

TIN OXIDE DOPPED CaCO₃ COATING ON PAPER FOR FLAME RETARDANCY AND PRINTABILITY PROPERTIES

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Valuable papers, such as checks, promissory notes, money or printing papers used in wallpaper laminates, must be resistant to burning. For this reason, different flame retardants are used in papers. However, generally, the flame retardants used negatively affect printability by creating a hydrophobic surface. For this reason, it is thought that the combination of flame retardants with a filler that will positively affect the printability of paper will be more suitable for such printable papers. For this purpose, this work aimed to obtain paper with good printability and delayed ignition properties by using calcium carbonate, which is a good paper filler, and tin oxide, which is a flame retardant.

In this study, starch-based paper coating formulations containing calcium carbonate and tin oxide individually and in combination in equal amounts were prepared and applied on office paper. Color, gloss, contact angle and flame retardancy properties of the produced papers were determined using a spectrophotometer, a glossmeter, a goniometer and LOI, respectively. Prints were made on the the obtained papers with the IGT C1 offset test printing machine, and the color and gloss properties of the prints were determined. As a result, it was determined that the flame retardancy properties of the papers were significantly increased with the tin oxide filler, while the combination of calcium carbonate and tin oxide improved both the printability and flame retardancy properties.

Keywords: flame retardant, paper coating, printability, tin oxide, calcium carbonate

INTRODUCTION

Paper is one of the two main inputs of the printing industry. The properties of the papers used are among the main parameters that affect their printability.¹ The printability parameters include color, gloss, absorbency, surface contact angle, surface porosity *etc.*² These properties can be imparted to paper during or after production.³ In order to gain these properties during production, resin, fillers and colorants can be added to the pulp as additives. After production, features such as surface properties and printability can be improved by surface coating processes, fillers added to the coating formulation, polymeric materials used in the formulation, to provide the desired properties in terms of printability. The whiteness, gloss and absorbency of paper are the most important parameters in terms of printability.⁴

Calcium carbonate is one of the most common fillers that can be added during the paper-making process or to coating formulations to be applied on paper surface.⁵ Thanks to its white color, it

provides contrast between the paper and the ink, thus increasing readability. Meanwhile, it also adjusts the surface energy of the paper, thus allowing the interaction with the ink to be established in the best way, and ensures sufficient absorbency. Calcium carbonate displays a narrow particle size distribution, which contributes to the structuring of the coated layer. The narrow particle size distribution gives the coated layer a less densely packed open structure, with high pore volume. The greater porosity of the pigment coating structures leads to faster dewatering and subsequently quicker immobilization of the coating on application. In principle, this leads to better coating coverage compared to the standard.⁶⁻¹⁰ Calcium carbonate is manufactured from large natural ore deposits. It is a common substance found in rocks, such as the minerals calcite and aragonite; its chemical formula is CaCO₃. Calcium carbonate is used in a variety of applications, for example, in the construction industry, medicine, paint and ink production,

paper production and as a reinforcing agent in the plastics industry.

In the printing industry, added value can be imparted to paper products by adding some extra features to them. For this purpose, next-generation products are developed in many areas. One of the special features that can be of high interest in papers is the low flammability feature. Fire retardancy or non-flammability can be of great importance in papers used for printing products such as money, checks, promissory notes or rare books. Moreover, it would be extremely important for human safety if papers used in laminates or wallpapers applied in domestic or public buildings did not ignite in possible fires or emit toxic gases. Most flame retardants used to impart hydrophobicity to paper affect its printability. Therefore, attention should be paid to the selection of a suitable flame retardant to be used in the production of printed papers.

Flame retardants are used to prevent the danger of burning. There are two conditions that are important for the use of a flame retardant. These are: to obtain the highest flame retardancy efficiency at the lowest cost and to have low toxicity/non-toxic properties. Inorganic tin compounds have received increasing attention in recent years as a means to meet the requirements of good flame retardance, smoke suppression, non-toxicity, and environmental friendliness. Tin compounds, such as zinc hydroxystannate (ZHS), zinc stannate (ZS) and tin oxide (SnO_2), have been demonstrated to have good flame-retardant and smoke-suppressant properties when added to various materials.¹¹⁻¹⁵ Tin oxides are effective even at low incorporation levels, and thus, their addition would have a small effect on the physical properties of the polymer. Tin oxides are white, of low toxicity, they do not discolour polymers and are safe to use as they produce less undesirable by-products than other additives. To impart the flame retardancy feature to paper, it can be added to the formulation during paper production, or applied to the paper surface as a coating.

However, considering that it is easy, cheap and sustainable to achieve this feature by coating the paper surface, it would be a more advantageous approach, since it would allow both a more homogeneous distribution of the flame retardant and more effective results due to the presence of the flame retardant on the paper surface, which comes in direct contact with the flame.

With these considerations, this study aimed to obtain paper with good printability and delayed ignition properties by using calcium carbonate as a paper filler and tin oxide as a flame retardant.

EXPERIMENTAL

Materials

Calcium carbonate, tin oxide and starch were purchased from Sigma-Aldrich, Turkey. All solvents were obtained from Merck, Turkey.

Methods

Flame retardant coating formulations were prepared according to Table 1, using calcium carbonate and tin oxide individually and in combination, water and starch.

In the preparation of the coatings, the binding part of the formulation was prepared first. For this, 10% (w/v) starch was added into distilled water heated to approximately 90 °C and mixed. At this temperature, the mixture was stirred at approximately 750 rpm for 10 minutes to allow the starch to swell. The produced mixture was then cooled to 50 °C and the filler material was added in the amounts given in Table 1. The coating formulations were applied immediately after preparation.

Before the coating process, the papers were conditioned for 48 hours under laboratory conditions. The obtained flame retardant paper coating formulations were applied using a laboratory type K303 Multi-Coater (RK Print Coat Instruments Ltd., United Kingdom), with Mayer Rod 2, at room temperature, with amounts of 0.1 g/m² to one side of 80 g/m² paper, at a speed of 2 m/min. The average thickness of the coatings was set to 3 µm. After the coating process, the papers were dried in the air for a day. The obtained coated papers were characterized in terms of color, gloss, wettability and flame retardancy properties.

Table 1
Paper coating formulations

Formulation	Calcium carbonate (%)	Tin oxide (%)	Starch (%)	Water (%)
F0	0	0	10	90
F1	5	0	10	90
F2	0	5	10	90
F3	5	5	10	90

Then, the uncoated and the coated papers with all the prepared coating formulations were printed with an IGT C1 test printing machine, using equal amounts of process magenta ink (DIN ISO 2846-1), at 300 N printing pressure and 0.2 m/s printing speed. The ink film thickness of all the printed samples was measured as 8 μm . Color measurements of the prints on differently coated and uncoated papers were made by the CIE L*a*b* method, using an X-Rite eXact spectrophotometer according to ISO 12647-2: 2013 standard.

Characterization methods

The flammability characteristics of uncoated and coated papers were determined by LOI measurements according to UL-94 VTM standard. The LOI values of the coated papers were measured using an FTT (Fire Testing Technology) type instrument.

The wettability of the coated paper was determined, measuring the contact angle by the sessile water droplet method (TAPPI T 458). Distilled water was used as standard wetting fluid in a Pocket Goniometer Model PG-X (FIBRO Systems AB, Sweden), program version 3.4. Images of water droplets were recorded using a CCD video camera. Surface free energies were calculated according ASTM D5946 standard test method, based on the contact angle.

The color measurements of the printed papers, with different coatings, were made by the CIE L*, a*, b* method, using an X-Rite eXact™ spectrophotometer according to ISO 12647-2: 2013 standard (measuring conditions: polarization filter, 0°/45° geometry, 2°

observer angle, D50 light source) in the range of 400-700 nm. Color differences among the samples were calculated according to the CIE ΔE^* 2000 ISO 13655 standard, by the relation:

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L^*}{k_L S_L}\right)^2 + \left(\frac{\Delta C^*}{k_C S_C}\right)^2 + \left(\frac{\Delta H^*}{k_H S_H}\right)^2} + R_T \frac{\Delta C^* \Delta H^*}{k_C S_C k_H S_H} \quad (1)$$

Gloss measurements of the coated papers and base paper were carried out with micro-gloss 75° geometry in accordance with ISO 8254-1: 2009, using a BYK-Gardner GmbH glossmeter, and the gloss measurements of the prints were carried out with a BYK-Gardner GmbH Micro-Tri-Gloss with 60° geometry in accordance with ISO 2813: 2014.

RESULTS AND DISCUSSION

In this study, different formulations of coatings were prepared and applied onto the paper surface to achieve both good printability and flame retardancy of the paper products. The coatings were prepared according to the ratios listed in Table 1, where calcium carbonate was added to improve the printability properties, while tin oxide was added to impart a flame retardant feature to the paper. The formulations were prepared successfully. The color and gloss values of the obtained papers coated with different formulations of coatings, as well as those of the blank (base paper), were measured and the results are shown in Table 2.

Table 2
Color and gloss values of coated and uncoated paper samples

Formulation	L*	a*	b*	ΔE_{00}	Gloss
Base paper	95.25	2.75	-10.25	Standard	5.6
F0	96.28	2.59	-9.83	0.69	28.2
F1	96.14	2.62	-11.49	1.02	25.9
F2	95.98	2.52	-9.13	0.92	25.4
F3	95.37	2.47	-10.10	0.36	24.1

Examining the data in Table 2, it can be observed that the color shifted towards yellow on the positive b axis when the coating containing only starch was applied on the surface of base paper (F0). This yellowing can be explained by the chromophore groups in starch, which caused this color shift. With the addition of calcium carbonate to the starch-based coating formulation (F1), the color shifted slightly to blue. The crystalline lamellar structure of the inorganic calcium carbonate refracted the incident light, which caused the color to shift to blue. With the addition of tin oxide to the starch-based coating formulation (F2), the color shifted towards the

light yellow color of tin oxide. In the case of the coating comprising the combination of both fillers (F3), the color achieved on the paper is closest to the color of the base paper. Because the negative shift (blue shift) on the b axis caused by calcium carbonate compensated for the positive shift (yellow shift) on the b axis caused by starch and tin oxide, the color difference was the lowest. For all the coatings developed, the color difference among the paper samples is so low that it cannot be perceived with the naked eye. The results obtained are consistent with previous studies.¹⁶

As regards the gloss values of the papers, it can be remarked that when the initial coating

formulation (F0) is applied to the paper surface, the surface becomes smoother and the gloss significantly increases, compared to the base paper. This is explained by the fact that the coating fills the gaps between the fibers on the paper surface, leading to less diffuse reflection. The addition of each individual filler (calcium carbonate (F1) and tin oxide (F2)) to the coating caused a slight roughness on the paper surface, leading to a decrease in gloss. When both fillers were added together to the formulation (F3), the roughness on the paper surface increased even more, subsequently leading to a further decrease in the gloss value. Nevertheless, the gloss values of all the paper samples (for all the coating formulations) remain about 5 times higher than that of the base paper. The results obtained are in line with those reported earlier.¹⁷

For printing grade paper, it is important that the surface energy of the ink be compatible with that of the surface to be printed. In this sense, the surface energy and contact angles of the produced papers were measured and the results are given in Table 3.

Examining the data in Table 3, it can be seen that when the surface energy decreases, the contact angle increases. In order to print on a

surface and ensure low ink consumption, the contact angle of the surface must be low. In F0 and F1 coated paper samples, the contact angle decreased, compared to the base paper, due to the H bonds formed by the H groups in the starch applied to the surface and the inorganic nature of calcium carbonate. This led to enhanced printability results. This trend has been documented in the literature.¹⁸ However, it was determined that the addition of tin oxide to the coating formulation (F2) caused a significant rise in contact angle and thus decreasing printability. On the other hand, in the coating where both calcium carbonate and tin oxide are used together, the increase in contact angle is less significant and the printability characteristic achieved is better, compared to the coating containing tin oxide only. Thus, a printable paper surface with a flame-retardant feature can be obtained.

LOI testing is widely used to determine the flame retardancy of materials. Therefore, in this work, the flame retardancy properties of the papers coated with different formulations were determined by LOI tests. The obtained LOI values of the uncoated and differently coated papers are shown in Figure 1.

Table 3
Contact angle and surface energies of coated and uncoated paper samples

Formulation	Surface energy (mJ/m ²)	Contact angle (°)
Base paper	34.7	83.9
F0	46.2	52.1
F1	45.6	53.9
F2	39.0	71.9
F3	41.1	66.2

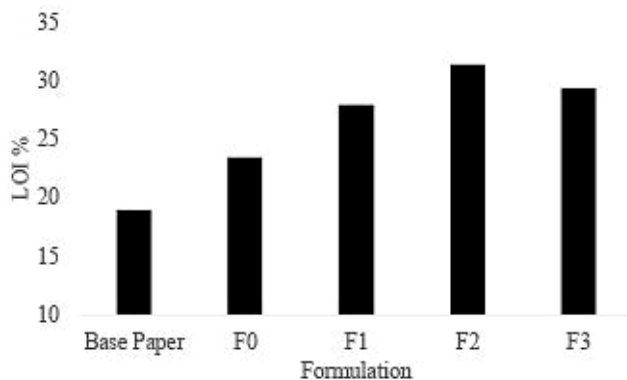


Figure 1: LOI values of of coated and uncoated paper samples

Table 4
Printability parameters of of coated and uncoated paper samples

Formulation	L*	b*	b*	ΔE_{00}	Gloss
Base paper	45.95	72.74	-3.83	Standard	2.3
F0	47.56	72.52	-3.49	1.58	15.8
F1	47.57	72.64	-4.12	1.48	14.4
F2	46.29	72.54	-3.28	0.47	14.1
F3	46.13	72.35	-3.94	0.29	13.7

The data in Figure 1 reveal that the starch coating (F0) applied on the base paper surface formed a slightly protective layer, which made ignition more difficult, compared to the uncoated base paper. By adding calcium carbonate to the coating formulation (F1), a semirigid structure was formed in the organic polymeric lattice and applying such a coating delayed the flammability of the paper. Meanwhile, the data indicate that significant flame retardancy was gained by adding tin oxide to the coating formulation (F2). When the coating formulation incorporated both fillers (F3), its application on paper led to significantly higher flame retardancy, compared to the uncoated base paper; although the flame retardancy was slightly lower than in the case of the coating containing tin oxide only. The results are in line with those reported in the literature.¹⁹ In terms of LOI values, an increase of 64% in the LOI value was determined in F2, compared to that of the base paper, and an increase of 54% was calculated in the case of F3.

Offset test prints were made on the paper samples coated with the obtained formulations. The color and gloss values determined for the printed papers are shown in Table 4. Analyzing the data tabulated in Table 4, the same trends regarding color changes can be observed as remarked above in the case of the unprinted papers. In other words, it was determined that, under the influence of the starch-based coating, the color of the paper turned slightly yellow; the addition of calcium carbonate caused a shift to blue, while that of tin oxide alone also contributed to a slight shift of the color to yellow.

At the same time, it has been found that using the two fillers together allowed the prints to reach the closest color results to those of the printed base paper. The color differences of the prints on all the coatings were found to be within the limits recommended by ISO 12647-2. As regards the gloss values of the prints, a decrease was determined, compared to the base paper. This decrease in gloss of all the prints can be explained

by the different light scattering of the pigment in the ink. Thus, as surface roughness increased because of the coating applied, this led to more diffuse reflection, and thus the gloss decreased. The obtained results are supported by the literature.²⁰

CONCLUSION

In this study, a suitable paper coating was successfully developed to ensure both printability (using calcium carbonate) and flame retardancy (using tin oxide) of the paper samples. For this purpose, coating formulations, with different compositions, were applied on office paper under laboratory conditions. The colors of the resulting papers slightly shifted to blue when a calcium carbonate coating was used, and to yellow when using a starch-based coating and the formulation incorporating tin oxide. When a combination of calcium carbonate and tin oxide fillers was used, the color achieved was the closest to that of the base paper. The gloss of the paper increased by approximately five times after the coating processes. Contact angle and surface energy measurements were made to evaluate the printability of the papers. Calcium carbonate contributed to good printability results, while tin oxide negatively affected printability. However, applying the coating formulation containing both fillers, the decrease in printability was prevented. By adding tin oxide to the coating, the flame retardancy properties of the papers were improved approximately twice. Offset test prints were successfully made on the coated papers and it was determined that the color results obtained were in line with those previously determined for the unprinted coated samples. Overall, this allowed concluding that the developed coating formulation containing both calcium carbonate and tin oxide imparted flame retardancy to the paper, while preserving its printability.

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