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#### OPTIMAL CONDITIONS FOR LAMINATING AND ADHESION OF WAX-BASED HOT MELT COATINGS ON PAPER.

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#### ABSTRACT

Wax based hot melts used for food packaging are blends of paraffin waxes, microcrystalline waxes and low density polyethylene whose characteristics are adapted to each specific application. The results of differential scanning calorimetry analysis at different cooling rates show that the crystallisation temperature of the polyethylene is a linear function of the logarithm of the rate of cooling. By extrapolating these results to very much greater cooling rates, we have assumed the existence of a critical rate of cooling for which the polyethylene and the paraffin wax crystallise simultaneously. By using finite element methods we have produced a heat transfer model that permits the rate of cooling at all points in the paper hot melt structure to be predicted throughout a manufacturing process.

#### INTRODUCTION

The wrapping of fresh food such as meat and cheese has been using paraffin wax coated paper for a long time. Modern waxbased hot melt coatings give paper the possibility to associate its natural properties of strength and printability with other properties like water and grease resistance, and impermeability to gases and flavours.

Nowadays base papers and hot melts are selected to suit each specific wrapping application. The producers choose the various raw materials and the processing conditions to suit the end use.

Wax based hot melts are often applied on paper by roll coating machines. The coatings are solidified in contact with chrome plated metal chill rolls.

The study of hotmelt coating can be conducted from several points of view. The present paper will be limited to the thermal and crystallising behaviour of hotmelt mixes during rapid cooling. A heat transfer model using finite differente methods permits the study of temperature variations in the thickness of coated papers during the contact with chill rolls.

#### I. COMPOSITION OF WAX BASED HOT MELTS.

Wax based hot melts used for food packaging are blends of paraffin waxes, microcrystalline waxes and polymers in quantities adapted to each specific application. We will point out a few features of each component.

Paraffin waxes are commercialy specified by their melting points. Commercial grades are generally range from 48-50°C to 62-64°C. Their molecular weight distribution depends on the mineral oil origin and from the conditions of distillation.

Paraffin waxes are mostly linear chain hydrocarbons whose molecular weights vary from 320 to 400. Purified paraffin waxes for food contact generally contain less than 0,5% oil. They are colourless in their molten state and hard, brittle, tasteless and odourless in the solid state. Paraffin crystals are macrocrystals (fig. 1). Paraffin waxes in the melting point range from 48°C to 60°C generally have two crystalline states. The orthorhombic state is stable below 40°C, and the hexagonal state is stable between 40°C and the meltirig point.

Microcrystalline waxes in particular contain cyclic and branched hydrocarbons. Their molecular weights vary from 450 to 1200. They are coloured from yellow to brown, they are often plastic and sometimes soft. They become liquid in the temperature range 60 to 95°C. Microcrystalline waxes for food wrapping often have melting points below 80°C and their oil fractions are less than 3%.

There are two types of branched chains:

- iso-paraffins have one or more branches per chain
- cycloparaffins possess a saturated ring.



Figure 1. Crystals of paraffin wax 54-56°C. Cooling rate 4°C/min.

Rings and branches are usually situated near the ends on the main chain. For higher molecular weights it is possible to find more complex chains, with for example several rings or branches on the same molecule. For one molecular weight, the more the chain is branched, the lower is its melting point.

The molecular weight of polymers used to blend with microcrystalline waxes and paraffin waxes varies between about 1,000 to 12,000.

The highest possible coating temperature is in the order of 140°C to avoid the risk of oxidation of the paraffin chains. The maximum viscosity allowed is about 500 mPa.s. The polymer fraction is consequently limited to about 20 %. Polymer addition increases firstly molten and solid adhesion. Secondly it improves gas and vapour barrier properties particularly when the paper is folded. At the same time the water repellency and non-stick properties of paraffin waxes are conserved.

For these reasons two types of polymers are often used in the blends: low density polyethylene (LDPE) and ethylene vinyl acetate (EVA) copolymers. EVA is used in small quantities as adhesion promoters, their polyethylenic fractions co-crystallise with paraffin chains. The melting point of the LDPE is generally 100-110°C.

The size of crystals of a blend of 90 % paraffin wax and 10 % polyethylene is comparable to that of microcrystalline wax (fig. 2).

For the same cooling conditions, crystal size as observed by a cross polarised optical microscope, does not change with the addition of a further 10 % microcrystalline wax.



Figure 2. Crystals of a 90% paraffin wax 10% microcrystalline wax blend. Cooling rate 4°C/min.

#### II. THERMAL ANALYSIS OF HOT MELT WAXES.

#### II.1. Behaviour at low cooling rates.

The cooling enthalpy curve of a paraffin LDPE mix as observed by a differential scanning calorimeter generally has three characteristic peaks (fig. 3):

- the crystalline phase change of paraffin between 15 and 30°C

- the solidification/ crystallisation of paraffin between

30 and 50°C

- the solidification/crystallisation of LDPE between



Figure 3. Thermal analysis of a 90% paraffin wax and 10 % polyethylene blend. Cooling speed 8°C/min.

The position of the LDPE crystallisation is a function of the percentage of polymer present. As the fraction increases so the position approaches that of the pure polymer.

X-ray diffraction analysis reconfirms the expected solid phases as a function of temperature. At 75°C only the LDPE is crystallised. At 40°C hexagonal paraffin is present and at 25°C orthorhombic paraffin is seen, as if it were pure paraffin but with smaller crystals.

Between 90°C and 55°C for a cooling rate of 8°C/min, the hot melt is composed of a solid phase of polyethylene and of a liquid phase of paraffin wax. Under 55°C, paraffin wax crystallises and the hot melt becomes completely solid. However the solid is not homogeneous since the paraffin and polyethylene crystals are separate.

By using viscoelastic analysis we demonstrate a difference between the modulus of a hot melt blend cooled at low

rates and the modulus of the same blend quenched in liquid nitrogen. The speed of chilling has an effect on the crystalline structure, and have also on the rheological properties.

## II.2. The change of polyethylene crystallisation temperature as a function of cooling rate.

The experimentally determined temperature of crystallisation polyethylene is a function of cooling rate (Ref. 1). The same result can be seen for polyethylene, paraffin wax blends?

Table 1 records the crystallisation temperatures of wax blends as determined by differential scanning calorimetry with cooling rates varying from 0.5 to 20°C/min.

Cooling rate (°C/min)	Wax B	Wax C	Wax E	Wax F	Wax G
0.5			87.6		
1	85	85	86	83.7	86.2
5	79.4	78.8,	82.7	77	83
10	77.2	77.3	77.9	76	80.1
20	76.8	76.8	77.1	75.7	77.3

 
 Table 1. Change of the crystallisation temperature of the polyethylene as a function of cooling rate.

Experimentally we find that the temperature of crystallisation varies linearly with the logarithm of the rate of cooling. Figure 4 shows an extrapolation of this observation.

The temperature of crystallisation of paraffin wax is largely independent of the rate of cooling, thus it is represented by a horizontal line in figure 4.



Figure 4. Evaluation of the critical cooling rate of a coating wax.

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The extrapolates of the polyethylene crystallisation meet the paraffin crystallisation line at cooling rates of 800 and 3000 °C/s. These values on the abscissa will be called the critical cooling rate.

When the rate of cooling is lower than the critical value, the solid coating is not homogeneous since the polyethylene crystallises first.

When the cooling rate is greater than or equal to the critical rate, the polyethylene and wax crystallise simultaneously. The molecules of polyethylene are not amalgamated into solid micels. They act as a large number of nucleation centers for potential crystallisation of the paraffin wax. In consequence there are very many, very small crystals which allows the explanation of the different rheological properties as already mentioned.

Crossed polarized light microscopic investigation of a hot melt coating on clear cellophane shows that the surface in contact with the chill roll has a finer crystal structure than the center of the coating where the crystals are larger. The rate of cooling was greater in contact with the chill roll.

#### III. CALCULATION OF HEAT TRANSFER IN HOT MELT COATING.

# III.1. Definition of the key terms in writing the heat flow equations.

The hot melt process comprises two main elements: the laminator and the chiller. The laminator contains the heat source, for this reason it is never in contact with the chiller. The coating of paper can thus be separated in three phases:

- a phase where the hot melt coating is applied to the paper by a coater

- a phase of transit between application and cooling

- a cooling phase.

We will consider the initial time to be the time when the hot melt coating is first applied to the base substrate by the applicator.

In the process of laminating, the two surfaces of the paper are successively put in contact with different parts of the laminating machine. The paper coating exchanges heat with the surroundings into its two surfaces.

We assume that the heat flow to the internal base substrate to be conductive and the external heat flow to be convective. We also assume that the inteface between the coating and the substrate is a flat plane with no penetration into the porous fibrous structure.

The paper coating and the surfaces with which it is in contact are both moving. Consider a coordinate system moving with the web in the plane Oxy on the surface of the coating. The direction Oz is perpendicular and points to the interior of the paper (figure 5).



Figure 5. Coordinate system used for the model of the heat exchanges during wax coeting.

The speed of the elements in the laminating machine are considered to be equal to the speed of the paper. It is assumed that there is no slip and that all thermal transfer in the xy plane is neglegible, thus we consider only transfer in the Z direction.

## III.2. Equations of heat flow for a two layer system and boundary conditions.

Let  $e_c$  and  $e_p$  be the thickness of the coating and the paper respectively. The equations for heat conduction in each of the two layers are:

$$\mathbf{a}_{c} \frac{\delta^{2} \theta_{c}}{\delta z^{2}} - \frac{\delta \theta_{c}}{\delta t} = 0$$
 (1)

and

$$a_{p}\frac{\delta^{2}\theta_{p}}{\delta z^{2}}-\frac{\delta\theta_{p}}{\delta t}=0$$
(2)

where  $\theta_c$ ,  $\theta_p$ ,  $a_c$  and  $a_p$  are the temperatures and thermal diffusivities respectively for the coating mix and the paper.

The thermal diffusivity is of a form given by:

$$a = \frac{\lambda}{\rho C_{p}}$$
(3)

 $\lambda$  is the thermal conductivity of the layer,  $\rho$  the specific gravity and C<sub>p</sub> the specific heat.

At the hot melt coating, paper interface the heat transfer is assumed to be solely by conduction. Thus thermal flux is conserved, the temperatures are the same if the contact resistances are assumed to be zero.

$$-\lambda_{\rm c} \cdot \left(\frac{\delta \theta_{\rm c}}{\delta z}\right)_{z=ec} = -\lambda_{\rm p} \cdot \left(\frac{\delta \theta_{\rm p}}{\delta z}\right)_{z=ec}$$
(4)

and

 $q_{c}(z=e_{c},t) = q_{p}(z=e_{c},t)$  (5)

 $\lambda_c$  and  $\lambda_p$  represent the thermal conductivities of hot melt and paper respectively.

Air temperature is assumed constant at  $\theta_{air}$  and heat loss from the surface of the hot melt coating and the paper are through convection only with radiation assumed to be neglegible. The coefficient of radiation is identical for the two surfaces since it is independent of the material properties. Thus the heat flow equations at the paper-air and the hot melt-air interfaces are given by:

$$-\lambda_{p} \cdot \left(\frac{\delta \theta_{p}}{\delta z}\right)_{z=ec+ep} = \alpha \cdot \left(\theta_{p} \left(z = e_{c} + e_{p}, t\right) - \theta_{air}\right)$$
(6)

$$- \lambda_{c} \cdot \left(\frac{\delta \theta_{c}}{\delta z}\right)_{z=0} = -\alpha_{c} \left(\theta_{c} \left(z = 0, t\right) - \theta_{air}\right)$$
(7)

When the surface of the wax or paper are in contact with a rotating element, it is assumed that the temperature of that is maintained constant at  $\theta_c$ . For neglegible contact resistance the surface temperature of the wax or paper is equal to this temperature.

If the contact resistance, R, is not neglegible, then the thermal equations of the elemental coated layers can be written:

$$-\lambda_{p} \cdot \left(\frac{\delta \theta_{p}}{\delta z}\right)_{z=ec+ep} = R(\theta_{p}(z=e_{c}+e_{p},t)-\theta_{e})$$
(8)

$$-\lambda_{c} \cdot \left(\frac{\delta \theta_{c}}{\delta z}\right)_{z=0} = -R(\theta_{c}(z=0,t) - \theta_{e})$$
(9)

The contact resistance is possibly due to a layer of air of thickness  $e_{air}$  and thermal conductivity  $\lambda_{air}$  between the rotating element and the substrate. Its value is approximately equal to:

$$R = \frac{\lambda_{air}}{e_{air}}$$
(10)

#### III.3. Initial conditions.

At time t=0, the temperature of the base and the temperature of the hot melt can be considered constant throughout their thickness. In this case their are respectively equal to  $\theta_{p0}$  or  $\theta_{c0}$ . When z is in the range  $e_c$  to  $e_c+e_p \theta(z,0)=\theta_{p0}$  and when z is between 0 and  $e_c \theta(z,0)=\theta_{c0}$ .

It is thus possible to define an initial temperature distribution through the thickness of the laminate.

The analytic solution of a system of equations written above is possible, for example by expressing the temperature as a function of Laplace transforms. The solution can be expressed by function of erf(c). The analytic solution of this type of equation is usually aided by a computer. Thus we have chosen to make a programme using numerical methods directly based on the principle of finite differences.

The thickness of the wax coating is devided into layers of thickness  $\Delta z_c$  and the paper into layers of thickness  $\Delta z_p$ . Time is devided into fractions of seconds  $\Delta t$ . The index, i, represents space

and the index, k, represents time. Thus the temperature of the i element at the kth instant would be expressed as  $\theta^{k}_{i}$ .

#### III.4. Expressing the equations in the Finite Difference Notation.

We expressed the second derivative of temperature with respect to z as follows:

$$\frac{\delta^2 \theta}{\delta z^2} = \frac{\theta_{i+1}^k - 2\theta_i^k + \theta_{i-1}^k}{(\Delta z)^2}$$
(11)

And the first derivative with respect to time:

$$\frac{\delta\theta}{\delta t} = \frac{\theta_i^{k+1} - \theta_i^k}{\Delta t}$$
(12)

Take m as the spatial index of a portion of wax at the interface of the coating/paper and n is the spatial index of the last portion of paper.

The wax coating is bounded by the segments with index 1 and m. It follows for  $2 \le i \le m-1$ :

$$\mathbf{a}_{c} \cdot \frac{\boldsymbol{\theta}_{ci+1} - 2\boldsymbol{\theta}_{ci}^{k} + \boldsymbol{\theta}_{ci-1}^{k}}{(\Delta z_{c})^{2}} - \frac{\boldsymbol{\theta}_{ci}^{k+1} - \boldsymbol{\theta}_{ci}^{k}}{\Delta t} = 0$$
(13)

The substrate is bounded by the segments with index m+1 and n. It follows for m+2 $\leq$ i $\leq$ n-1:

$$a_{p} \frac{\theta_{p_{i+1}}^{k} - 2\theta_{p_{i}}^{k} + \theta_{p_{i-1}}^{k}}{(\Delta z_{p})^{2}} - \frac{\theta_{p_{i}}^{k+1} - \theta_{p_{i}}^{k}}{\Delta t} = 0$$
(14)

The temperatures of the wax segment at m and the substrate at m+1 are equal. Furthermore the thermal fluxes are equal. It follows:

$$\theta_{cm}^{\ k} = \theta_{p_{m+1}}^{\ k} \tag{15}$$

and

$$-\lambda_{p} \frac{\theta_{p_{m+2}}^{k} - \theta_{p_{m+1}}^{k}}{\Delta z_{p}} = -\lambda_{c} \frac{\theta_{c_{m}}^{k} - \theta_{c_{m-1}}^{k}}{\Delta z_{c}}$$
(16)

In the case where the substrate or coating are in contact with a rotating element with no contact resistance, their surface temperatures are equal to the temperature of the rotating element.

In the case of contact with air, it follows, at the substrate surface (i=n):

$$-\lambda_{p} \frac{\theta_{p_{n}}^{k} - \theta_{p_{n-1}}^{k}}{\Delta z_{p}} = \alpha . (\theta_{p_{n}}^{k} - \theta_{air})$$
(17)

and at the coating surface (i=1):

$$-\lambda_{c} \cdot \frac{\Theta_{c2}^{k} - \Theta_{c1}^{k}}{\Delta z_{c}} = -\alpha_{c} (\Theta_{c1}^{k} - \Theta_{air})$$
(18)

In the first phase of coating, the wax hot melt is in contact with the coating head thus the temperature is assumed constant and equal to  $\theta_{ce}$ . For all k≥1,

$$\theta_{c1}^{\ k} = \theta_{ce} \tag{19}$$

The non coated face of the substrate is initially in contact with ambient air or with a rotating element. The initial temperature of the substrate and the coating can be considered to be constant in the z direction. If we assume constants, for all  $2 \le i \le m$ :

$$\theta_{ci}^{1} = \theta_{c0}$$
 (20)  
and for all m+1≤i≤n:

$$\theta_{p_i}^{1} = \theta_{p0} \tag{21}$$

## III.5. Expression of the temperature at time k+1 in terms of the temperature at k.

The temperatures at time k+1 are devided from those at k by the following formulae, devided in part from the preceeding formulae.

For i=1 in the case where the coating is in contact with a rotating element at constant temperature  $\theta_{ce}$ ,

$$\theta_{c1}^{\ k} = \theta_{ce} \tag{22}$$

For i=1 in the case where the coating is in contact with air,

$$\theta_{c1}^{k} = \frac{\alpha \cdot \theta_{air} + \frac{\lambda_{c}}{\Delta z_{c}} \theta_{c2}^{k}}{\frac{\lambda_{c}}{\Delta z_{c}} + \alpha}$$
(23)

For 2≤i≤m-1,

$$\theta_{c_i}^{k+1} = \theta_{c_i}^k + a_c \frac{\Delta t}{(\Delta z_c)^2} (\theta_{c_{i+1}}^k - 2\theta_{c_i}^k + \theta_{c_{i-1}}^k)$$
(24)

For i=m and i=m+1,

$$\theta_{p_{m+1}}^{k} = \frac{1}{\frac{\lambda_{c}}{\Delta z_{c}} + \frac{\lambda_{p}}{\Delta z_{p}}} \left( \frac{\lambda_{c}}{\Delta z_{c}} \theta_{c_{m-1}}^{k} + \frac{\lambda_{p}}{\Delta z_{p}} \theta_{p_{m+2}}^{k} \right)$$
(25)

and

$$\theta_{cm}^{\ k} = \theta_{p_{m+1}}^{\ k}$$
(26)  
For m+2≤i≤n-1,

$$\theta_{\mathbf{p}_{i}}^{\mathbf{k}+1} = \theta_{\mathbf{p}_{i}}^{\mathbf{k}} + \mathbf{a}_{\mathbf{p}} \frac{\Delta t}{(\Delta z_{\mathbf{p}})^{2}} (\theta_{\mathbf{p}_{i+1}}^{\mathbf{k}} - 2\theta_{\mathbf{p}_{i}}^{\mathbf{k}} + \theta_{\mathbf{p}_{i-1}}^{\mathbf{k}})$$
(27)

For i=n in the case where the free face is in contact with a rotating element at constant temperature  $\theta_{\text{pe}}$ ,

$$\theta_{p_1}^{\ \kappa} = \theta_{pe} \tag{28}$$

For i=n in the case where the free face is in contact with air,

$$\theta_{p_{n}}^{k} = \frac{\alpha.\theta_{air} + \frac{\lambda_{p}}{\Delta z_{p}} \theta_{p_{n-1}}^{k}}{-\frac{\lambda_{p}}{\Delta z_{p}} + \alpha}$$
(29)

In the case where temperatures of coating and substrate are considered constant at the initial instant it follows for all i $\ge$ 2,

$$\theta_{ci}^{1} = \theta_{c0} \tag{30}$$

and

$$\theta_{p_i}^{1} = \theta_{p0} \tag{31}$$

The rate of cooling in a segment i,k is given by

$$v_i^k = \frac{\theta_i^{k-1} - \theta_i^k}{\Delta t}$$
(32)

# IV. DETERMINATION OF THE THERMAL PARAMETERS OF THE WAX COATING AND THE PAPER.

#### IV.1. Coefficient of convection for heat transfer between paper and the surrounding air.

We are going to evaluate the order of magnitude of the coefficient of convection. To simplify the model we consider it for one given speed of coating. In the range of speed considered (100-300 m/min) the Reynolds number for the coating mix is greater than 10,000; the mix is thus turbulent and in this case the coefficient of convection  $\alpha$  is expressed in kcal.m<sup>-2</sup>.h<sup>-1</sup>.°C<sup>-1</sup>. After integrating over the thickness of the coating with the appropriate limits:

$$\alpha = 0,036.\lambda_{air}.(v^{-0.8}).Pr^{\frac{1}{3}}.L^{-0.2}.u^{0.8}$$
(33)

 $\lambda_{air}$  is the thermal conductivity of air. As it is obtained as a function of temperature,  $\theta$ , by Kelvin's experiment via Sutherland's formulae:

$$\lambda_{air}(\theta) = \lambda_0 \sqrt{\frac{\theta}{293}} \frac{1 + \frac{125}{293}}{1 + \frac{125}{\theta}}$$
(34)

we take  $\lambda_0 = 0,0192 \text{ kcal.m}^{-1}.h^{-1}.^{\circ}C^{-1}$ . Pr is the Prandtl number corresponding to the flow of air at the surface of the sheet. We consider it constant and equal to 0.1353. L corresponds to a unit distance, u is the speed of flow, given in this case by machine speed.  $v(\theta)$  is the kinematic viscosity of air obtained from:

$$\nu(\theta) = \frac{\mu(\theta)}{\rho(\theta)} \tag{35}$$

where  $\mu(\theta)$  represents the dynamic viscosity and  $\rho(\theta)$  the specific gravity: 1.205 kg.m<sup>-3</sup> @ 20°C, and 1.146 @ 30°C.  $\mu(\theta)$  expressed in Pa.s is given by:

$$\mu(\theta) = \mu_{20^{\circ}C} \sqrt{\frac{\theta}{293}} \frac{1 + \frac{113}{293}}{1 + \frac{113}{\theta}}$$
(36)

with  $\mu(20^{\circ}C)=1.82$  Pa.s and  $\theta$  expressed in kelvins.

The order of magnitude of the coefficient of convection  $\alpha$  is between 5 and 15 for 100-300 m/min machine speed and 20°-40°C ambient temperature.

#### IV.2. Amount of heat loss by wax due to phase change.

The solid and liquid states are outside the range of temperatures where phase changes take place, heat absorbed by or lost from the hot melt is proportional to the change in temperature. This is not the case for change of phase, effectively these are exothermic in the case of cooling and endothermic in the case of heating.

Paraffin wax, microcrystalline wax and polyethylene are not monomolecular products. In the same crystal of hot melt there exist many types of molecules of differing molecular weight and when this melts or crystallises the phase change occurs throughout. Thus it is not possible to define a simple latent heat of phase change nor the contribution of each molecule to the heat exchange take place during change of phase.

The thermal flux flow in the hot melt coating at the time of phase change is a complex function of temperature which is known thancks to the analysis of a differential scanning calorimeter. Figure 6 represents for a wax, B. In the absence of change of phase this is largely equal to the specific heat of the mix.



Figure 6. Differential scanning calorimetry. Derivative of heat flow with respect of time as a function of temperature. Cooling rate 8°C/min.

For the purposes of modeling we assume the change in flux to be modeled by a change in specific heat of the material. The specific heat of the wax in the range of temperature of a phase change is a function of temperature. This function is composed partly from the differential scanning calorimeter results (fig.6). A similar function is used when the wax is reheated to gain a complete endothermic picture of the heat of fusion.

#### IV.3. Thermal parameters of hot melt coating and paper.

The thermal conductivity  $\lambda$  and the specific heat  $c_p$  of paper are assumed constant whatever the temperature in the range of coating temperatures 10-140°C.

$$\lambda_{p} = 0.04 \text{ kcal.m}^{-1}.\text{h}^{-1}.^{\circ}\text{C}^{-1}$$
 (37)

$$c_{p} = 0.3 \text{ kcal.kg}^{-1} \circ \text{C}^{-1}$$
 (38)

The specific gravity of paper is assumed equal to 800 kg.m<sup>-3</sup>.

The thermal conductivity of the hot melt coating is measured at 0.2 kcal.m<sup>-1</sup>.h<sup>-1</sup>.°C<sup>-1</sup>. The specific gravity of hot melt

coating assumed constant at 850 kg.m<sup>-3</sup>. It would be equally possible to take account of the changes in phase. However we have not done this because these variations depends on the rate of cooling among other things. Thus the data at our disposal are not adequate to define a sufficiently representative function of the temperature.

#### V. RESULTS.

We will develop three simulations of cooling. At the initial time, the paper and coating are in contact with a chill roll surface maintained at a constant temperature.

## V.1. Influence of the exothermic flux of the crystallisation of the hot melt.

Figure 7 represents the development of temperature as a function of time during chilling of the coating. Case n°1 does not take account of the exothermic flux of crystallisation: the specific heat of the hot melt is constant. In the second case, the heat of crystallisation is taken account of in the form of a variable specific heat vs. temperature function as described in the paragraph IV.2.

The temperature of the hot melt coating decreases rapidly by comparison with that of the substrate. After 5 milliseconds, the temperature of the wax is below  $40^{\circ}$ C, ie. it is crystallised. By comparison the temperature of the substrate at the same time is between 40 and 90°C.





The rate of cooling is not constant throughout the sheet. The greater the distance from the chill roll the lower the cooling rate. For a given coating thickness, the rate of cooling of the coating is lower when the latent heat of crystallisation is taken into account (case n°2). The difference is even greater at greater distances from the cooled surface. Because of the heat liberated by the crystallisation, the cooling curve reaches a plateau at about 55°C.

#### V.2. Influence of coat weight on the rate of cooling.

Figure 8 shows the temperature as a function of time at the interface between the coating and the substrate when the coating is in contact with a chill roll.

The greater the coat weight, the lower the average cooling rate of the coating.

Furthermore the greater the distance from the chill roll, the more the speed of cooling is effected by a change in the coat weight.



Figure 8. Influence of coat weight on the rate of cooling.

Finally in the temperature band 45-60°C, the curves obtained show clear evidence of a plateau symptomatic of the exothermic phase change due to crystallisation.

#### V.3. Influence of the temperature of the chill roll.

Figure 9 shows the development of temperature as a function of time at the interface of the coating-substrate for different chill roll temperatures.



Figure 9. Influence of the surface temperature of the chill roll on the rate of cooling. Coat weight 12 g.m<sup>-2</sup>.

The cooler the chill roll surface, the quicker the coating is cooled.

#### V.4. Conclusions.

The rate of cooling of an 8 to 16 g.m<sup>-2</sup> coating close to the chilled surface is about  $10^6$  °C.s<sup>-1</sup>. However it is very much slower at the coating substrate interface ( $5.10^3 - 5.10^4$  °C.s<sup>-1</sup>). The rate of cooling of a coating decreases significantly as the distance from the chilled surface increases. For a cooling of 12 g.m<sup>-2</sup> the rate is of the same order of magnitude as the critical cooling rate according to simulation.

The exothermic release of heat considerably reduces the cooling rate throughout the coating. This is particularly true at greater distances from the chill roll.

The transfer of heat by convection at the surface of the coating and the support are neglegible compared with the internal heat transfer by conduction. When a sheet is in an open draw the changes in heat within the sheet rapidly reduce its internal temperature gradient.

#### GENERAL CONCLUSIONS AND PERSPECTIVES.

In this study we have sought to characterise the thermal changes in the coating mix and the substrate in the coarse of hot melt coating. When the coating mix is chilled at tens of degree per minute the polyethylene crystallises before the paraffin wax.

The results of differential scanning calorimetry at different cooling rates shows that the crystallisation temperature of the polyethylene is a linear function of the logarithm of the rate of cooling. By extrapolating these results to very much greater cooling rates, we have assumed the existence of a so called critical rate of cooling of the order of several thousands of degrees Celsius per second for which the polyethylene and the paraffin wax crystallise simultaneously.

By using finite element methods we have produced a heat transfer model that permits the rate of cooling at all points in the paper hot melt structure to be predicted throughout a manufacturing process. We have shown how temperature, and rate of cooling vary through the film thickness. For given substrate grammage, coating grammage and initial conditions the model allows the chill roll conditions to be specified to at least acheive the critical cooling rate.

Complementary measures of moisture permeability rate, and coating substrate bonding have shown that products cooled at or above the critical cooling rate behave better than products cooled more slowly (Ref. 2).

Considering the difference in thermal diffusivities, the speed of cooling of the substrate is very much slower than that of the coating. The simulation of the industrial coating process shows that the gradient of temperature in the substrate and coating are such that this can in certain cases reheat the coating in particular if the duration of cooling and quantity of heat removal are not sufficient. In this case the crystallisation of the wax and in consequence the characteristic properties of the coating are very much diminished.

The model allows the evaluation of coating conditions found on the production machine. Thanks to these results it is now

possible to determine improvements in the coating process whenever the coating conditions are not optimal.

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 HELLY C., "Etude de l'enduction des cires hot melt sur un support cellulosique. Détermination des conditions optimales de l'enduction", thèse de Docteur Ingénieur, Institut National Polytechnique de Grenoble (1993).

## **Transcription of Discussion**

## OPTIMAL CONDITIONS FOR LAMINATING AND ADHESION OF WAX BASED HOT-MELT COATINGS OF PAPER

C Helly

#### ERRATA:

Figure 3 (p503) and Figure 6 (p514) should be as follows:



Figure 3. Thermal analysis of a 90% paraffin wax and 10 % polyethylene blend. Cooling speed 8°C/min.



Figure 6. Differential scanning calorimetry. Derivative of heat flow with respect of time as a function of temperature. Cooling rate 8°C/min.

## Dr T Uesaka, PAPRICAN, Canada

I would like to ask a question on some of the mathematics. You included the effect of the phase change, in particular heat loss due to the phase change of wax in the change in the specific heat, is it a kind of tight procedure. Is there any numerical effect on your calculation?

### **C** Helly

The calculations take into account the complete picture of crystallisation of polyethylene and the crystallisation of paraffin wax and the fast change too.

### T Uesaka

Was this heat loss due to the phase change of the wax? It actually becomes an independent term in the heat transfer equation. It seems to be different from just including such change, in the 'A' term. I am wondering if it is a right procedure?

### C Helly

For each temperature we recalculate the specific heat of the wax to take into account these variations.