

Chatter and Soft Tissue Production: Process-Driven Mechanisms

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ABSTRACT

Chatter is a creping process abnormality that can result in a loss of sheet integrity, increased waste, and, in severe cases, damage the Yankee dryer surface. In this paper, a number of process and operational conditions are reviewed that can lead to the initiation and propagation of doctor blade vibration and chatter. A basic review of Yankee coating characteristics, vibration mechanisms, and force dynamics help describe what happens at the tip of the doctor blade. Examples of sheet, coating, and Yankee dryer surface chatter are presented. Studies are reviewed that illustrate how variation in process conditions can result in the appearance of chatter and how this condition can be minimized.

INTRODUCTION

The tissue industry continues to be challenged by the marketplace to improve product quality and reduce manufacturing costs. To accomplish these goals, a number of process changes have been adopted that directionally lead to product and process improvements. In the Light Dry Crepe (LDC) process, some of the changes have led to the evolution of "chatter."

Chatter is a term used by tissue makers to describe the appearance of cross-direction defects in the sheet, marks in the Yankee coating, and, in severe cases, grooves in the metallic surface of the Yankee dryer (See figures 1, 2 a and b, and 3 a and b).

Chatter in tissue making is caused by out of plane movement related to vibration of the tip of the creping doctor blade. This vibration can be mechanically or process-induced. Traditionally, studies have focused on mechanically-induced, harmonic, or sympathetic vibration caused by external stimulation. The vibrations are generally classified as one of three types (Figure 4) (Naterwalla 2007):

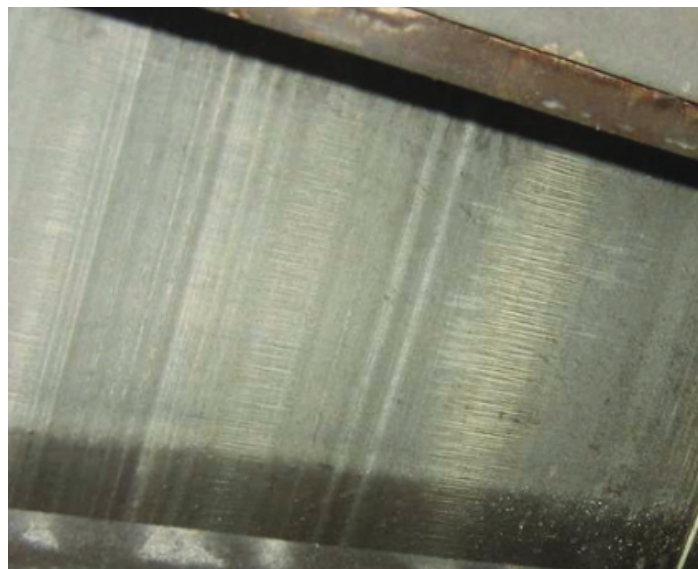


Figure 2a - Bands of coating chatter

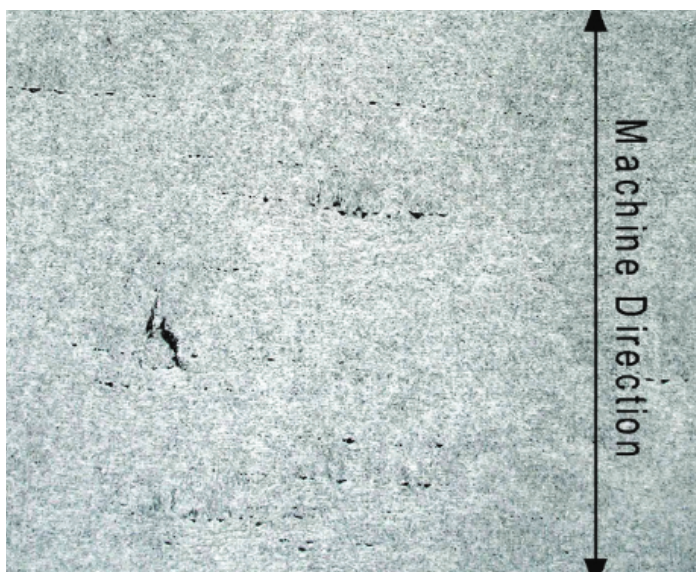


Figure 1 - Sheet chatter



Figure 2b - Full-field coating chatter

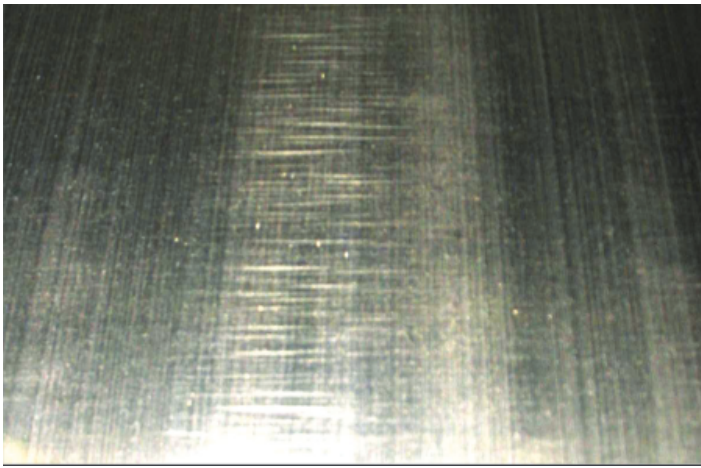


Figure 3a - Band of dryer surface chatter

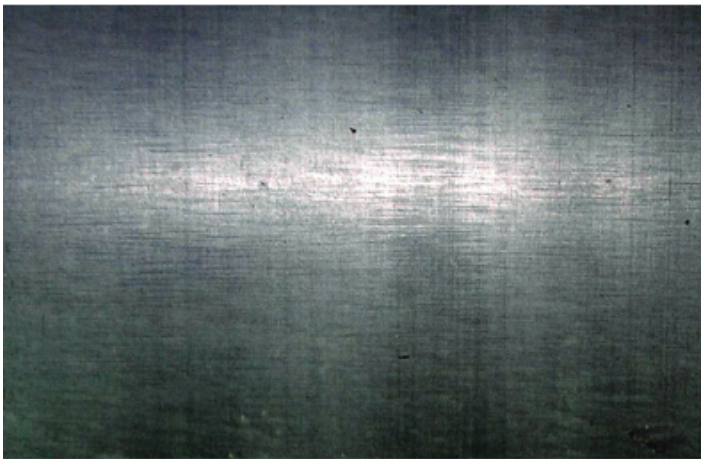


Figure 3b - Full-field dryer surface chatter

1. **Free Vibration** - Related to the natural, characteristic vibration of the system. It needs an initial impact, but the amplitude decays with time.
2. **Forced Vibration** - Dependent on an external exciting force (i.e., an unbalanced shaft). The frequency and amplitude of motion are dependent on the characteristics of the external source.
3. **Self-Excited Vibration** - Occurs when a steady input of energy is converted into movement that has characteristics of frequency and amplitude. The amplitude increases with time.

A general equation of motion has been presented that characterizes vibration, $F\sin(t)$, at the tip of the doctor blade utilizing a mass of the system, m , a dampening constant, c , a stiffness factor, k , and a displacement, x , relative to a specific time, t . (Corboy 2003, Apple 2007)

$$F\sin(t) = m(dx^2/dt^2) + c dx/dt + kx \quad (Eq. 1)$$

This equation helps the tissue maker understand the critical factors related to sympathetic and/or harmonic vibration. The impact of process-driven self-excited vibrations are also defined by this equation. Should the doctor blade tip be caused to move out of plane a specific distance, x , a characteristic vibration will develop. If the amplitude of the vibration is sufficient, chatter can

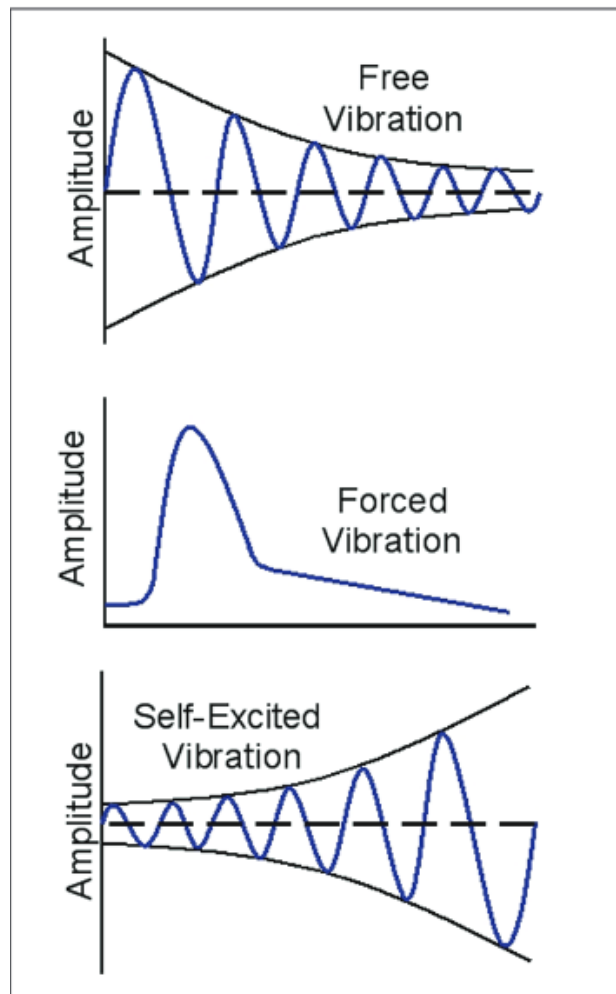


Figure 4 - Three types of vibrations

occur on the dryer surface.

Although many occurrences of chatter have been directly related to excessive mechanically-induced vibration, a significant number have been related to process changes. These changes are generally related to softness improvement and productivity initiatives. Typically they include:

- Increasing machine speeds
- Creping at lower moisture
- Higher adhesion creping
- Use of functional chemical additives

These process shifts can have a direct impact on the characteristics of the Yankee coating. The Yankee coating is the interface between the doctor blade tip and the Yankee dryer surface. Changes in its characteristics will significantly impact creping dynamics. If specific creping forces reach a critical level, the doctor blade tip can start to vibrate at higher and higher amplitudes. This movement can lead to generation of chatter marks in the coating, the sheet, and on the Yankee dryer surface. Generally, this process is progressive. If chatter is observed in the sheet, or the coating, it is probable that these conditions will escalate to a point where Yankee damage may occur. Corrective actions should be taken as soon as possible.

DYNAMICS OF PROCESS- INDUCED CHATTER

The System

Chatter occurs at a discrete location in the process - the tip of the doctor blade in contact with the Yankee surface. Figure 5 helps with orientation and defines system elements around the doctor blade tip. As shown in the figure, the tip of the doctor blade normally travels in a softer layer of coating below the sheet, and is supported by harder layers of coating resident next to the dryer surface. Supporting and opposing forces determine the exact position and travel of the doctor blade tip in the coating. These forces include:

- The normal force, N , of the blade to the Yankee surface.
- The force of the rotating dryer pushing the coating and sheet into the doctor blade. This causes the doctor blade tip to shear through the coating and can be called "Effective Tip Movement".
- The tangential resistance is a function of a number of process conditions, including the characteristics of the Yankee coating and adhesion of the sheet to the dryer, as described in Eq. 2.

It should be noted that, although, chatter is due to out of plane movement and vibration of the blade tip, the process change that drives this phenomenon could originate at any point in the tissue making process.

TANGENTIAL RESISTANCE →

$$f[(\mu_k F_N), (m\Delta v), G', C_x, P] \quad (\text{Eq.2})$$

Where:

F_N = normal force of the doctor blade tip

$-\mu_k$ = coefficient of kinetic friction, dependent on surface characteristics

$-m$ = mass of coating material, m_c , and sheet, m_s , on the dryer. The mass associated with the sheet is a function of basis weight and a sheet adhesion factor, A , (0 to 1). Here, $m = (m_c + m_s A)$

$-v$ = surface velocity of Yankee moving the coating and sheet into contact with the tip of the creping doctor blade

$-G'$ = elastic behavior of the coating developed on the Yankee at the current velocity

$-C_x$ = tendency of the coating adhesive to become hard or react with other chemistries in the process

$-P$ = pocket angle, $P = (90 - \theta + \alpha)$

PROCESS-DRIVEN MECHANICS

In the creping process, the tip of the doctor blade rides in the Yankee coating in a relatively stable manner. Although some out of plane movement is normal, the amplitude is minimal. Optimization of the creping process is accomplished by controlling mechanical elements around the doctor blade tip and managing the three-dimensional characteristics of the Yankee coating (Stitt 2005). Elimination of conditions that lead

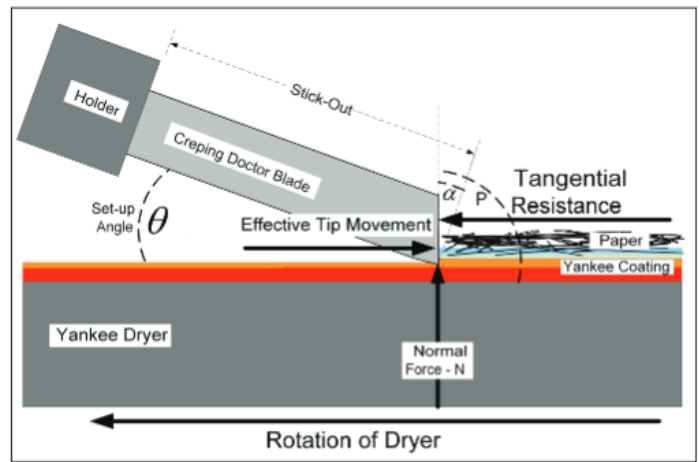


Figure 5 - The system of interest when defining chatter

to hard coatings, excessive vibration, and chatter is critical to the optimization of the creping process. The following mechanistic model can be very useful in understanding how process conditions can lead to the appearance of chatter:

1. Process conditions develop that cause changes to the viscoelastic properties of the Yankee coating – the coating becomes harder. The total tangential resistance increases as coating modulus and friction increase. As total resistance increases, a point is reached where a phenomenon known as "stick-slip" begins (McMillian 1997) (Figure 6 a-d). It is important to realize that these conditions can develop in localized discrete areas, be in defined circumferential bands, or on the entire Yankee dryer surface.

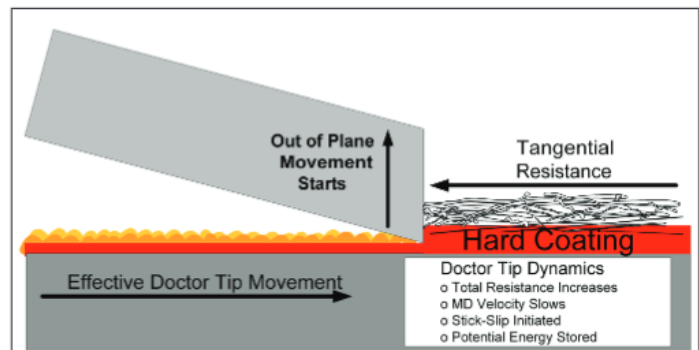


Figure 6a - High resistance to MD movement encountered

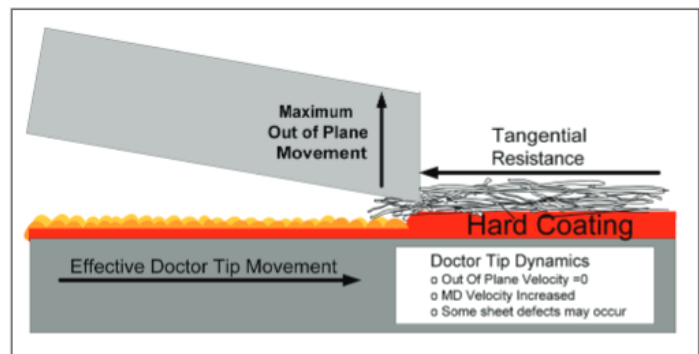


Figure 6b - Blade tip rises away from dryer surface

2. The blade tip can no longer traverse evenly through the coating, and the velocity in the machine direction (MD) drops toward zero. At this point, the blade becomes "stuck" (Figure 6a).
3. The force imposed by the rotating Yankee reaches a point that exceeds the static "stuck" condition. The tip of the doctor blade will either lift out of the coating plane or push through the hard coating, removing it. If the coating material is sufficiently hard, the blade tip rises out of the coating plane, following the path of least resistance. As the blade tip rises, the pressure (psi) at the blade tip drops and potential energy is stored ($\frac{1}{2} kx^2$, where k is a stiffness factor, and x is displacement). Velocity of the tip in the MD increases (Figure 6b).
4. When the doctor blade tip reaches its maximum elevation, out of plane velocity drops to zero. The blade tip then accelerates back toward the Yankee surface. The stored potential energy changes to kinetic energy ($\frac{1}{2} mv^2$, where m is the mass of the blade and holder and v is the downward velocity). The impact force, F_i , (Eq. 3), of the doctor blade tip is sufficient to penetrate the Yankee coating (Figure 6c).

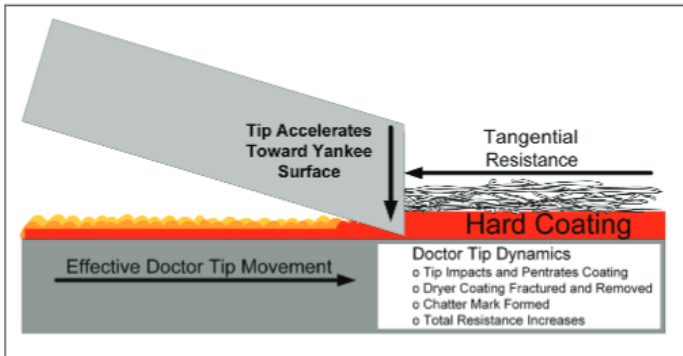


Figure 6c – Blade tip moves back toward surface, penetrating Yankee coating

$$F_i = m \, dv/dt$$

Where: (Eq. 3)

m = mass of the door system

dv = change of velocity at the doctor blade tip as it comes in contact with the Yankee dryer

dt = time of a single contact event to come to zero velocity

5. The increased downward speed at the tip of the doctor blade and the short impact time causes the coating to appear very hard and brittle. The molecular network of the coating does not have sufficient time to absorb and distribute the energy. The coating fractures and chips away from the Yankee surface. Normally, the coating is thick and hard enough near the dryer surface to resist penetration and protect the Yankee. Although some of the energy is absorbed by the coating and the Yankee surface, a significant portion is converted and dissipated as heat and/or sound.
6. As the blade tip penetrates deeper into the coating,

tangential resistance increases dramatically, leading to stick-slip-induced cyclic movement or vibration. If this induced vibration frequency, f_s , and the natural vibration frequency, f_n , (Eq. 4) of the system are synchronous (Eq. 5), a high amplitude, resonant, and self-excited vibration can develop. The increased amplitude at the doctor blade tip will result in increased cyclic impact forces on the Yankee dryer surface and, eventually, chatter.

$$f_n = (1/2\pi) \sqrt{k/m} \quad (\text{Eq.4})$$

$$f_s/f_n = 1 \rightarrow \text{Can lead to chatter} \quad (\text{Eq.5})$$

Where:

f_s = the induced vibration due to stick-slip

f_n = the natural frequency of the system (Hz)

k = doctor blade stiffness

m = the mass of the system

7. This process repeats (Figure 6d) as long as the Yankee coating is hard enough and tangential resistance is high enough to support the tip movement. Occasionally, process conditions will develop that result in impact forces sufficient to cause tip penetration of the entire Yankee coating. When this occurs, the doctor blade will strike the metallic surface of the Yankee dryer. If the impact force is sufficiently high, the Yankee surface can be damaged, as metal is removed in a cross-direction groove shape (chatter). The normal force (pressure) exerted by the doctor blade tip on the Yankee surface during routine operations ranges between 1,000 - 5,000 psi (6.9 - 34.5 MPa), with spikes at doctor blade changes to 15,000 - 20,000 psi (103 - 138 MPa), or greater. The impact force, F_i , of the blade on the Yankee surface during tip vibration, that leads to chatter, can be estimated to exceed 200,000 psi (1379 MPa).

The coating characteristics that lead to process-driven chatter usually do not self-resolve. In this condition, the doctor blade tip can no longer traverse evenly through the coating. Damage to the Yankee dryer surface usually results from excessively hard adhesive Yankee coatings. These coatings cause high frictional forces and tangential resistance at the doctor blade tip, which amplify the stick-slip phenomenon. Additional Yankee surface chatter can develop with each rotation. If the tip of the doctor blade catches the trailing edge of a previous chatter mark, the energy within the system can amplify out of plane movement. The resulting impact force can be very high. Often, this forced movement is followed by a period of free vibration. Chatter marks generally increase in size and number. In a typical tissue making operation, this process is repeated millions of times. Process reliability issues or Yankee damage can and will occur if the process is not modified or adjusted.

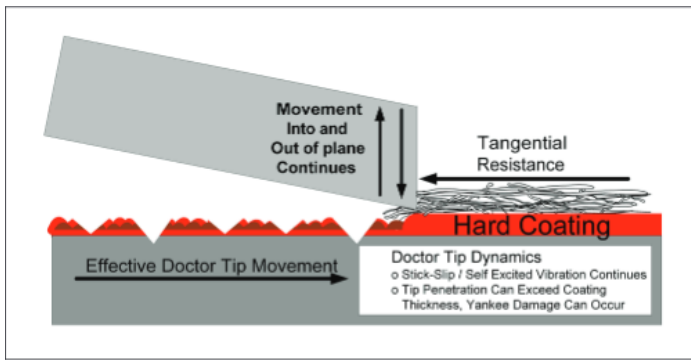


Figure 6d – Stick-slip cycle is repeated, resulting in chattered dryer surface

PROCESS CONDITIONS THAT LEAD TO HARD COATINGS AND YANKEE CHATTER

Machine Speeds

Ever since tissue machines were invented, manufacturers have continually attempted to run faster and more efficiently. Some modern light dry crepe (LDC) machines operate with Yankee speeds in excess of 6500 fpm (1980 mpm). A number of process conditions have changed as a result of increasing machine speeds to improve productivity. Dwell times around the Yankee have in general decreased. Of particular importance to creping was the decrease in dwell time between the spray boom and the suction pressure roll (SPR). This has resulted in less time for coating stabilization prior to sheet lamination at the SPR nip. Yankee coating packages have changed to meet these needs. Customized multi-component coating systems are very popular and are optimized for each machine's unique operating conditions (Archer 2005). Generally, this requires faster film formation and stabilization while still providing appropriate adhesive and viscoelastic properties. Additional drying capacity is required to match increased productivity. Yankee dryers are running at 120 - 130 psi (827 - 896 kPa) and hoods are consistently running between 850° and 950°F (450° - 510°C). Steam showers are in common use to improve creped sheet moisture profiles and increase total drying capacity. Temperatures on the surface of the dryer have increased. Reduced dwell times, increased temperatures, and chemical changes in the adhesive can lead to coatings that become hard and/or variable during normal operations. The creping operating window becomes smaller.

Changes in Yankee coating characteristics have been observed as tissue machines operate at higher speeds. Typically, the coating behaves as if it is harder. Normally, a loss of sheet control is noticed that appears to be related to a loss of adhesion. Coating chatter has developed in some operations. Laboratory explorations (Furman 2004) utilizing shear storage modulus, G' , as a coating hardness indicator (Figure 7) confirms the machine observations. These studies show that G' of the Yankee coating increases with an increase in test frequency. The coating behaves as if it is harder. In the test procedure, increasing frequency is analogous to increasing Yankee speed. This data is consistent with earlier Time Temperature Superposition (TTS) studies that showed similar shifts in the modulus of polymers with increased testing frequency (Van Gurp 1998, Ferry 1980).

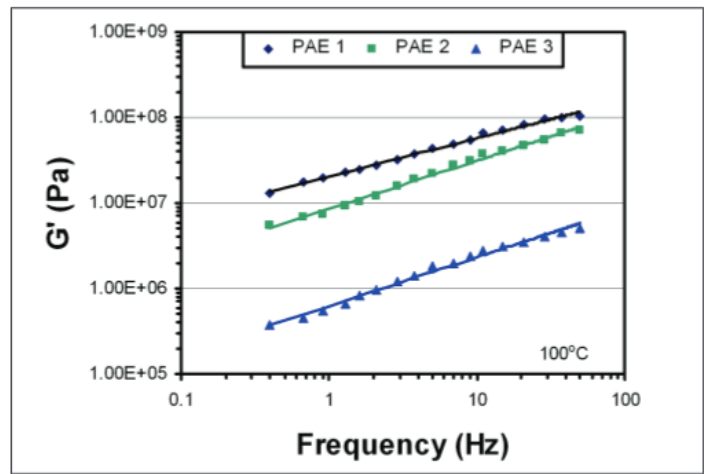


Figure 7 – Impact of Yankee speed (frequency) on shear storage modulus, G' , of a PAE coating (Furman 2004)

As noted in Eq. 2, increases in G' and velocity, v , can result in higher tangential resistance. G' increases as internal resistance, or friction develops within the coating. Generally, the resistance of the coating follows non-Newtonian behavior and appears to be pseudoplastic at higher speeds. Velocity increases the force exerted on the doctor blade by the mass of the coating and sheet through Newton's second law, $F=ma=m\Delta v$. The change in coating characteristics and the impact of the coating on the doctor blade tip cause the increase in tangential resistance. Eventually, a point is reached where stick-slip movement at the doctor blade tip occurs, resulting in vibration and formation of chatter.

Low Moisture, High Adhesion Creping

Lower moisture creping usually results in higher sheet and Yankee surface temperatures. The higher temperatures drive off additional moisture in the sheet and Yankee coating. Yankee coating characteristics change as moisture content decreases. Lower moisture containing coating materials have higher glass transition, T_g , and G' values (Figures 8 and 9) and appear harder and more brittle (Furman 1993). Thermosetting Yankee coatings cross-link to a higher degree, while other materials dehydrate on the Yankee surface. Natural cellulosic materials dehydrate and become harder. Inorganic materials that precipitate from inter-fiber water become part of the coating (Oliver 1980, Furman 2007). The Yankee coating composite that develops on the dryer surface is noticeably harder and has a higher degree of internal friction. Tangential resistance at the doctor blade to movement through the coating increases.

Typically, tissue makers will change the coating package composition to increase the adhesion of the sheet to the Yankee dryer. A common strategy is to increase the amount of the adhesive applied through the spray boom, while decreasing the amount of release and/or modifier. Often, total add-on rates are also increased. The resulting shifts in the coating package favors sheet adhesion, but can result in a harder coating. With increased adhesion, more cellulosic debris and inorganic materials are integrated into the matrix. Figure 10 demonstrates the impact that different coating components can have on G' .

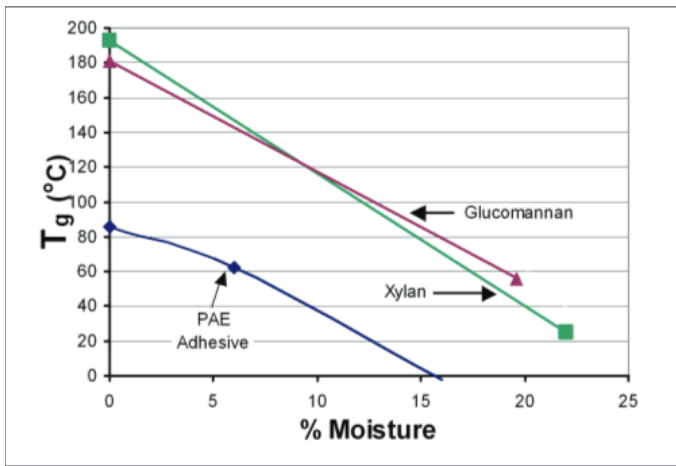


Figure 8 – Impact of moisture on coating T_g (Furman 1993)

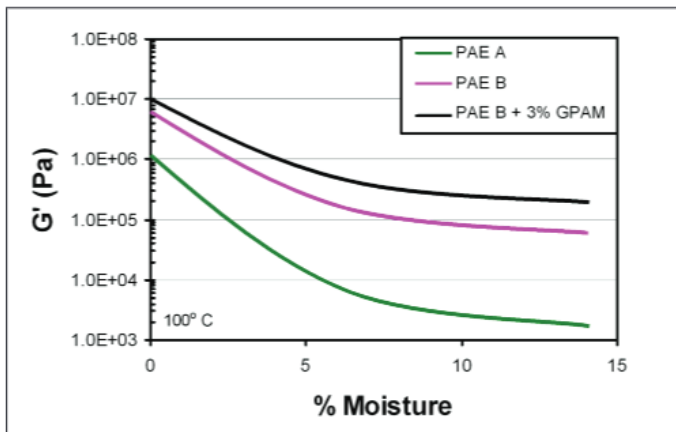


Figure 9 – Impact of moisture on shear storage modulus, G' , of a PAE coating

A common problem that occurs during low moisture, high adhesion creping is the appearance of hard deckle edge deposits and bands. These deposits can result in chatter in the sheet, coating, and on the Yankee dryer surface. Higher temperatures, at the deckle edge of the sheet, force coatings to thermoset and/or dehydrate faster. Over time, these deposits build in size, both in cross direction and out of plane. Cross-direction deposits can eventually penetrate under the trim and move into the sheet area. If this happens, it is possible to experience edge cracks and loss of deckle edge sheet control. Out of plane deposits can become very thick and hard. As the deposit builds, the doctor blade tip rides further away from the Yankee surface. This lifting of the blade effectively reduces doctor loading in adjacent areas. Stick-slip dynamics, caused by the hard edge deposit, lead to excessive vibration and coating chatter. Coating chatter in these deposits serves as a template, causing sympathetic vibration and chatter to appear in adjacent areas or across the doctor blade.

Functional Chemistries

Achieving functional properties in bath tissue products sometimes requires the use of unique chemical additives. A good example of this is the use of Temporary Wet Strength (TWS), glyoxylated poly-acrylamide resins. TWS resins are used to increase the short-term wet tensile strength of bath tissue

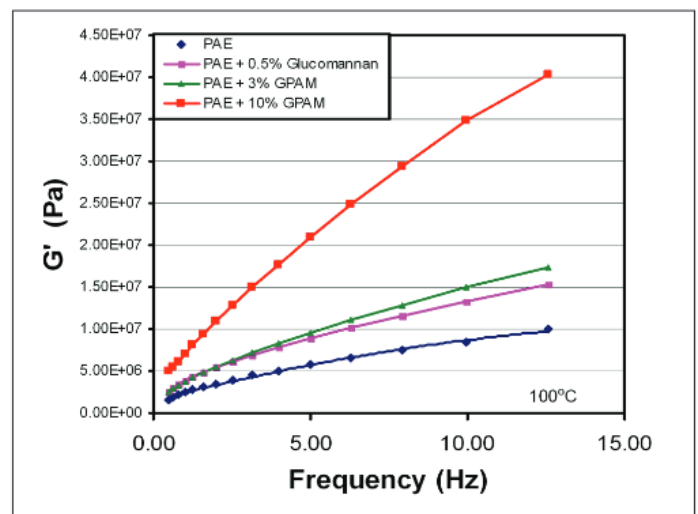


Figure 10 – Impact of composition on shear storage modulus, G' , of a PAE coating

products. With increased wet tensile strength, the tissue strength maker has the option of decreasing the total dry tensile strength of the product while assuring the product will function as intended. By reducing tensile, the tissue maker will observe a reduction in stiffness. The tissue will appear softer.

TWS resins are introduced into the stock approach system prior to the headbox. Some of the material attaches to long fibers as intended, while a portion becomes associated with fines, colloids, and dissolved contaminants. The sheet is formed, transported, and transferred to the Yankee for drying prior to being creped. During the drying process, some of the TWS resin-laden fines and colloidal materials migrate through the sheet due to the Dreshfield effect, and become a part of the coating (Furman 2007). TWS materials that migrate to the surface of the dryer can chemically react with Polyaminoamide Epichlorohydrin (PAE) adhesive materials that were applied through the spray boom. This reaction between TWS and PAE resins can form a coating with a high-crosslink density that tends to become harder and less adhesive. Laboratory studies validate what is observed in the field. Figures 9, 10, and 11 illustrate the impact of a typical TWS additive on commercial PAE adhesives. In Figure 11, note that the adhesive peel force decreased while G' increased significantly. Both results are consistent with a harder coating. If these conditions persist, the coating can become very hard. Tangential resistance at the tip of the blade can increase to a point where stick-slip motion is initiated and chatter is observed on the Yankee surface.

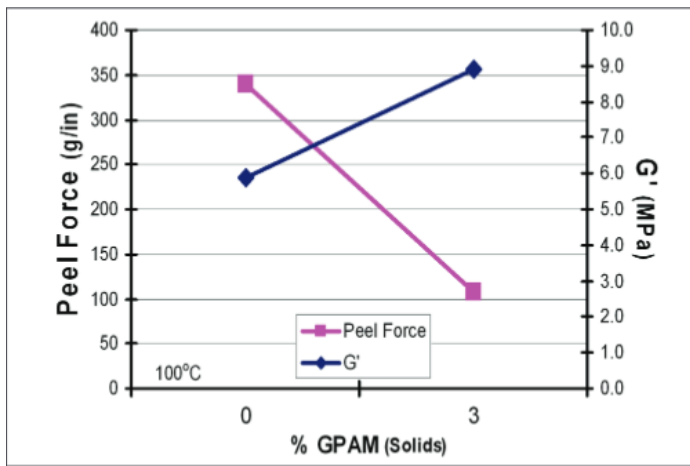


figure 11 – Impact of temporary wet strength on peel force and shear storage modulus, G' , of a PAE coating

MANAGING TO MINIMIZE THE OCCURRENCE OF CHATTER

Process conditions and variation can result in chatter on the Yankee dryer. Unfortunately, there is no single actionable solution that will prevent its appearance. There are, however, a number of directional moves that will minimize the occurrence of chatter and Yankee damage. These moves can be implemented alone or in combination, but will require rigorous monitoring to evaluate the impact on the process. If the issue is a minor appearance of coating chatter, small changes may be appropriate. In contrast, if chatter appears in the metallic surface of the Yankee dryer, a more aggressive action plan is advisable. In either case, the appearance of chatter should be taken very seriously.

General Action Plans

- Reduce variation throughout the tissue making process – this is critical to minimizing the impact of any of the process changes discussed above.
 - Conduct a full machine audit to identify both mechanical and process variation that could result in the observed incidence of chatter.
- Develop and implement a plan focused on reducing variation related to the appearance of chatter on the Yankee surface.
- Monitor the Yankee dryer and doctor blades to identify the occurrence of coating or Yankee chatter.
 - Visually observe the surface of the Yankee dryer with a timed strobe light. Note the appearance and characteristics of any coating chatter present.
 - Consider use of vibration and thermographic monitoring technologies to identify conditions that lead to excessive vibration.
 - Monitor doctor blade wear rate and CD variability as an indicator of Yankee coating characteristics.
- Characterize creping system mechanics
 - Evaluate the stiffness potential of existing Yankee doctor holders and strong backs.

- Evaluate the damping potential of mechanical elements. Consider shifting from pneumatic loading cylinders to hydraulic systems around the Yankee.

Process-Driven Action Plans

These are focused on at either managing the current operating conditions or changing coating characteristics to open the operating window.

- Optimize creping doctor set-up and operation
 - Stiffen the creping doctor blade – This tends to reduce the out of plane movement due to the “stick-slip” phenomena, while at the same time, forces the blade through some harder coating materials that will develop on the dryer. If vibration does occur, the amplitude will be reduced but frequency will increase.
 - Reducing the doctor blade stick-out to thickness ratio will stiffen the doctor blade and can be tried very easily.
 - Increasing the doctor blade loading effectively stiffens the system. This should only be attempted if it is believed that there is sufficient “acceptable” coating on the dryer. Coating add-on strategies should be reviewed and adjusted to fit this operating condition.
 - Consider an adjustment or replacement of components to increase the stiffness of the creping doctor assemblies.
- Increase the set-up angle (θ in Figure 5) – Changing this angle results in more aggressive removal and management of harder Yankee coatings. Care should be taken with this approach, as it is likely that stick-out, bevels, and loading may need to change. Doctor blade wear should be monitored and coating type and add-on strategies adjusted.
- Optimize Yankee coating characteristics
 - Soften the Yankee coating – Typically, the quest for tissue softness and higher speed results in harder coatings. If there is sufficient coating on the dryer, but it appears to be too hard, a change in coating package composition would be advisable.
 - For slight shifts in characteristics and optimization of existing coatings, consider using softening modifiers. Avoid materials that tend to separate from the adhesive/coating matrix (release oils). At higher temperatures, these materials tend to lead to development of non-uniform three-dimensional coatings with very hard surfaces just below the sheet-coating interface. Instead, utilize modifying materials that tend to remain evenly distributed in the coating (Furman 2004, Grigoriev 2005). These materials are more efficient in attenuating formation of harder coatings due to higher temperatures on the Yankee dryer surface.
 - For significant shifts in process capability, consider a change to a softer non-thermosetting adhesive platform. Have appropriate modification technologies and resources available for process optimization (Archer 2005).

- Eliminate edge deposits
 - Consider use of appropriate edge deposit control technologies. These can be mechanical, chemical, or a combination of the two (Archer 2006). By minimizing edge deposits, breaks and edge-induced chatter can be reduced.

CONCLUSION

The pursuit of increased production and improved quality will predictably continue. Softness and productivity improvements can be achieved with changes to existing processes. However, some of these changes have been associated with a stick-slip phenomenon and vibration at the tip of the doctor blade. Excessive vibration can develop and lead to appearance of chatter on the Yankee surface. A number of process modifications have been reviewed to minimize the occurrence of chatter and its impact on machine operations and stability.

REFERENCES

- Apple, Chan Lok Shun, www.personal.cityu.edu.hk/~bsapplec/forced.htm.
- Archer, S. Furman, G., Llanos, C., "Coating Space – A 3-D View of Creping Cylinder Coatings," Associacao Brasileira Tecnica de Celulose e Papel Conference, ABTCP, Brazil, October 2005.
- Archer, S., Furman, G., Daily W., "Creping Optimization – Look One Step Back," Tissue World Americas Conference, Miami, Florida, March 2006.
- Archer, S., Furman, G., "Method for Targeted Application if Performance Enhancing Materials to a Creping Cylinder," US 7,048,826 B2, May 23, 2006.
- Corboy, W., "Vibration Induced Yankee Surface Wear – An Overview of Chatter," Tissue World Conference, Nice France, March 27, 2003.
- Ferry, J., "Viscoelastic Properties of Polymers," Wiley, New York, 1980.
- Furman, G., Su, W., "A Review of chemical and physical factors influencing Yankee dryer coatings," Nordic Pulp and Paper J., Vol. 8 no. 1, 217-222, 1993.
- Furman, G., Grigoriev, V., Su, W., Kaley, C., "Effects of Modifying Agents on Adhesive Film Properties – Findings Toward Improved Yankee Coatings," Tissue World Americas Conference, Miami, Florida, September 2004.
- Furman, G., Phillips R., Archer, S., "Wet End Impacts on Creping – Part 1 – The Effect of Retention Aids on Yankee Coating," Tissue World, Nice France, March 2007.
- Grigoriev, V., Cloud, R., Furman, G., Su, W., "Development of New Methods for Characterizing Yankee Coatings," 13 th Fundamental Research Symposium, Cambridge, UK, September 2005
- McMillian, A., "A Non-Linear Friction Model for Self- Excited

Vibrations," Journal of Sound and Vibration, 205(3), 323-335, 1997.

Naterwalla, U., "Chatter-Free Milling and Optimized Material Removal," Ingersoll Cutting Tool Co., [http:// www.mmsonline.com/articles/article_print1.cfm](http://www.mmsonline.com/articles/article_print1.cfm), 2007.

Oliver, J., "Dry creping of tissue paper – a review of basic factors," Tappi, Vol. 63, No 12, 91-95, December 1980.

Stitt, J., "Every Yankee Has Its Coating," Tissue World, April-May 2005, pp. 22-26.

Van Gorp, M. "Time Temperature Superposition for Polymeric Blends," www.rheology.org/sor/publications/rheology_b/jan98/van_Gorp&Pallmen.PDF, Jan 1998

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