Modern refiner pulp mills can produce mechanical pulps at brightness and strength levels suitable for the production of high quality papers. Paper made from these pulps has attractive optical and printing properties such as high opacity, high bulk, and high stiffness. However, rapid light-induced yellowing of high-yield pulps remains a significant impediment to their broader use [1-3].

The discolouration is due to photochemical reactions of lignin [3-13]. The many methods of inhibiting yellowing that have been attempted can be classified into two main groups: 1) lignin modification [7, 8, 14-17]; 2) addition of chemicals that either stop the photochemistry or redirect the subsequent reactions to avoid coloured products (see reviews by Heitner [18] and Leary [13].)

The most successful chemical additives are ultraviolet light absorbers (UVAs) and radical scavengers (RS). UVAs preferentially absorb the damaging UV light and dissipate the energy harmlessly as heat. Radical scavengers trap the radicals formed during light irradiation, and stop the photochemical reaction from producing chromophores. Both additives are used, separately or together, to stabilize paints, varnishes, automobile coatings and plastics. While these additives improve the light stability of high-yield pulps, the amounts required for effective colour stabilization are too high to be practical [6, 10, 19-26].

Recently Paprican and Ciba Specialty Chemicals developed a hindered hydroxylamine radical scavenger (RS) that effectively inhibits yellowing at modest doses [27]. When combined with a UVA, exceptional brightness stability is possible [28-30]. In collaboration with Ciba Specialty Chemicals, a mill trial was carried out at an eastern Canadian mill that produces machine finished coated (MFC) paper from 100% alkaline peroxide mechanical pulp (APMP). The inhibitors were applied onto the paper surface as part of a pigmented coating formulation. Laboratory studies [31] showed that when using a combination of RS and UVA as inhibitors, a viscosity modifier was needed to maintain an acceptable coating rheology at high solids content. A simpler solution was to use TiO₂ as a UVA, in place of an equivalent mass of the ground calcium carbonate (GCC) in the coating formulation. While TiO₂ is generally used in the paper industry as a scattering pigment, it also absorbs UV light strongly. A combination of 1.05% TiO₂ and 0.3% RS (on air-dried coated paper) significantly improved light stability and had no effect on the rheology of the coating colour. Therefore, this combination of inhibitors was selected for the mill trial. This paper will report the results of the mill trial and the following long-run pilot printing trial.
scavenger (RS), a hydroxylamine (4-hydroxy-2,2,6,6-tetramethyl-N-hydroxypiperidine) salt (Ciba® PAX-2067, Ciba Specialty Chemicals). TiO₂ replaced 5% of the GCC in the coating formulation, while RS was incorporated into the formulation as an additive. The inhibitor charges were based on the weight of the air-dried coated paper. Sodium hydroxide was used to adjust the pH of the coating formulation to about 8.9. The coating colour was prepared in a mixing tank and afterwards, the pH was adjusted to verify that differences the brightness to the PC number, the less the paper has yellowing.

Characterization of the Coating Colour

The TiO₂ content in the paper was determined using an Inductively Coupled Plasma (ICP) Emission Spectrometer (Model AtomScan 25 from Thermo Jarrell Ash). The TiO₂ content was calculated from the TiO₂ content, assuming that TiO₂ and the RS were coated proportionally onto the paper.

Paper Machine

The paper machine is a fourdrinier machine equipped with two online short-dwell blade coaters. The paper was coated on one side first, dried in contact with a set of steam cylinders, and then coated on the other side. The machine speed was about 600 m/min.

Brightness Stability Test

The effect of yellowing inhibitors on brightness stability was examined using both accelerated and ambient light exposure conditions. Accelerated photolysis was done in a metal box with eight, 8W cool-white fluorescent lamps positioned 19 cm above the samples (Luzchem Research Inc.). These lamps are similar to those used in common North American office lighting. The box was ventilated to maintain the temperature inside at about 30°C during the exposure period. In the ambient tests, the sample was exposed to normal office fluorescent light (24 hours a day) plus the sunshine through a south-facing window. Yellowing inhibition was monitored by the decrease in paper brightness and the increase in b*.

Physical Property Tests

After standard conditioning, the samples were tested for their structural, strength, optical, and surface properties according to appropriate TAPPI standard testing methods.

Characterization of the Coating Colour

The coating colour was characterized by measuring its low shear viscosity, high shear viscosity, and water retention value. Low shear viscosity was measured at 35°C with a Brookfield viscometer (#5 spindle at 100 rpm). A Hercules Hi-shear viscometer (DV-10) was used to measure the high shear viscosity up to 4400 rpm at 35°C with No. A Bob. An AA-GWR Water Retention Meter (Model 150) was used to measure the water retention value of the coating colour at room temperature.

Long-Run Heatset Offset Printing Trial

The printing trial was done at the Institut des Communications Graphiques du Québec (ICGQ) in Montreal. The test form contained a variety of features designed to allow instrumental measurement of ink density, contrast, dot gain, print through, and ink trapping. There were also two photographs for visual evaluation.

The trial samples were printed on a Harris M110 heatset offset printing press, which consists of 4 printing units in the order of black, cyan, magenta, and yellow. The press speed was about 360 m/min. Mid-tack inks for heatset (7-8 at 1 minute and 25°C) from Sun Chemicals were used. The settings of the press remained unchanged during the entire printing trial. 57,000 copies were printed on each of
the two trial papers. The densitometric measurements were done on samples collected every 10,000 copies, with an Auto-tracking Spectrophotometer (ATS) from X-Rite. The fountain solutions were characterized before and after the trials by their conductivity, surface tension, and pH.

RESULTS AND DISCUSSIONS

Brightness Stability

The trial started after collecting four tons of control paper. Then two batches (3200 L each) of coating colour containing inhibitors, 5 pph TiO₂ and 1.4 pph radical scavenger (equivalent to 1.05% TiO₂ and 0.3% RS on weight of air-dried coated paper) were prepared. The mill trial lasted about 4 hours. Four trial samples with various inhibitor charges were collected in the middle and at the end of the trial. The samples were analysed for the actual TiO₂ content in the paper (Table II). Table II shows that the maximum amount of TiO₂ on these samples was about 64% of the target charge (0.67% TiO₂ vs. target of 1.05%). To make sure that we added the right amount of inhibitors during the preparation of the mill trial coating colour, a sample of mill-made colour was taken from the mixing tank and used to coat the paper by a laboratory CLC coater. The base paper was also coated with a laboratory-prepared colour that contains the target inhibitor charge. Figure 1 shows that the laboratory and mill-made colours produced similar inhibition, suggesting that mill colour in the mixing tank contained the right amount of inhibitors for target charge. However, the inhibitor concentration in the feeding tank of the two online coaters was diluted, most likely by the remaining control colour in the storage tank or within the circulation lines.

Figure 2 shows that the bottom side of the paper had higher brightness stability than the top side for both control and inhibited samples. Figure 2 also shows that good yellowing inhibition was nonetheless obtained in the mill trial. The brightness decrease for paper treated with 0.67% TiO₂ and 0.18% RS was less than 7 points (bottom side) after 12 days of continuous accelerated light exposure. This is similar to the sample treated with the target charge (1.05% TiO₂ plus 0.3% RS) by a laboratory CLC coater (Figure 3). PC number was used in Figure 3 to compensate for the slight difference in initial brightness between laboratory and mill samples.

To explain the discrepancy between mill and laboratory trials in the inhibitor charge required for the same inhibition level, we measured the coat weight, coating coverage, and coating thickness uniformity using the SEM and image analysis technique as described in the Experimental section. Table III shows that in the mill trial, the bottom side had a higher coat weight and coating coverage than the top side. This could be further illustrated by the SEM micrographs in Figure 4. For this coated paper, the yellowing inhibition came from the combined effects of inhibitor and pigment coating. Since the latter depends strongly on the coating coverage, a higher coating coverage gives a more stable paper [34]. This explains why the bottom side had higher brightness stability than the top side. Since only the bottom side of the mill sample had the target coat weight, which is also similar to that of the laboratory sample, the data on brightness stability in the rest of the report is the result for the bottom side.

Table III shows that at a similar coat weight, the inhibited paper produced in the mill trial had a higher coating coverage than the one from lab trial (97.5% versus 91.8%). As a result, the mill trial sample had the same inhibition at a much lower inhibitor charge, as compared with the laboratory one. Table III also shows that at a similar coat weight, the mill control had a slightly higher coating coverage than the laboratory one (96.8% versus 93.5%), which explains why the mill control had a slightly higher brightness stability than the laboratory one, as shown in Figure 3.

Figure 5 shows the yellowing inhibition obtained under ambient light exposure conditions. After 90 days of exposure to office light, the paper treated with 0.67% TiO₂ and 0.18% RS lost 2.8 ISO bright-
ness points, compared with 7.0 points for the control, a 60% reduction in brightness loss. Also the difference in brightness between these two samples increased with time. After one year of exposure, there was a difference of 9 points in ISO brightness. Note that the samples were exposed to light 24 hours a day, which is more severe than normal office conditions. Figure 9 shows that control and inhibited samples lost about 1.8 points, compared with 7.0 points for the control.

As shown in Table V, the yellowing inhibitors had a negligible effect on the structural and strength properties of the paper. For example, similar Parker Print Surf (PPS), air permeability and breaking length were obtained under the same calendering conditions for the samples treated with and without inhibitors. However, the inhibited sample had a higher ISO opacity than the control sample (93.8% vs. 92.1%), mainly due to the high scattering coefficient of TiO₂ [36].

We also measured the coating thickness uniformity of paper cross sections by SEM and image analysis. Figure 10 shows that the inhibited sample had a lower coefficient of variation (C.O.V.) for the coating thickness, indicating that the inhibited sample had a more uniform coating thickness than the control, on both sides of the paper.

The most popular test for measuring the pilling resistance of paper is the IGT surface strength test, which simulates letterpress and offset printing conditions. Control, 12000 1.55 1.32 1.32 0.98 30 27 31 19 21 10 11 .03 .03 .02 .03 68 83 63
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Runnability and Coating Colour Characterization

There were no runnability problems during the trial. The control and inhibited coating colours were sampled and tested for their rheological properties including low- (Brookfield) and high-shear viscosity (Hercules), thixotropy, and water retention value.

Figure 8 shows that the control and inhibited coating colour had similar viscosity curves. Figure 8 also shows that these two coating colours had similar thixotropic characteristics. There was a hysteresis loop between the increasing shear rate (up) and the decreasing shear rate (down) curves. A thixotropic coating colour is defined by its potential to have its structure reformed, when the colour is allowed to rest for an extended period of time. Table IV lists the corresponding data for these two coating colours had similar low-shear viscosity.

The water retention characteristic of a coating colour is its ability to maintain an aqueous phase in contact with the pigment and latex particles. It may affect the coat weight, coating runnability, and paper end properties. Water retention value is also an indication of the migration of coating colour aqueous phase into the paper [35].

The water retention characteristic and the water retention characteristics of paper are obtained under the same calendering conditions for the samples treated with and without inhibitors. However, the inhibited sample had a higher ISO opacity than the control sample (93.8% vs. 92.1%), mainly due to the high scattering coefficient of TiO₂ [36].

We also measured the coating thickness uniformity of paper cross sections by SEM and image analysis. Figure 10 shows that the inhibited sample had a lower coefficient of variation (C.O.V.) for the coating thickness, indicating that the inhibited sample had a more uniform coating thickness than the control, on both sides of the paper.

The most popular test for measuring the pilling resistance of paper is the IGT surface strength test, which simulates letterpress and offset printing conditions.
Both control and inhibited papers had an IGT pick speed of about 2 m/s.

**Long-Run Heatset Offset Printing Trial**

The main purposes of the printing trial were: (1) to compare the print quality of inhibited and control papers; (2) to evaluate the influence of print length on the printing characteristics of these two papers. The prints from control and inhibited papers were compared by absolute solid ink densities, dot gain at 50%, print contrasts at 70%, print through, and ink trapping.

In general, there was no significant difference between control and inhibited papers. Both papers had similar print density, ink trapping, and print contrast (Table VI). Table VII shows that there were negligible changes in the fountain solutions during the printing trial. There was no detectable amount of radical scavenger in the fountain solution after the print trial. This is important, as material extracted from coatings into the fountain solution can interfere with the ink-water balance on the press, and with colour trapping [37].

Some differences were observed between the control and inhibited papers during the trial, and will be discussed in the following sections.

**Print through**

Table VI shows that the inhibited paper had a lower print through than the control. This is expected since the inhibited paper had a higher opacity due to the high scattering coefficient of TiO₂, as shown in Table V.

**Magenta on top side and black on bottom side of the paper samples**

Table VI shows that, in general, the dot gain at 50% was similar on both papers. However, after 34,000 copies, the dot gain of magenta on the top side and black on the bottom side of the inhibited paper were higher than those on the control paper. Correspondingly, the print density
also increased, as shown in Figure 11. Print density increases with dot gain, through a non-linear function based on the Murray-Davis equation [38]. Coincidentally, there was a web break right after 34,000 copies. The longer the printing run, the higher the dot gains at 50% half-tone blocks. Visually, Caucasian skin tones appeared more reddish and darker on the inhibited paper. This could be due to either the improper colour control after the web break, or to ink piling and micro picking problems of the paper. In either case, a good printing operator should be able to adjust the colour density quickly back to normal.

The analysis of tape pulls from the black unit shows that slightly more picking occurred on the inhibited paper. The picks were mainly dried ink, pigments and fibres. This could be due to an insufficient amount of binder in the formulation containing the inhibitors. TiO2 has a larger surface area than GCC, and usually requires more binder. Also, during the preparation of the colours containing inhibitors, the operator accidentally added 5 pph more clay than needed. A small increase of binder portion in the coating formulation could solve this picking problem.

**SUMMARY**

A mill trial was done to test a yellowing inhibition system on a machine finished coated paper made from 100% alkaline peroxide mechanical pulp. The inhibitor system contained rutile TiO2 as an UV absorber, a hydroxylamine radical scavenger (RS). The main findings are:

1. The yellowing inhibitors improved light stability. After 90 days of exposure to office light, the paper treated with 0.67% TiO2 and 0.18% RS lost 2.8 ISO brightness points, compared with 7.0 points for the control, a 60% reduction in brightness loss. The brightness difference between these two samples increased to 9 points after one year of exposure.
2. Compared to the laboratory sample, the mill trial sample had similar brightness stability at a much lower inhibitor charge.

This was attributed mainly to a higher coating coverage in the mill sample.

3. The inhibitors had no negative effect on initial brightness nor on brightness stability under ambient dark conditions.
4. The inhibitors had no effect on the coating colour rheology. No runnability problems were encountered in the trial.
5. The yellowing inhibitors had no effect on structural and strength properties of the paper. The inhibited paper had a higher ISO opacity because of the higher scattering coefficient of TiO2 that was added into the formulation as an UV absorber.
6. A handset offset printing trial of 57,000 copies was performed on the mill trial samples. Both papers had similar print density, ink trapping, and print contrast. The inhibited paper had a lower print through, but slightly more picking on the blanket. The picking could be due to an insufficient amount of binder in the inhibited coating colour containing TiO2.

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**REFERENCES**


Résumé: Nous avons procédé à des essais en usine d’un inhibiteur de jaunissement pour du papier couché apprêté sur machine contenant de la pâte mécanique au peroxyde alcalin. L’inhibiteur était composé d’un capteur de radicaux hydroxylamine freiné et de dioxyde de titane. La perte de blancheur après 90 jours d’exposition à un éclairage de bureau était de 60 % inférieure à celle du contrôle. L’inhibiteur était composé d’un capteur de radicaux hydroxylamine freiné et de dioxyde de titane. La perte de blancheur après 90 jours d’exposition à un éclairage de bureau était de 60 % inférieure à celle du contrôle.

Keywords: Mechanical Pulps, Coated Papers, Yellowing, Inhibitors, Titanium Dioxide, Hydroxylamine, Paper Properties.


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