## Technical Paper Segment





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# NEW GENERATION COATING ADDITIVES AS TOTAL BINDER REDUCTION IN COATING FORMULA AND RENEWABLE COATING BINDERS

#### SUMMARY

Pigment coating is applied to surface of paper and board in order to improve their printability and to reduce amount of fibrous raw materials. Synthetic latexesare widely used as coating binder; these binders are petroleum-based and are non-renewable. In contrary, starch, as a renewable raw material, has been used as a coating co-binder for several decades. A technique based on graft-copolymerization was applied to produce a modified starch, namely KLIC10.

Development of the starch was established on an idea to improve binding properties of starch per unit mass while maintaining a good flow ability in coating color. With these characteristics, LHH concept was introduced to the market with KLIC 10 application. The concept greatly benefits paper mill who seeks a cost saving and environmental friendly strategies for coated paper production.

Application of KLIC 10 under LHH concept was feasible in several production trials of coated paper. Two reference production trials of the starch based on heavyweight and lightweight coated paper are outlined. Reduction of synthetic latex consumption would lead to potential cost saving of more than 100,000 USD per year depending on specific production parameters.

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Pigment coating is applied to surface of paper and paperboard in order to improve their printability (1) and to reduce amount of fibrous raw materials (2). Coating color consists of several components that play different roles in coated paper. The main component is pigment, which acts as ink absorption and light scattering elements, shares about 80-95 weight % depending on coating formulation. Another major componentis binder that help binding of pigment to base paper and binding pigment together. Synthetic latexes, i.e. styrene butadiene (SB), styrene acrylate (SA), and polyvinyl acetate (PVAc) latexes, which derived from petroleum, are widely used as coating binder (3). Besides these synthetic binders, there are also binders which derived from natural polymers, i.e. starches, proteins, and celluloses (3).

Starch has been recognized by papermakers as coating co-binder for several decades. In recent years, there has been an industrial trend to increase usage of starch in coating formulation (4). This is partly due to high production cost associated with petroleum-based binders. Moreover, these petroleum-based binders are non-renewable. BP (5) estimated that global proved oil reserves will be sufficient for only about five decades and this would critically affect availability of petroleum-based products. In contrary, starch is a natural-based and renewable resource; it is a promising choice of binder in resource-and cost-wise strategies fora long term coated paper production.

#### LITERATURE

Traditionally, in order to apply starch as a coating cobinder, starch is modified by reducing its molecular weight utilizing different techniques, i.e. acid thinning, oxidation, thermo-chemical conversion, or enzymatic conversion. Recently, different strategies on development of coating starch have been reported by several research groups. Glittenburg (6) reported on thermally modified starches with a good rheological characteristic with metered size press coating. Shin et al (7) mentioned an application of starch nanoparticles in coating formulation and their rheological characteristics under high shear rate. A study on possibility for applying starch in top coating, with various pigment combinations, was also reported (8). An attempt to achieve higher than 50% latex replacement in pre-coat formulation, with latex to

starch replacing ratio of 1:1, was likely possible (4).

Despite sharing similar idea to improve application of starch in coating formulation, none of the reports has clearly mentioned a concept on improvement of binding properties of coating starch which potentially leads to coating color formula with less total binder.

Based on our experience on developing modified starch for papermaking combined with recent fundamental knowledge in coating technology, a graft-copolymerized coating starch with enhanced binding property as well as good rheological behaviors in coating suspension was developed. The starch was named KLIC 10.

Utilization of KLIC 10 is able to achieve LHH concept in coating formulation, which are Less total binder, High starch part, and High coating solid. Less total binder and high starch part benefit not only on cost reduction but also on conservation of the world's limited resources on petroleum-based binders. High coating solid poses several advantages such as reduced binder migration during coating application and improved printability of coated paper as well as improved drying rate of coating layer which reduces drying energy (9). In 2011, Lertwanawatana et al (10) first introduced KLIC 10 in an international symposium. Results from a pilot coater trial indicated that application of KLIC 10 in coating formulation at 1-2 pph could be able to reduce total binder content by up to 25%. Coating color containing KLIC 10 provided acceptable rheological properties and improved water retention to reference latex-based formulation. While the coated paper showed markedly improved pick resistance and similar optical characteristics to the reference.

Following a successful pilot-scaled trial, the starch has been tested in production-scaled in several paper mill in order to prove viability of LHH concept. Two case studies of production trials for coated paperboard and lightweight coated (LWC) paper are given here as successful references.

#### **RESULTS AND DISCUSSION**

The first reference mill trial (coated paperboard)

Table 1 shows coating color formulations in this experiment along with their properties. All coating colors showed shear thinning rheological behavior in

range of measured shear rate. Addition of KLIC10 for 11.5 pph while reducing latex for 1.5-3 pph did not
significantly affect viscosity at low shear rate as
measured by Brookfield viscometer at 100 rpm.
Viscosity at high shear rate, about 130,000 s<sup>-1</sup> as
measured by Hercules high shear viscometer (FF bob;
6600 rpm), in trial 1 and trial 2 formula increased by 4-7
cPs compared to reference. This was partly due to
higher viscosity of continuous phase (11) since KLIC 10

is water-soluble. However, these values were still in an acceptable range. As for water retention, slightly better water retentions were observed in KLIC 10 containing formulas. According to these finding, it was highly likely that KLIC 10 would not adversely affect run-ability of coater and the mill decided to test KLIC 10 in a production trial; detailed coating formulations are showed in Table 2.

Table 1: Coating formulation and properties of coating color in the first reference (coated board)

| Formulation                      | 0/ C - L J          | Reference | Trial 1 | Trial 2 |  |
|----------------------------------|---------------------|-----------|---------|---------|--|
| Formulation                      | %Solid              | Part      | Part    | Part    |  |
| 1.Pigment                        |                     |           |         |         |  |
| -CaCO <sub>3</sub>               | 75                  | 100       | 100     | 100     |  |
| 2.Binder                         |                     |           |         |         |  |
| -Latex SB; Stryronal 510D        | 50                  | 9         | 6       | 7.5     |  |
| -Starch; ExcelCoat 65            | 40                  | 2         | 2       | 2       |  |
| - Starch; KLIC10                 | 95                  | 0         | 1.5     | 1       |  |
| 3.Additive                       |                     |           |         |         |  |
| - Thickener; Sterocoll FD        | 25                  | 0.15      | 0.15    | 0.15    |  |
| Coating properties               | Unit                |           |         |         |  |
| %Solid content                   |                     | 64        | 64      | 64      |  |
| pH                               |                     | 9.0       | 9.0     | 9.0     |  |
| Brookfield(100 rpm); 0 hr(35°)   | (cPs)               | 490       | 555     | 527     |  |
| HERCULESFF 6600 rpm; 0 hr(25°)   | (cPs)               | 36        | 43      | 40      |  |
| AA GWR,gsm 1.5 bar,120 sec; 0 hr | (g/m <sup>2</sup> ) | 144       | 137     | 132     |  |

Table 2: Coating formulation during production trial in the first reference (coated board)

| Formulation         | % Solid | Reference formula | Trial formula |  |  |
|---------------------|---------|-------------------|---------------|--|--|
|                     | 76 SOHU | Part              | Part          |  |  |
| 1.Pigment           |         |                   |               |  |  |
| - CaCO <sub>3</sub> | 75      | 100               | 100           |  |  |
| 2.Binder            |         |                   | The second    |  |  |
| - Latex             | 50      | 9                 | 6.5           |  |  |
| - Starch            | 20      | 2                 | 2             |  |  |
| - KLIC10            | 95      | 0                 | 1.2           |  |  |

Key parameters monitored during the trial were stiffness, brightness, and pick resistance (IGT method). Time course on key parameters of coated paperboard during the trial were displayed in Figure 1 to 3. All key parameters didn't significantly change during the trial period. Pick resistance of trial formula (total binder = 9.7 pph) were comparable to reference formula which contains 11 pph of total binder. Benefit of KLIC10 formula on cost saving could be systematically presented in Table 3. Costs of binder were based on dry weight as USD unit (2014 data).KLIC 10 formula clearly showed cost saving of about 90 USD per batch. Under full production capacity of the mill, by applying KLIC 10, it would be possible to save up to nearly100,000 USD per year. The mill concluded that KLIC 10 was applicable under real production conditions regarding qualities of coated paperboard.

Figure 1 : Stiffness of coated paperboard during the production trial

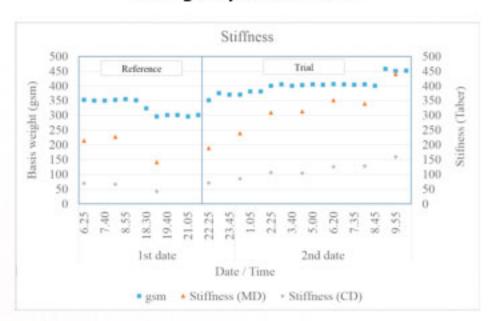


Table 3: Cost simulation for KLIC10 formulain the first reference (coated board)

| Binder                              | Cost<br>(USD per dry kg) | Current<br>formula | Current<br>cost | KLIC10<br>formula | KLIC10<br>cost |
|-------------------------------------|--------------------------|--------------------|-----------------|-------------------|----------------|
| KLIC 10                             | 1.7                      | 0                  | 0               | 1.2               | 2.04           |
| Starch                              | 0.7                      | 2                  | 1.4             | 2                 | 1.4            |
| Latex                               | 2.6                      | 9                  | 23.4            | 6.5               | 16.9           |
| Total cost                          |                          |                    | 24.8            |                   | 20.34          |
| Total binder cost saving            |                          | 1                  | 8               | 9                 | 6              |
| Latex consumption per ye            | ear                      | 40                 | 00              | Ton               |                |
| Coating starch consumption per year |                          | 45                 |                 | Ton               |                |
| Potential cost saving per year      |                          | 99,181             |                 | USD               |                |

Figure 2 : Brightness of coated paperboard during the production trial

Figure 3 : Pick resistance of coated paperboard during the production trial





The second reference mill trial (LWC paper)

Table 4 shows coating color formulations in this experiment along with their properties. Pigment was solely kaolin clay in order to produce high smoothness LWC paper from single coating. In laboratory trial

formulations, latex was replaced by KLIC 10 at ratio of 2:1. Viscosity at low shear rate and high shear rate slightly increased by addition of KLIC 10 for 1-1.5 pph. Water retention of the coating colors containing KLIC 10 were marginally improved from reference.

Table 4: Coating formulation and properties of coating color in the second reference (LWC paper)

| Farmulation                      | 0/5-114             | Reference | Trial 1 | Trial 2 |  |
|----------------------------------|---------------------|-----------|---------|---------|--|
| Formulation                      | %Solid              | Part      | Part    | Part    |  |
| 1.Pigment                        |                     |           |         |         |  |
| -Kaolin clay; Kaofine 90         | 100                 | 100       | 100     | 100     |  |
| 2.Binder                         |                     |           |         |         |  |
| -Latex SB; Stryronal 510D        | 50                  | 8         | 6       | 5       |  |
| -Starch; ExcelCoat 65            | 40                  | 5         | 5       | 5       |  |
| - Starch; KLIC10                 | 95                  | 0 1       |         | 1.5     |  |
| 3.Additive                       |                     |           |         |         |  |
| - Dispersant; PA-40              | 50                  | 0.3       | 0.3     | 0.3     |  |
| Coating properties               | Unit                |           |         |         |  |
| %Solid content                   |                     | 60        | 60      | 60      |  |
| pH                               |                     | 9.0       | 9.0     | 9.0     |  |
| Brookfield(100 rpm); 0 hr(35°)   | (cPs)               | 560       | 627     | 610     |  |
| HERCULESFF 6600 rpm; 0 hr(25°)   | (cPs)               | 35        | 37      | 37      |  |
| AA GWR,gsm 1.5 bar,120 sec; 0 hr | (g/m <sup>2</sup> ) | 93        | 84      | 84      |  |

Table 5 : Cost simulation for KLIC10 formulain the second reference (LWC paper)

| Binder                              | Cost<br>(USD per dry kg) | Current<br>formula | Current   | KLIC10<br>formula | KLIC10<br>cost |  |
|-------------------------------------|--------------------------|--------------------|-----------|-------------------|----------------|--|
| KLIC 10                             | 1.7                      | 0                  | 0         | 1                 | 1.7            |  |
| Starch                              | 0.7                      | 5                  | 3.5       | 5                 | 3.5            |  |
| Latex                               | 2.6                      | 8                  | 20.8      | 6                 | 15.6           |  |
| Total cost                          |                          |                    | 24.3      |                   | 20.8           |  |
| Total binder cost saving            |                          | 14                 | .4        | 9                 | 6              |  |
| Latex consumption per ye            | ear                      | 7,0                | 00        | Te                | on             |  |
| Coating starch consumption per year |                          | 2,200              |           | Ton               |                |  |
| Potential cost saving per           | I cost saving per year   |                    | 1,532,510 |                   | USD            |  |

During the production trials period, there was smoothly transfer from reference formula to trial formula and didn't face any run-ability problems. The LWC paper produced had achieved mill standard pick resistance as well as optical characteristics, comparable to reference formula. Total binder in coating formulation could be decreased by 1 pph (from 13 to 12pph). Cost simulation based on dry weight as USD unit (2014 data) can be found in Table 5. Potential cost saving per year was huge up to 1.53 million USD. This number was much larger than the first case due to different in production capacity and consumption of latex.

It is worth noting that the cost saving models
presented here were based on the data from 2014 and
global crude oil price has recently dropped
considerably. Presently, actual cost saving benefit
would be somewhat lower than the estimated value.

#### CONCLUSIONS

Shortly after the introduction of KLIC 10, several production trials have been conducted. This paper briefly summarizes two successful production trials of KLIC 10 application as an additive to reduce total binder in coating formulation. Information obtained from laboratory study is useful for paper mill to make a decision on production trial. Coating colors containing the starch were applicable not only with paperboard but also with lightweight paper. Rheological properties of coating color, machine run-ability and pick resistance of coated papers produced were comparable to corresponding reference formulations that contained higher total binder. Paper mill could save production cost substantially by application of the starch. LHH concept combined with KLIC 10 application has been proofed to be valid and operable in resource- and cost-wise strategies for a long term coated paper production.

#### **EXPERIMENTAL**

#### The first reference mill trial (coated paperboard)

Paper mill in this case produces coated paperboard.

The mill used a minute amount of modified starch in pre-coat formulation. Reference formula was

Latex:starch (9:2). KLIC 10 was proposed, following Less total binder concept, to replace synthetic binder (latex) in pre-coat formulation at ratio of about 2:1 to 1.5:1.

A lab-scaled experiment was carried out in order to test whether rheological properties under low shear rate and high shear rate as well as water retention characteristics of coating color containing KLIC 10 were comparable to the reference formula. KLIC 10 was applied at 1 or 1.5 pph with latex to starch replacing ratio of 2:1 to 1.5:1. Pigment was 100% GCC (FMT 60). An SB latex (BASFStyronal 501D) and a modified starch (SMS ExcelCoat 65) were used as binder and cobinderin reference formula, respectively. Thickener was BASF Sterocoll FD. Solid contents of coating colors were estimated by oven dry method. Brookfield viscometer (LV type) and Hercules high shear viscometer (FF bob; 6600 rpm) were employed to estimate viscosity of coating color at low shear rate and high shear rate, respectively. Abo-Academy gravimetric water retention (AA-GWR; 1.5 Bar, 120 seconds) was used to evaluate water retention value of coating colors. Detailed coating formulations and properties of coating color are showed in Table 1. After laboratory verification on properties of coating color, a production trial was conducted based on experimental data. KLIC 10 was applied at 1.2 pph while lowering part of latex by 2.5 pph (about 2:1 replacing ratio) for pre-coat formulation. The mill produced 300-450 g/m<sup>2</sup> coated paperboard. Base paper was produced by a cylinder machine. Coater was off-machine with a metering bar applicator. Coating color was applied on top side with coat weight of approximately 13 and 12 g/m² for pre-coat and topcoat, respectively. Detailed coating formulations are showed in Table 2; exact type and name of chemicals are confidential though. The trial was conducted for 2 days. Time course on key properties of coated paperboard during the trial were displayed in Figure 1

#### The second reference mill trial (LWC paper)

Another success story of KLIC 10 was based on a production trial at a LWC paper mill. Basis weight of paper was 60 g/m<sup>2</sup> with single coating. The mill used

modified starch at nearly half amount of total binder. Reference formula was latex:starch (8:5). KLIC10 was proposed, following Less total binder and High starch part concept.

A lab-scaled experiment was carried out. KLIC 10 was applied at 1 or 1.5 pph with latex to starch replacing ratio of 2:1. Pigment in this case was 100% clay (Thiele Kaofine 90) dispersed with a dispersant (HOPAXPA-40). An SB latex (BASF Styronal 501D) and a modified starch (SMS ExcelCoat 65) were the latex and modified starch

used in reference formula. Properties of coating color were evaluated in the same manners as previously described in the first case. Detailed coating formulations and properties of coating color are showed in Table 4.

Evaluation of performance of KLIC 10 under production trial was done. Based on reference formula (8:5; total binder = 13), the mill decided to replace latex by 1 pph of KLIC 10 at ratio of 2:1, resulting in trial formula of latex:starch:KLIC 10 (6:5:1; total binder = 12).

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