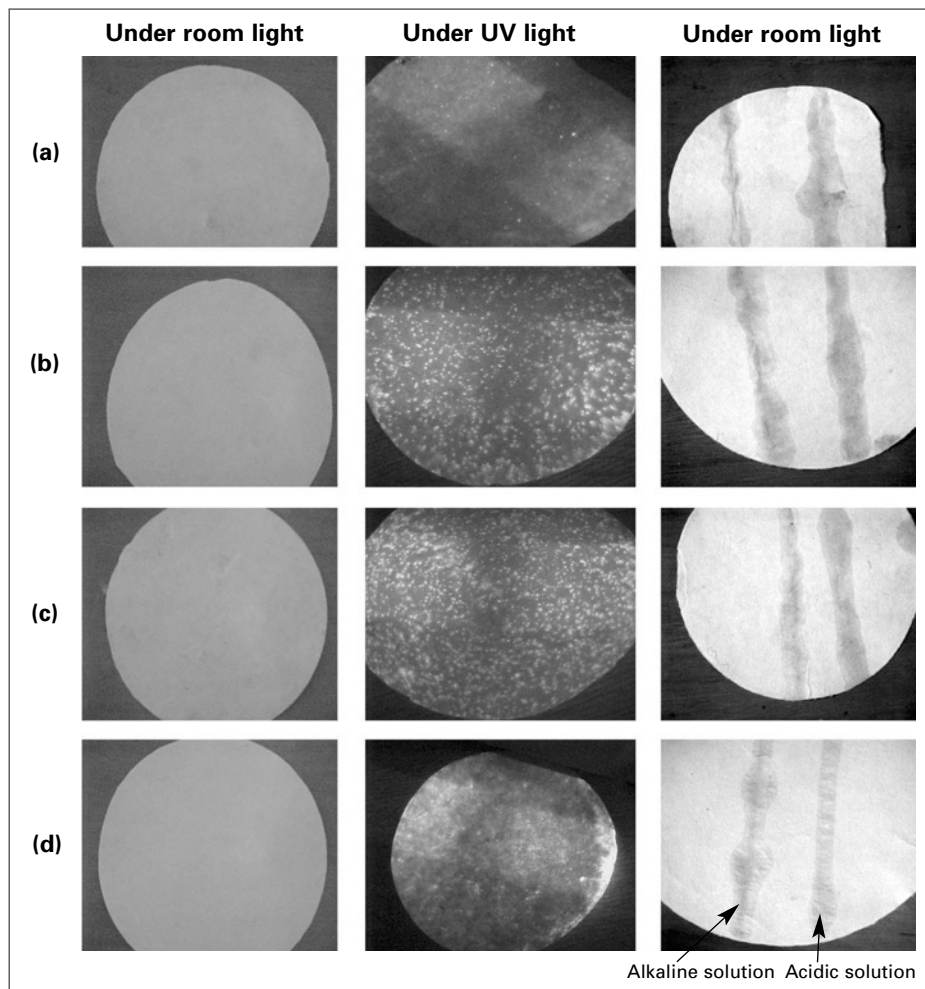
Transition metal ions

Figures 2b and 1b show the difference between the presence and absence of transition metal ions with fluorescent sodium dye. With transition metal ions, a yellow-green color developed when an alkaline solution was used. Under ultraviolet lighting, yellow fluorescence spots were seen except in the sample containing Cu^+ . The use of metals provides specific coloring or dyeing properties as the metal becomes chemically bonded to the dye as a part of the paper manufacturing process [8].

The molecules in the solution of nickel chloride are converted into complex cations via four $-\text{ONa}$ groups from two fluorescein sodium molecules. The complexing agents in these compounds is nickel ion, which replaces sodium in two $-\text{ONa}$ groups. The ligands are the oxygen atoms of these two $-\text{ONa}$ groups, with two other oxygen atom bonded to another group that does not lose sodium atoms. The structure of the complex formed between the nickel ion and the fluorescein sodium is shown in Figure 4.

Almost every molecule exists in its lowest energy state, which is usually called the “ground” state. The absorption of a quantum of electromagnetic radiation in the ultraviolet and visible regions occurs in a very short period of time (approx. 10^{-15} s) and results in the promotion of an electron to an orbital of higher energy. As a result, the state of the molecule is also changed [7].

Transition-metal compounds in which the bonding is predominantly covalent are sometimes quite like main-group compounds with similar stoichiometry, but they can show striking differences [9]. The molecule absorbs this energy, uses it to rearrange its bonding electrons, and changes from its ground state to an excited state [9]. In the case of fluorescent agents, the energy difference is much larger, so it takes much longer for the molecule to lose its energy after it absorbs UV light. The first-order rate constants for fluorescence are between 10^6 s^{-1} and 10^9 s^{-1} [8].



3. Effect of adding fillers and cellulose derivatives: (a) kaolin, (b) starch, (c) cellulose sulfate, and (d) methyl cellulose.

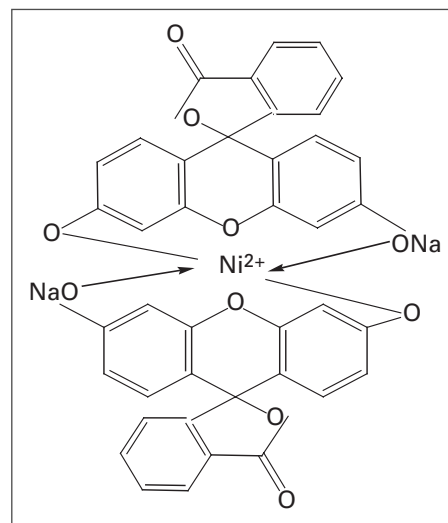
The left side of Fig. 5 shows the ground state configuration of Cu^+ (10d). According to the Crystal-Field Theory, the crystal field stabilization energy (CFSE) is equal to zero, and no spectrum appears under UV light. On the right side of Fig. 5, the ground state configuration of Ni^{2+} (8d) for nickel chloride hexahydrate in a weak crystal field has the structure of $\text{trans}[\text{NiCl}_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ [10]. We get $\text{CFSE} = 12$ by adding up the individual electron energies for the high-spin case, and the fluorescence spots appear under UV light according to spin allowance (i.e., $\Delta S = 0$).

Fillers

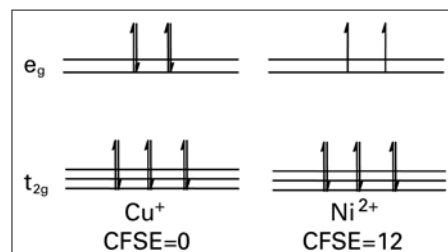
Interesting results were observed when methyl cellulose, cellulose sulfate, kaolin, and starch were added as fillers in the presence of sodium fluorescent dye (Figs. 3 and 1b). The paper turned yellow when drops of alkali were added. Under UV light, a fluorescent yellow-green color was detected (Fig. 3).

Fillers have always been important raw materials in papermaking, and they are now used for various purposes in many paper and paperboard products [11]. Starch is the most used additive that is derived from renewable raw material [12]. Soluble cellulose derivatives are also used in specialized applications [13]. The yellow fluorescent color appears as a result of the adsorption of the starch and kaolin with the fluorescent furnish components.

The filler particles are rarely attached to the actual fiber surface in the wet state. Instead, they are attached to fine fragments and fibrils that are part of the fibers or are attached to the fibers by electrostatic forces [11]. The color appears because the fiber network is disrupted as a result of the inclusion of the filler particles with fluorescent dye. Dispersion into monomolecular layers on fiber is important in ensuring effectiveness; hence, to function well, the flu-



4. The complex formed between the nickel ion and the fluorescein sodium.



5. Ground state configuration of transition metal ions.

orescent agent should form a monomolecular layer [5].

The presence of the kaolin reduces the yellow fluorescence spots, as Fig. 3a shows. Certain kaolin fillers may reduce brightness since they may counteract the fluorescence by being slightly yellow and dull [8].

Cellulose derivatives

Cellulose sulfate and methyl cellulose act as carriers, and they further enhance the performance of the fluorescent agents. The appearance of the fluorescent color under the UV light is caused by the negative charge on the sulfate group for the cellulose sulfate or, for methyl cellulose, by the lone pair of electrons on the methoxyl group. The fluorescent color appears because the UV light excites the electrons.

For fluorescent agents, the measure of the efficiency of fluorescence is the quantum yield, ϕ_f , which is as important as the UV light absorption. The quantum yield is a measure of the number of fluorescent agent molecules which, once excited, lose their energy to the ground state by fluorescence and not by other

means [8]. The presence of electron-withdrawing groups, such as $-\text{SO}_3\text{H}$ in cellulose sulfate, may decrease the fluorescence (smaller ϕ_f), whereas electron-donating groups, such as $-\text{OCH}_3$ in methyl cellulose, may increase it [8]. This mechanism accounts for the fact that the fluorescence spots appear larger in the case of methyl cellulose than in the case of cellulose sulfate (Figs. 3d and 3c).

CONCLUSIONS

By using transition metals, fillers, and cellulose derivatives with fluorescent dye, papermakers can produce papers that have special characteristics that are difficult to reproduce but easy to identify. The use of such specialty papers in paper money and security documents serves to prevent or discourage counterfeiting and the forgery of banknotes.

In our experiments, we produced specialty papers by using fluorescent dye along with either transition metals, cellulose derivatives, or fillers. These papers were identified with UV light and/or alkaline and acidic solutions. Consequently, papermakers can produce identifiable papers with special characteristics by using fluorescent dyes and transition metals or cellulose derivatives as additives. **TJ**

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INSIGHTS FROM THE AUTHORS

Specialty papers have long served to prevent or discourage counterfeiting and the forgery of banknotes and other security documents. In this research on the preparation of specialized paper, we carried out trials to identify and characterize the effects of additives in specialty paper, concentrating primarily on the effects of transition metals and cellulose derivatives.

One difficult aspect of the work was the percent addition of the transition metals. We solved this difficulty by using transition metals in small percentages. The use of transition metals with fluorescent dye causes fluorescent spots to appear under UV light. The transition metal ion absorbs the energy and changes from its ground state to an excited state. The paper's fluorescence under UV light depends on this change in the ground state.

When either methyl cellulose or cellulose sulfate is used, the fluorescent spots appear in the whole paper. The performance of the cellulose derivatives depends on the nature of the substituted groups—electron-

donating groups in methyl cellulose and electron-withdrawing groups in cellulose sulfate.

Mills can benefit from this information by using compounds with different configurations to act as carriers for the fluorescent dyes, leading to the appearance of the fluorescent color under UV light. Our next step will be to produce safety papers with a fluorescent compound obtained from the same raw material—the pulp.

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