Fouling in the paper machine wet end

TIMO KALLIO AND JUHA KEKKONEN

ABSTRACT: DLVO theory roughly explains the adsorption behavior of colloids and polymers on partially wettable oxide and polymer surfaces. Therefore, at moderate salt conditions, fouling can be explained in terms of charge, where an oscillating net charge in process water leads to fouling. Other key elements that affect fouling include Lewis acid–base reactions, steric and long-range hydrophobic interactions, viscoelasticity, and the contact area of contaminants. For controlling fouling in paper machines, the types of anti-fouling surfaces that can be developed include photocatalytic and electrically controlled surfaces, surfaces with minimized adhesion properties, and hydrophilic and strongly hydrophobic surfaces.

Application: Deposits lead to fouling problems, but it is possible to design anti-fouling surfaces for paper machine parts under wet conditions.

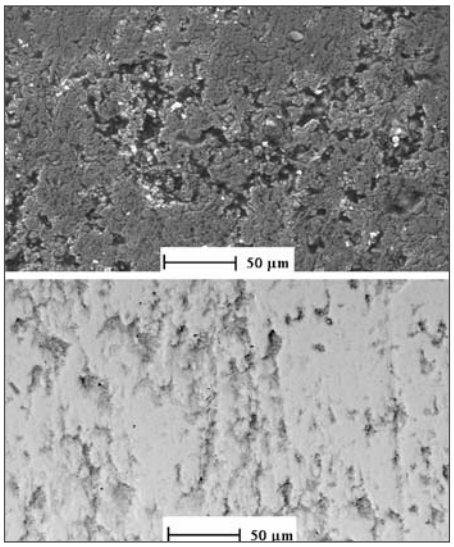
Deposits that collect on paper machine parts (**Figure 1**) may damage the parts, interrupt the papermaking process, decrease dewatering, and diminish paper quality. The fouling of tubes exacerbates pressure and energy losses.

Polymers such as polyurethane and polyamide and oxides such as chromium and aluminum oxide are widely used in the paper machine wet end, especially in ceramic rolls. In our studies, we have concentrated on the properties of oxide and polymer surfaces and the adsorption kinetics of dissolved and colloidal substances. These areas have been relatively poorly studied, although some other studies related to fouling have been published [1–6].

DEPOSIT FORMATION

The formation of deposits is a highly complex phenomenon for several reasons. First, process conditions vary on paper machines. The pH, the concentration and quality of ions, the content of different gases, and the temperature fluctuate. The quality of raw materials, including pulp and broke, varies as well. These variations are different on each machine, and the formation of deposits depends strongly on the particular conditions in each individual process.

Second, the substances that can form deposits can be hydrophilic, hydrophobic, soft, or hard. They can be particles, polymers, or even liquids. They can be pitch emulsions, alkenyl succinic anhydride (ASA), or some forms of alkyl ketene dimer (AKD). The size varies from surfactants of a few nanometers to fibers several millimeters long. The most common substances in process water are colloidal in size (less than 1 μm) and are controlled by surface forces [7].



1. Two SEM images from a fouled ceramic roll are shown. The upper image is from a relatively clean part of the roll and the lower image is from a strongly fouled part of the roll. Note how the small grazes (seen in the upper image) are filled with deposits in the lower image.

Third, deposits can be formed by different substances as a result of aggregation, coagulation, adsorption, reactions, or by release from the paper web. Microbiological activity may also cause deposits. Several surface forces have an influence on the formation of deposits.

Finally, deposit formation is affected in many ways by external circumstances. As process surfaces are showered and cleaned, deposits are subjected to forces from mechanical cleaning. The influence of hydrodynamic and mechanical forces on deposits depends on the surface morphology and the mechanical softness or hardness (viscoelasticity) of the deposits. The thickness of water films on surfaces varies in different parts of the paper machine.

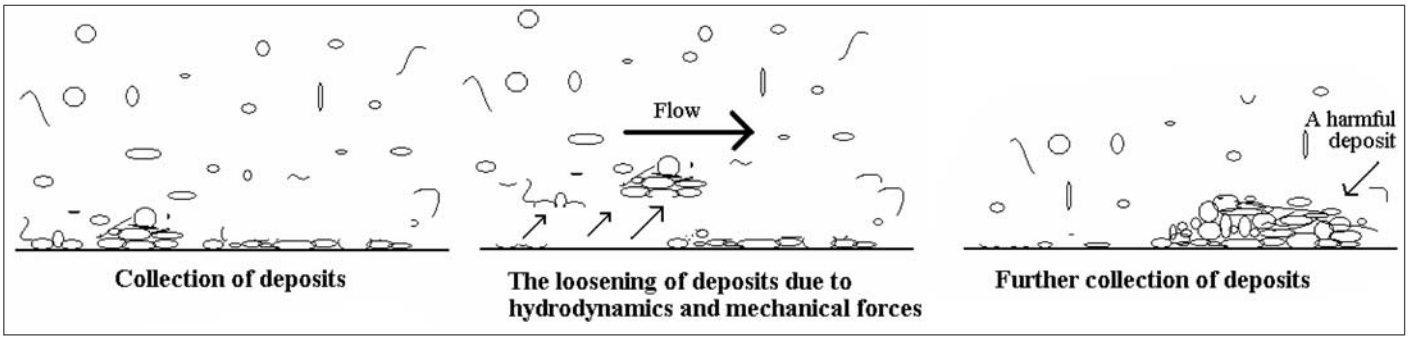
To simplify the complexity of the problem [8], we have divided the formation of deposits into three main steps. In the first step, the substances are brought into contact with the surface. In Step 2, the deposits adhere to the surface. In the third step, the fouled surface collect further deposits. Deposits that cause problems can be seen as "residues" that have survived all of the steps.

As **Fig. 2** shows, some of the substances collect on the surface but do not stay there because of their low adhesion. Some collect and adhere well but are not able to collect further deposits, in which case the fouling stops. Some deposits collect, adhere well, and are also able to collect further deposits.

FACTORS THAT AFFECT FOULING

Solution conditions and paper machine surfaces

The fouling of the surface in wet conditions mainly depends on the interactions between process water substances and clean or fouled paper machine surfaces. The role of bringing deposits in contact with the surface is strongest in places with still water, where there is no force to remove the fouling substances. Adsorption determines the formation of



2. Examples of fouling mechanisms.

deposits if the surface is continuously under water and the size of the fouling substances is colloidal (less than 1 μm).

The role of surface forces was demonstrated in experiments with anionic and cationic oxide surfaces and polyurethane surfaces. The results indicated that the adsorption of dissolved and colloidal substances is strongly dependent on the net charge of both the oxide surface and the substances in the process water. Thus, if the substances in the process water have an anionic net charge, anionic and hydrophilic, or partially wettable, surfaces should be favorable to diminished fouling, since no adsorption of wood materials occurs on hydrophilic silica at low or moderate salt concentrations [9–12].

However, anionic surfaces are susceptible to fouling by cationic substances. Thus, if the oxide surface is anionic in the pH range used in papermaking, cationic compounds such as polyelectrolytes or polyelectrolyte complexes adsorb on the oxide or on polyurethane surfaces [8, 14]. Since wood materials are anionic by nature, process water can only be made cationic with cationic additives. If small amounts of cationic additives are used, anionic complexes are formed. If the oxide surface is anionic, there should be no adsorption of these compounds. However, more additions of cationic compounds lead to the formation of neutral complexes and finally to cationic complexes. These compounds are likely to adsorb on anionic oxides and contribute to the fouling of equipment surfaces [11, 12].

On the other hand, if equipment surfaces are covered with an oxide that is cationic in neutral or weakly acidic conditions, such as Cr_2O_3, Fe_2O_3, or Al_2O_3 [14], the oxide surface placed in anionic process water will be swiftly covered by adsorbed wood materials [11, 15]. Therefore, after this initial step, further fouling of these surfaces depends mainly on the interactions of compounds that form the first adsorbed layer. Presumably, these compounds are mainly hemicelluloses in thermomechanical pulp (TMP) model dispersions [10, 11].

Thus, if the oxide surface and the dissolved and colloidal substances are oppositely charged, adsorption on oxides or on polyurethane apparently cannot be avoided [10–13]. Therefore, to minimize fouling, equipment surfaces and substances in process water should have the same type of charge, whether positive or negative, and the substances in process water should be stable in terms of net charge. The second best option is for the equipment surface and process water to have opposite signs of net charge, with the substances in the process water being stable in charge. In this case, a thin adsorbed layer forms, but excessive fouling should not take place. The adsorbed layer may even protect the surface against pitch deposits.

The worst case occurs when the substances in the process water are not stable and oscillate between an anionic and a cationic net charge. The oxide's initial sign of charge is not important, and multiple layers of dissolved and colloidal materials grow on the surface [9–12]. In addition, large flocs seem to form in the process water each time the charge equivalence is reached [12, 13]. It seems likely that such flocs also contribute to the fouling of equipment surfaces. Experiences in paper mills support the idea that an oscillating net charge in process water lends itself to fouling.

The fouling is therefore explained mainly in terms of charge and roughly according to DLVO theory in moderate salt conditions. (DLVO is a classic theory that provides explanation on colloid stability. It is named for researchers Derjaguin, Landau, Verwey, and Overbeek.) The concentration of negative ions affects the adsorption behavior of positively charged substances, and positive ions affect the behavior of negatively charged substances. As DLVO theory predicts, the influence of charge on adsorption becomes negligible at high salt concentrations. A high salt concentration means tens of mmol/L for divalent ions (Ca_2^+, SO_4^{2-}) and over 300 mmol/L for monovalent ions (such as Na^+ and Cl^-). For trivalent ions (Al^{3+}), the amounts are even lower than for divalent ions.

Fouling that stems from charge does not encompass fouling that arises from nonionic polymers such as polyethylene oxide [12]. In addition, very hydrophobic surfaces adsorb wood materials from TMP dispersions and pitch dispersions [11]. However, clean oxide and polyurethane surfaces are partially wettable in normal atmospheric conditions [16]. Therefore, adsorption arising from hydrophobic interactions appears to take place only if the surface is fully covered by hydrophobic contaminants.

Hydrodynamics and mechanical forces

While interactions between fouling substances and paper machine parts lead to fouling, the layer of deposits can be detached through hydrodynamic and mechanical forces. One example of the influence of mechanical forces is a "snowfall" discovered at one paper mill. Large amounts of white deposit were collected on a press section surface. However, a doctor blade was brought to bear on the deposits, and large amounts of white deposit fell to the floor. As a result, no problems occurred with deposits.

The stronger the deposit adhesion, the more difficult it is to detach the deposits. In places controlled by strong mechanical forces and hydrodynamics, fouling is mainly driven by adhesion. Only those substances that are able to adhere strongly to clean or fouled surfaces cause fouling. Viscoelastic (sticky) contaminants usually adhere well because of their large contact areas. In addition, if chemical bonds are formed between the surface and the deposit, and between deposited particles and other deposited particles, the adhesion of the deposit increases. Experiences from paper mills indicate that the layer of deposit often becomes compact and sticky under strong flow and mechanical forces.

Flow usually inhibits the adsorption of colloids, but it may accelerate the collision of larger particles. Under strong flow, the role of electro-osmotic force diminishes.

In some cases, a doctor blade may accelerate the spreading of deposits on the surface. This spreading increases the contact area of deposits, causing fouling to worsen. Surfaces also wear under mechanical forces. The doctor blade cleans the surface, but it may also alter the surface properties.

ANTI-FOULING SURFACES

Controlling the conditions in the process water is the most important factor in reducing paper machine fouling. However, the surface properties of paper machine parts can also significantly affect fouling problems.

Hydrophilic surfaces

Colloidal wood resin adsorbs less on hydrophilic silica than on hydrophobic surfaces, as **Table I** shows. Many liquid hydrophobic substances, such as AKD **(see Figure 3)** and ASA, adhere less on hydrophilic surfaces than on hydrophobic surfaces (with low surface energy) [17,18]. Therefore, it would be better for a surface to be hydrophilic if that surface is continuously under water.

Water drops do not flow down the side of a hydrophilic, vertical surface as fast as they flow down the side of a hydrophobic surface. Inside a water drop, deposits have more time to reach the surface if it is hydrophilic. Therefore, for a surface where there is a vertical water splash, such as in a tank, strong hydrophilicity can be disadvantageous.

Silicon dioxide contact angle	Deposited amount after 25 s, mg/m^2	Deposited amount after 100 s, mg/m^2
90°	0,2-0,25	0,85-0,9
70°	0,2-0,25	0,6-0,65
50°	0,2	0,2

I. Wood resin deposits in an unstable dispersion on silicon dioxide surfaces with contact angles of 90°, 70°, and 50°. (Dichlorodimethylsilane was used to create the wettability gradient. Electrolyte conc. = 100 mM $CaCl_2$. pH = 6.5.) [11]

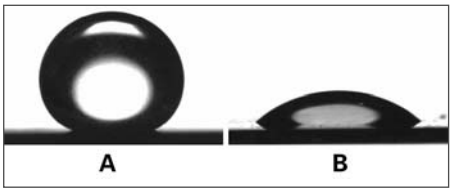
Hydrophobic surfaces

It has been proposed that the use of fluorinated polymers [19] or so-called "lotus" surfaces [20] could reduce problems with deposits. These approaches may be beneficial in some applications, but our studies indicate that the use of hydrophobic surfaces under wet conditions in a paper machine also involves limitations.

Fluorinated polymers. Flourinated material typically has low surface energy, and flourinated materials are therefore strongly hydrophobic. The adsorption of wood resin droplets increases when the surface energy of the material falls. Very intensive fluorination may therefore increase fouling if the process water contains hydrophobic contaminants. Potential hydrophobic contaminants such as pitch droplets and AKD wax are usually stabilized with a crust of polymers. However, if the crust of polymers covers them inadequately, substances often adsorb more easily.

Strongly hydrophobic (fluorinated) surfaces may be useful in areas of vertical splash. Splashes often cause fouling, because the fouling substances are brought into contact with the surface on drying. In addition, Lewis acid–base bonds that cause deposits to adhere to the surface are formed more easily when the splashes dry. However, if the surface is strongly hydrophobic, the splashes quickly roll away from the tank surface, and the fouling substances do not have time to attach to the surface. Hydrophobic surfaces may also remain relatively clean in the dry part of the paper machine.

Lotus surfaces. The lotus effect is based on rolling drops of water that can clean the surface. Lotus surfaces are hydrophobic (with a contact angle as high as 160° reported). Their hydrophobicity is partly related to their regular morphology [21]. The contact area of a lotus surface can be fairly high.



3. Spreading of liquid AKD-wax in ultrapure water on hydrophilic (3A) and hydrophobic silicon dioxide (3B). AKD wax contact angles 139° (3A) and 27° (3B). SiO_2 contact angles 20° (3A) and 100° (3B). [18]

The use of lotus surfaces on paper machines is limited. Drops of water cannot roll down the side if the surface is completely under water, so the lotus effect cannot be achieved on immersed surfaces such as those in tubes. The lotus effect can be applied on surfaces that are dry and wet intermittently, such as on rolls and places where water splashes. However, the large contact area of lotus surfaces can be problematic.

So far, it has only been proven that the lotus effect works when the fouling substance is composed of rigid particles [22] with an apparently small contact area. To our knowledge, the influence of the lotus effect has not been proven for viscoelastic and sticky contaminants. Because the deposits in the paper machine wet end are often viscoelastic, the large contact area of lotus surfaces may increase deposit adhesion. Since a water drop is a macroscopic object controlled largely by gravity, a surface that behaves as a lotus surface in static conditions does not behave the same way in moving process conditions. The lotus effect may also disappear rapidly when the lotus surface wears.

Wet surfaces operating in contact with the web

The design of anti-fouling rolls, belts, and other moving, wet surfaces operating in contact with the paper web is especially problematic. These surfaces need to release the paper web easily, and they need to be designed with increased cleanliness in mind.

Capillary forces and gas bubbles in contact with the surface affect web release [23, 24]. The paper web is better released on rough and hydrophobic surfaces, partly because capillary forces between the web and the surface decrease with increasing hydrophobicity and surface roughness. Hydrophobic, rough surfaces also collect gas bubbles more easily than do hydrophilic, smooth surfaces. However, as discussed, it could be favorable if anti-fouling surfaces operating in wet conditions were hydrophilic and smooth. Therefore, it can be difficult to design anti-fouling surfaces in contact with the paper web.

Other properties

Electric potential is used on steel surfaces in tanks to alter the oxide layer by forming oxygen radicals, which are able to decompose organic or biological contaminants [25–27]. However, the electric potential on conducting surfaces has an influence on electrostatic interactions and affects fouling.

Photocatalytic materials may have a future in paper machines because they are able to catalyze the composition of organic contaminants under UV light. The photocatalytic effect is based on oxygen radicals that are formed on TiO_2 surfaces [28]. The main disadvantage is the need for UV light, which can be problematic to arrange on a paper machine, since the process water scatters light.

The properties of the paper machine surface should stay stable against chemical stress and mechanical wearing. Changes in surface properties are, after all, a potential source of disturbances.

CONCLUSIONS

In studying the mechanisms involved, we have concentrated only on the effects of wood materials, synthetic polymers, and inorganic particles. However, fouling caused by microbes [29] and inorganic ions [2] is also important at paper mills. Deposits from the paper web may also adhere to surfaces. In addition, the role of hydrodynamics and mechanical forces has not yet been fully taken into consideration.

Therefore, clarification of the combined effects of all these substances and mechanisms represents a challenge for future research in this area. Applying photocatalytic, strongly hydrophobic, or electrically controlled surfaces to the paper machine are interesting new innovations, but their exact influence on fouling needs to be studied further. **TJ**

ACKNOWLEDGEMENT

We thank the National Technological Agency of Finland (TEKES), especially the "Clean Surfaces 2002–2006" Technology Program, as well as Metso Paper Rautpohja, for their financial support. We would also like to thank Juhani Vestola for fruitful discussions and Jussi Laurila (Tampere University of Technology) for the SEM figures.

LITERATURE CITED

1. Thornton, J., "Dissolved and colloidal substances in the production of wood-containing paper," Ph.D. thesis, Åbo Akademi University, Turku, Finland, 1993.
2. Caulkins, D., and Wildman, J., *Pulp & Paper* 62(6): 89(1988).
3. Sjöström, J., "Detrimental Substances" in *Pulp and Paper Production*, Kirjapaino Pika Oy, Turku, Finland, 1990.
4. Back, E.L., "Resin in Suspensions and Mechanisms of its Deposition," in *Pitch Control, Wood Resin and Deresination* (E.L. Back and L.H. Allen, Eds.), TAPPI PRESS, Atlanta, 2000, p. 151.
5. Holmberg, M., "Pitch and Precipitate Problems," in *Papermaking Chemistry* (L. Neimo, Ed.), Gummerus Printing, Jyväskylä, Finland, 1999, p. 223.
6. Holmberg M., "Paper Machine Water Chemistry," in *Papermaking Chemistry* (L. Neimo, Ed.), Gummerus Printing, Jyväskylä, 1999, p. 205.
7. Nylund, J., Lagus, O., and Eckerman, C., *Coll. Surf. A* 85(1): 9(1994).
8. Kallio, T., Kekkonen J., and Stenius P., *J. Adhes.* 80(10–11): 933-969 (2004).
9. Kekkonen, J., and Stenius, P., *Nord. Pulp Pap. Res. J.* 14(4): 7(1999).
10. Kekkonen, J., and Stenius, P., *Colloids Surfaces A* 156(1–3): 33(1999).
11. Kekkonen, J., and Stenius, P., *Nord. Pulp Pap. Res. J.* 16(1): 4-11 (2001).
12. Kekkonen, J., Ph.D. dissertation, Helsinki University of Technology, Helsinki, 2001.
13. Kekkonen, J., seminar handout, AEL-METSKO Paperikoneen saostumat, 6-7.2.2002, Imatra.
14. Parks, G.A., and de Bruyn, P.L., *J. Phys. Chem.* 66: 967 (1962).
15. Kekkonen, J., and Stenius, P., *Progr. Coll. Polym. Sci.* 116: 57-66 (2000).
16. Giese, Jr., R.F., Wu, W., and van Oss, C.J., *J. Disp. Sci. Tech.* 17: 527-549 (1996).
17. Lindfors, J., Ylisuvanto, S., Kallio, T., *et al.*, *Colloids and Surfaces A*, 256: 217-224 (2005).
18. Ylisuvanto, S., Lindfors, J., Kallio, T., Laine, J., Stenius, P., unpublished 2003.
19. Kilpeläinen, R., Taipale, S., Marin, A., *et al.*, "Forming Fabrics," in *Paper Making Science and Technology Part 8, Stock Preparation and Wet End* (H. Paulapuro, Ed.), Gummerus Printing, Jyväskylä, 2000, p. 253.
20. Reichel, W., *Wochen. Papierfabr* 125(13): 649 (1997).
21. Herminghaus, S., *Europhys Lett.* 52(2): 165-170 (2000).
22. Barthlott, W., and Neinhus, C., *Planta* 202(1): 1-8 (1997)
23. Silanter, M., M.Sc., thesis, Helsinki University of Technology, 1997.
24. Paulapuro H., "Wet pressing," in *Paper Making Science and Technology Part 8, Stock Preparation and Wet End* (H. Paulapuro, Ed.), Gummerus Printing, Jyväskylä, 2000, p. 284.
25. "Savcor Microbiological AntiFouling—solution for improving paper process performance," Savcor Group Ltd. Oy, August 2005, http://www.savcor.com/process/maf.php.
26. Abd-El-Kader, H., and El-Raghy, S.M., *Corrosion Science* 26(8): 647(1986).
27. Gervasio, D., Song, I., and Payer, J.H., *J. Applied Electrochemistry* 28(9): 979-992 (1998).
28. Fujishima, A., Rao, T.N., and Tryk, D.A., *J. Photochemistry & Photobiology, C: Photochemistry Reviews* 1(1): 1-21 (2000).
29. Kolari, M., Ph.D. thesis, University of Helsinki, 2003.

Received: December 27, 2004
Revised: May 1, 2005
Accepted: June 15, 2005

This paper is also published on TAPPI's web site <www.tappi.org> and summarized in the October *Solutions! for People, Processes and Paper* magazine (Vol. 88 No. 10).

INSIGHTS FROM THE AUTHORS

We decided to pursue this line of research because fouling in the paper machine is not a very studied field scientifically. Also the financiers of our research group had interest in this topic.

Our research with Dr. Juha Kekkonen was the first time that the adsorption of fouling substances on solid surface was studied. There are some studies related to fouling, but the interactions between solid surfaces and process water substances had not been studied.

Fouling in a paper machine is an extremely complex phenomenon. Therefore, we had to use some simplifications when we designed our experiments. This was the most challenging aspect of the research.

According to our studies, the fact that paper mills do foul is not a surprise. On the contrary, I sometimes wonder why paper mills don't experience even more fouling than they do today. The conditions in paper mills are ideal for fouling, and yet in some cases mills can run months without any particular problems with deposits.

The results we have achieved through this research can help papermakers understand problems with fouling and to resolve those problems. These results can also be used when antifouling paper machine parts are designed for a paper machine. Continuing industry research is exploring the development of antifouling paper machine parts and paper chemicals (AKD, ASA etc.) that foul less.

Kallio

Kallio is with the Dept. of Forest Products Technology, Laboratory of Forest Products Chemistry, Helsinki University of Technology, P.O. Box 6300, Vuorimiehentie 1, Espoo, FIN-02015 HUT, Finland; Kekkonen is with J.M. Huber Finland Oy, Telakkatie 5, FIN 49460 Hamina, Finland. Email Kallio at Timo.Kallio@hut.fi.

Kekkonen

COMING NEXT MONTH IN *TAPPI JOURNAL*:

Laboratory- and mill-scale study of surfactant spray flotation deinking

by Greg DeLozier, Yulin Zhao, Yulin Deng, David White, Junyong Zhu, and Mark Prein As the cost of quality waste paper continues to escalate, loss of saleable fiber within flotation rejects becomes both environmentally and economically unacceptable. The ability of surfactant spray technology to reduce fiber loss without detriment to pulp brightness gains has been demonstrated during both laboratory- and pilot-scale flotation deinking investigations. This paper documents the successful transfer of this technology to a single flotation unit within the deinking line of a mill producing newsprint from 100% secondary fiber. Initial results suggest that the loss of fiber across the unit was reduced by more than 50% without obvious detriment to final pulp quality.

Effect of thermal treatment on the structure of PCC particles

by P. Ferreira, J. Velho, M. Figueiredo, and A. Mendes Controlled combustion of paper is usually used to determine filler content, but it can also be a valuable tool to isolate the mineral particles for extra characterization and/or additional applications. However, it is known that the ashing temperature greatly affects the filler particles. This paper provides an analysis of the thermal treatment on the PCC particles structure, and evaluates the potential of the ashing method to isolate these particles from filled papers.

Production experience with curtain coating for woodfree coated paper

by Michael Trefz and Uwe Fröhlich For a long time, papermakers have been dreaming of non-impact coating: applying a perfect layer of coating on the surface without any mechanical impact on the paper. Curtain coating is now opening new possibilities for coated papers. The target of the trial presented here was to produce a single coated (C1S), glossy woodfree paper (70 - 80 g/m^2) with a curtain coater. Different coat weights were applied to evaluate their influence on the final quality. The work also included a variation of the base paper roughness, achieved with different levels of pre-calender line load. The coating color used for the trial was a blend of fine calcium carbonate and clay with a SB-latex. In a series of pre-trials on a pilot coater, the optimum solids content and viscosity were confirmed for the curtain coater. After coating, the produced rolls were calendered on a pilot multinip calender and heatset offset printed in a commercial printing shop. A blade coated paper was printed as a reference. Results with the curtain coated paper showed that a quality similar to blade coated paper can be achieved, demonstrating the applicability of the curtain principle for graphic paper grades.

PLUS: How polymers strengthen filled papers; exclusive Author Insights, and more. **www.tappi.org**