SURFACE TREATMENT: SIZEPRESS TRADITION, CURRENT DEVELOPMENT AND A PIGMENTED CHEMICAL FUTURE

P.A.C. Gane
Vice President Research and Development
Paper and Pigment Systems
Omya AG
CH 4665 Oftringen
Switzerland

ABSTRACT

Evolution of surface improvements on paper are driven by technical needs, in respect of printing and writing, economical drivers, such as mineral versus fibre cost and market niche exploitation, runnability and aesthetic requirements. From the simple anti-feathering absorption control of hydrophobisers, such as starch, to the sophistication of digital printing, the need to modify the surface of paper is an accepted criterion for investment in our industry. Simple pond and roll application has, through increases in speed and the application of pigmentising, developed in recent times to controlled film application processes. The demands throughout these developments for the scientific understanding of the interactional processes between fluids and substrate: absorption, hydraulic penetration, basepaper fibre debonding and roughening: and the complex rheology of pigment suspensions, based on stability, surface chemical and hydrodynamic criteria, have usually been met retrospectively. The machine concept or application is developed, installed, trouble-shooting achieves compatibility in the industrial environment and only latterly does the question of optimisation through a thorough scientific analysis come to the fore. By studying the models and accepted design criteria that have emerged throughout this evolution, it is proposed that advances through extrapolation of the models and by seeking new untried dimensions of the models can be made which can act to fuel the development further. Notwithstanding that current knowledge in multivariate applications inevitably remains inexact, the author attempts to demonstrate how the concepts available today could be extended to build potential for development in the future. Mechanics of suspension flow, dewatering and network absorption remain the primary controlling parameters and a critical review of past and present assumptions and new research is timely in order to re-fashion the directions that can be deduced. Rates of absorption as a function of available fluid volume arising from the resistance dynamics of rapid dewatering provide a key opportunity for improving surface coating holdout especially in the challenging on-machine context where the timescale for hydrophobising is too short and the wettability and moisture profiles are at their most critical. On the basis of this review, it is proposed that high rate absorption, through the use, for example, of ultra-high surface area filler pigments in the substrate, together with rapid low solids immobilisation of pigmentised formulations with disparate coating and basepaper permeabilities, provides a means of maximising the potential for surface treatment applications both at high speed and in the context of sophisticated niche product development. The roles of basepaper and pigment structure are therefore also an integral part of the review.

Keywords: surface treatment, filmpress, coating holdout, digital printing, absorption, porosity, network modelling

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INTRODUCTION

Usually, the words "surface treatment" suggest the traditional application of size to the surface of paper to provide surface and internal strength and resistance to absorption. Utilisation of low solids starch films which penetrate the surface structure and enhance internal bonding has been a major development factor in controlling the surface characteristics for improved printing ink holdout (1). This technology is still the basis today for enhancing the balance between the pointwise hydrophobising of internal sizing and the overall toner adhesion characteristics and linting control necessary for high throughput laser and xerox printing of general office papers and especially for inkjet printing (2).

Further applications are seen in the area of coated papers where surface sizing of the basepaper is sometimes used to provide strength and reduced absorption for subsequent, often off-machine, blade coating. This practice is particularly common where single pigmented coating layers are applied, for example using a short dwell coater (3). The need for using pigments that are generally quite fine compared with the pore structure of a basepaper to achieve surface gloss in single coating means that the closure of the basepaper is an important factor in reducing the penetration of these fine pigments into the underlying bulk structure and, importantly, in controlling the surface roughening arising from wetting and hydraulic impression of the water phase of the coating colour into the basepaper (4).

Between the extremes of uncoated paper and coated paper lies an area where papermakers seek to enhance surface properties either for speciality grades or for superior quality of commodity grades such as newsprint (5). There are still large parts of the papermaking spectrum where surface treatment could be used to enhance printability and optical properties and the development of more sophisticated formulations and applications systems continues to make such advances reality (6).

Environmental issues also play their part in determining the role of surface treatment technology. The need to retain papermaking chemicals efficiently within the mill wet end brings ever more pressure on the loading levels in the white water system. These loadings can be relieved effectively and efficiently by adopting the strategy of applying the chemical and pigment characteristics to the paper via a closed circuit surface treatment system (7).

DESIGN AND OPERATION OF THE SIZEPRESS

Adoption of the traditional flooded nip concept, Fig. 1, where size solution is introduced to the paper in a pond formed between the press rolls, relies on the absorption of the paper to determine the level of starch pickup as a function of machine speed, pond depth, nip pressure and nip width. These absorption characteristics are in turn reliant on the basis weight of the substrate, its density, surface smoothness, porosity and capillarity. The capillarity is a complex function of fibre surface energy, greatly influenced by the developing internal size, moisture content and temperature (8), and the network structure of the paper. The dominance of hydraulic pressure penetration over hydrophobic resistance to absorption becomes the critical parameter as speed and pressure in the nip increase (9), especially for on machine treatment where internal sizing in any case fails to develop in modern neutral papermaking systems on the timescale between the press section and the sizepress.

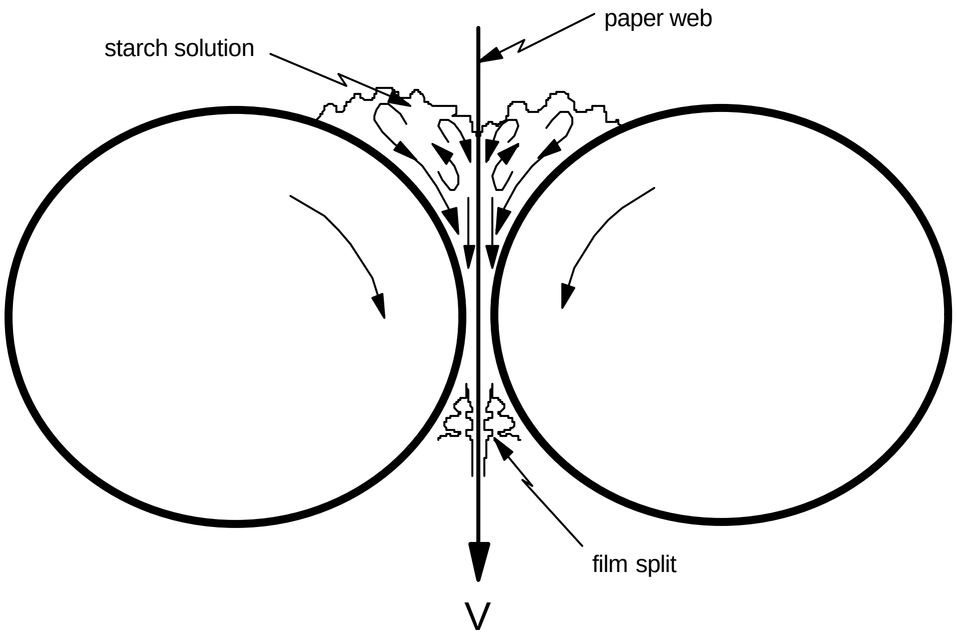

Fig. 1 Flow vortices in a flooded nip sizepress – horizontal configuration with vertical web run.

The molecular weight, amylose:amylopectin ratio, concentration and temperature of the starch solution determine its viscosity and hence flow characteristics on the sizepress

(10). The linear polymer chain of amylose creates the most viscosifying effect and is responsible also for the film-forming character of starch, whereas the amylopectin with its more branched structure makes the solution more flowable. Typical ratios in nature are 27 % amylose and 73 % amylopectin with speciality fractionated grades also available. To counter thickening (setback) tendency, modified (e.g. oxidised) starch is used and enzyme converted starch allows for lower temperature solubilisation whilst maintaining film forming properties. With these options, solids content of starch solutions may be varied from 3 % up to typically 9 % by weight, achieving a pickup in the range of 30 - 50 kg of starch per tonne of paper (11, 12).

Many causes for uneven film pickup and deposition arise from the flow characteristics of a flooded nip press. For example, the highly turbulent flow due to unstable vortices can entrain air, reject the solution from the nip entry and even translate into secondary flow behaviour giving banding similar to the short dwell coat weight banding which used to exist before the introduction of premetering/internal flow elements in the coating head chamber (13-15). Film split at the exit of the nip is also a potential problem for uneven surface pickup. The relationship between speed, the speed-correlated acceleration effects of roll diameter, and these defects limit the use of the flooded nip at high machine speeds and for pigmentation or higher solids coating colours.

Developments in sizepress technology

Increasing roll diameter has been the first step in ameliorating the accelerations experienced at nip entry and exit. Designs have been promoted where the pond boundaries have been isolated from both rolls and web by using the so-called Apron system, Fig. 2, in which baffles were mounted either side of the inlet flow (16). Experience proved this approach to be unsatisfactory in practice due to wear and the discontinuity of flow at the apron edges leading to deposition of dried starch arising from thermal drying at the hot frictional boundary and viscoelastic die-swell effects.

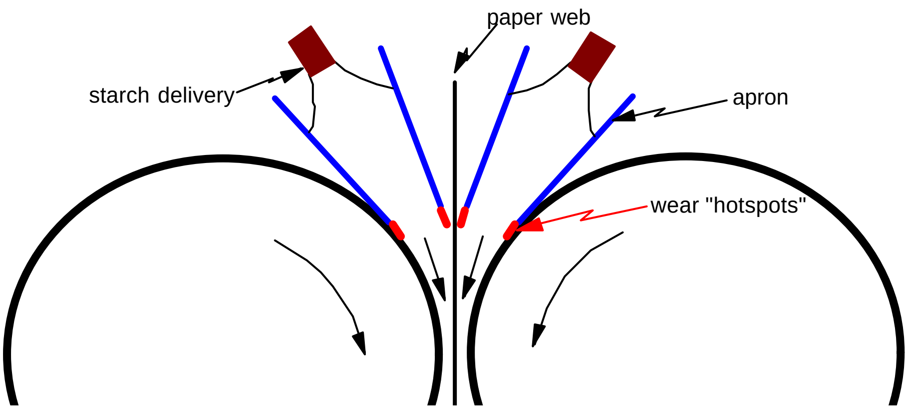

Fig. 2 "High speed sizepress" using aprons to isolate the inlet flow.

Using the analogy of treating the starch solution as a printing ink, the gateroll sizepress (Fig. 3) uses a train of rollers to distribute the solution evenly into a thin film and then onto the large diameter application rollers. The dynamics of the roller train are an important factor in determining the quality of the film. Roll cover design and differential rotation speeds are crucial in minimising film split patterns as the advantage of higher solids starch applications are offset often by film split unevenness (17) and picking or linting of the surface which is in itself a function not only of separation force but also of the increased hydrodynamic pressure associated with higher solids solutions. The advantages of improved holdout have been recognised from this technique and developments, especially the "transfer roll coater" in Japan, have allowed for modified synchronised loading dynamics (later modified for European applications (18)), whereby the adoption of either polyurethane or Neoprene covers in the range of ~ 55 - 80 P&J (90 - 95 Shore A) (where deformation, P&J, is expressed in units of 0.01 mm under a load of 1 kgf (9.81 N) applied to a standard incompressible sphere of 8 mm^2 cross sectional area) on the applicator rolls, matte finished chrome or steel rolls are also reported (19), reducing wear to acceptable levels, with softer outer rubber rolls (70 - 75 Shore A) has enabled the successful broadening of application to pigmented coating formulations primarily in the so-called lightweight Beetoko grades which cover both woodfree and woodcontaining papers used for catalogues, magazines and newspaper inserts (20, 21). The installation rate in Japan has been as high as 6 units per year in the middle of the 1990s. These developments required not only hardware design improvements but also improvements in formulation chemicals to allow for increasing solids of pigmented coating colours, for example plate-out resistant latices, to prevent the build-up of sticky films on the transfer rolls due to surface drying and shear-induced film forming, for which the Japanese were pioneers leading to the world's first successful large scale coated news grade designed by the Nippon Paper Co. for the improved print definition required for the complex script characters of the Japanese language.

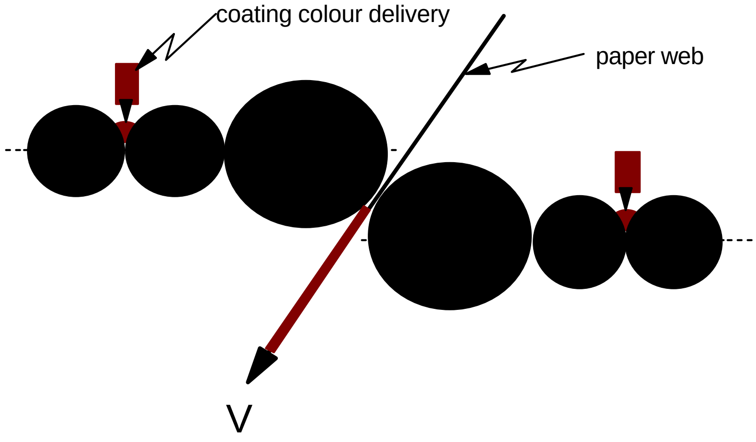

Fig. 3 Gateroll sizepress (or transfer roll coater) configuration.

Following the gateroll developments and demonstrated grade opportunities identified in Japan, European and North American development moved toward constructing a compact design of metering of the film onto the applicator rollers required to allow retro-fitting of metered sizepresses to existing paper machines in the space previously occupied by puddle-type presses. Fig. 4 shows the distribution worldwide of the different types of metered sizepress, taken from H. Tomita and H. Morita (20) from a compilation made in 1994, and shows the rapid adoption in the US and Europe of the premetering concept in its various forms. These premetering designs have adopted a range of principles all aimed at applying a thin even film of solution or coating to the application roll directly. In the case of pigmented formulations the demands on wear and scratch resistance have meant that blade metering onto the roll has progressively given way to rod metering either using a grooved or profiled rod for volumetric control at slower speeds and lower solids content (22) or a larger diameter smooth rod operating under hydrodynamic lubrication pressure, Fig. 5. Various diameters of rod are in use depending on the coat weight desired and the rheological properties of the coating ranging from as small as ~ 12 mm up to ~ 50 mm (23, 24).

The practical design success of the filmpress has come as much from materials research as from the purely applications standpoint. A main area of advancement, as also in calendering today, has been in the design of polymer roll coverings for the control of hardness, deformation differentials between the component rolls and basepaper and the surface chemistry characteristics in relation to wettability and film-carrying uniformity. Despite the sophistication of polymers available, it is mostly reported that mills have adopted the solution most suitable for them on a trial and error basis (19). The reason for this may well lie in the difference between the standard static hardness measurement (deformation, P&J) compared with the actual dynamic response in the running condition. Modern roll covers are elastomers, including natural rubber, Neoprene, Nitrile, hydrogenated Nitrile, polyurethane and epoxy, and show a visco-elastic deformation response which is therefore a function of both amplitude and rate of deformation and differs over the range of temperatures, pressures and speeds experienced in operation.

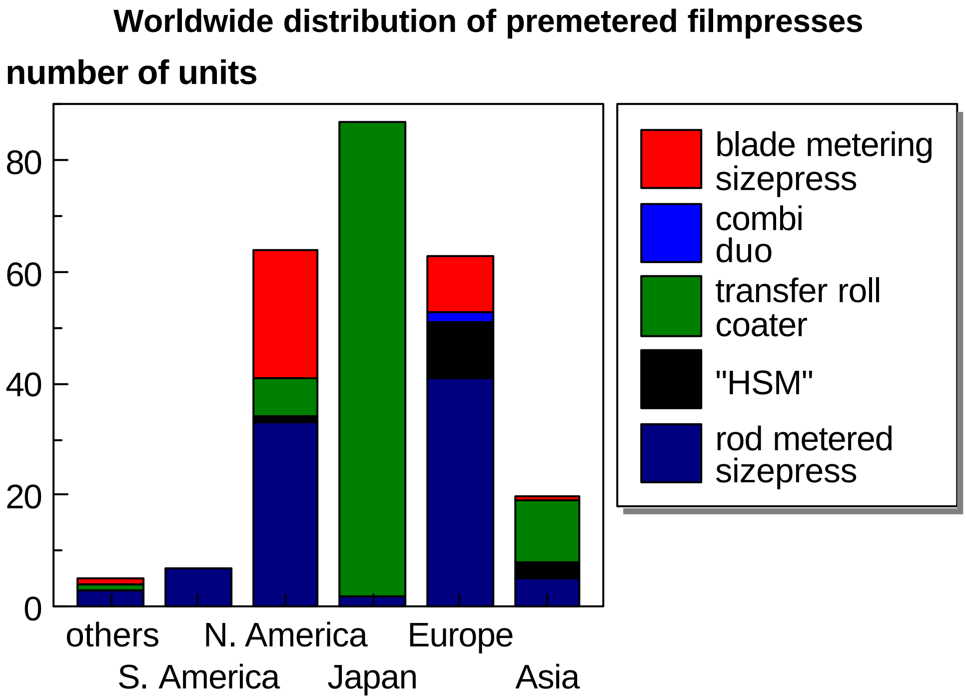

Fig. 4 Worldwide distribution of the different types of premetered filmpress units (17).

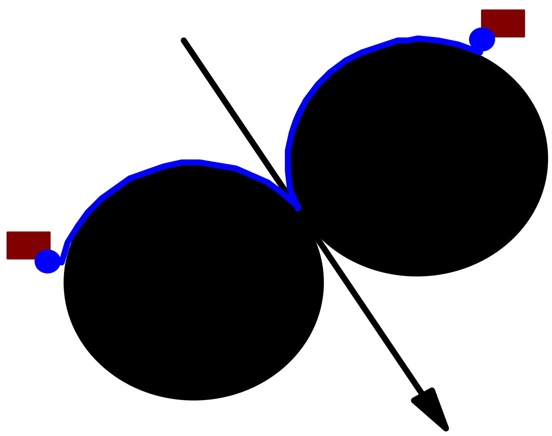

Fig. 5 Direct metering onto the application roll using a smooth rod.

RUNNABILITY OF PIGMENTED COATING COLOURS ON THE METERED SIZEPRESS

(1) AT THE METERING HEAD

Today, the emphasis is increasingly on pigmented film transfer and the filmpress, or metered sizepress as it is now most commonly defined (MSP), which is seen more as a coater than as a starch applicator, either directly as a two-side coating operation or as a two times single side coating system avoiding the air turn and problems of contacting wet coating surfaces and also avoiding two-sidedness due to asymmetric exit from the two-side coating nip. Quality of the film applied to the applicator roll is dependent on the film split characteristics at the exit of the premetering rod and the quality applied to the paper is a function of the transfer and film split characteristics between the backing rolls and the basepaper. The advantages of the MSP include the ability to apply even coat weight at low application weights - contour coating (19, 25) – and the improved runnability of light weight basepapers as well as the economy of installation as a potential precoating device in multi-coated woodfree grades (26, 27). These properties have been the subject of intense research and have included formulation studies (28, 29), rheological criteria (28, 30, 31) as well as pigment comparisons (28, 32).

Metering[1] with blades

The relation between coating solids and speed is critical, as with blade coating on paper, except that conditions for scratching are even more prevalent due to the unforgiving surface of a continuous applicator roll. Contamination and aggregate build-up under the blade, either from colour contamination or picking/linting of the basepaper, cannot be accommodated as in the case of a basepaper within surface roughness and voidage. Therefore, low speeds are problematic, especially in the bevelled blade mode which was the commonplace configuration previously for starch metering. Solids contents of 60 - 65 % can be applied under viscosities of 750 - 1 300 mPas at 30 s^{-1}. Adoption of bent blade configuration partly alleviates the problems of scratching but the system has always been regarded as sensitive especially as coat weight control becomes less dependent on coating solids under the lubrication dynamics of the confining blade nip entry. At speeds much above 1 000 $mmin^{-1}$, coating non-uniformities quickly arise (31).

Wire wound rods

The volumetric metering of colour results in a linear coat weight relationship for given applied pressure in relation to the free void space under the wire wound rod. Wire diameters range typically from 0.2 mm to 0.5 mm (33) and the rod is rotated slowly so that wear is even and to allow flushing of trapped particles under the rod. Pressures can be varied by pneumatic tube and the coat weight correlation is dependent on applicator roll hardness – the softer the roll the higher the coat weight. Pigment choice is critical in respect of abrasion (34) and this is a limiting factor as many lightweight and ultra

[1] It is useful to be clear about definitions in the following sections: the premetering of the colour onto the applicator rolls is usually defined as metering and the application onto the paper is made by the applicator rolls.

lightweight coatings demand specialised high opacity or high surface area pigments which traditionally tend to be abrasive, e.g. calcined clay. High solids coatings also tend to increase wear (31) and though operational viscosities can be as high 1 000 - 1 200 mPas at Brookfield 30 s^{-1}, the practical limit usually falls into the range of 200 - 800 mPas (33, 35, 36).

An operating range of film thickness can be identified by modelling the lubricational flow (37) using capillary number (= viscosity x speed / surface tension) as a function of wire diameter. Wire marks are predictable at low speed, and at high speeds ribbing is predicted with a pitch greater than the wire diameter. Levelling rate is an important parameter for the quality of a coating metered by a wire wound rod as inevitably there is a volumetric periodicity arising from the wire winding and is found to be proportional to the film thickness and surface tension and inversely proportional to viscosity. Despite the acceptance of this model, we must be aware of the limitations as it refers to an homogeneous purely viscous fluid. This is a gross simplification both for starch solutions which are visco-elastic and for pigmented coating colours which have non-linear visco-elasticity and have undefinable surface tension while the pigment and binder particle size in itself distorts the meniscus-forming properties of the fluid diluent such that the findings in relation to surface tension are ineffectual compared to the visco-elastic properties of real coating colours. However, the limitations as predicted are easily realised in practice.

Metering with smooth rods

As described above, the metering is defined by hydrodynamic forces (38). This method allows an increase in speed over 1 000 $mmin^{-1}$. Film thickness increases with speed and coating solids content and its control is much more flexible during running than either of the previous techniques. High shear viscosity gives a good indicator of the attainable maximum film thickness at a given speed, rod pressure and rod diameter (39). Applied coat weight is very dependent on the colour-basepaper interaction, or pick-up, in respect to the dewatering properties of the coating colour and the relation to the immobilisation solids of the coating colour (35, 36, 38-40). The role of this proposed contact filtercake is held as fundamental in determining the actual wet film thickness which undergoes film splitting at the nip exit and the balance between the desired level of dewatering and the application in question must be made. For example, at slow speed, on machine, water retention must be sufficiently high to prevent excessive solids rise in the web nip and ensuing orange peel patterning, whereas at high speed impulse dynamics are needed to be large enough to generate an immobilisation to combat excessive wet film thickness and resultant misting (21, 41-43). In extreme cases, at high speed, misting and/or dry build-up of coating colour can exist at the exit of the rod nip and problems similar to blade whiskering or stalagmite formation can occur (18, 44).

(2) MISTING AT THE NIP

The runnability advantages of the MSP, in relation to web run characteristics on-machine and reduced breaks in lightweight grades, have in many cases concentrated the impetus for economic papermaking on higher speed applications. Also, inevitably, the application window of coat weight has been sought to be broadened in attempts to make more traditional single coated LWC, and even MWC, replacing blade coating techniques (45-47). This has met with mixed success, partly because of the coating coverage and structure characteristics – which will be discussed later – but largely due to the presence of misting at the exit of the paper web from the application nip. The following sections review some of the fundamental aspects discussed regarding this misting phenomenon in the context of the mechanisms and solutions proposed (30, 41, 42) .

COLOUR RHEOLOGY – moving from a homogeneous fluid to a pigment suspension

The continuing increases in coating speed and solids concentration today dramatically reduce the timescale over which strain is applied to the coating colour and at the same time increase the magnitude of the strain in the critical metering and application regions. This shortening of the time interval under which stresses are developed in the colour brings the question whether visco-elasticity can become a predominant factor in describing the rheological response of the coating suspension. The review by Triantafillopoulos (48), which draws on work from a wide range of authors, highlights the parameters under which visco-elasticity may be important. It concludes, however, that it is difficult to visualise fully the effect elasticity might have on runnability phenomena. Furthermore, the difficulty of reproducing the conditions under which runnability problems arise has prevented a realistic laboratory appraisal. Elasticity, therefore, has at worst been implicated in potential solidification of the colour and at best been thought to be of benefit in assisting levelling after film splitting (49).

How does this visco-elastic property arise in a pigmentised coating colour? It is necessary to work with the realistic concept of an interacting system of solid particles, dispersed in a fluid by a balance of repulsive and attractive forces and destabilised by a combination of osmotic and adsorptive equilibria acting between the particles, their surfaces, and concentrations of dissolved polymers in the fluid phase. This picture correlates well with the static and transitional structures probed by oscillation and controlled stress rheometry (50, 51). Factors which predominate in defining changes in pigment packing structure during high speed coating include both the interactional forces between the particles, the particles and their fluid environment and changes in relative solids concentrations. Essentially, the elastic or storage modulus, G', derives from the interacting long and short range forces that form the colour solid-solid and solid-liquid structures. Conversely, the purely viscous or loss modulus, G'', reflects the frictional aspect of flow both within the fluid phase and between the fluid and the structure of the suspension solids. In effect, G' is the parameter describing the multitude of interactions which try to return the colour to the structural state it had before any strain was applied. Consequently, G'' describes the potential for absorbing energy, (i) by an irreversible change in the structure which allows flow to occur and (ii) during the flow itself. These stress-related moduli can be considered to act orthogonally, and a combination of the two, **G***, creates a stress, t, with a phase-lag relationship, d, in respect to the applied strain, g, under an applied angular oscillation frequency, w,

$$\mathbf{G}^* = G' + \mathrm{j}G'' \qquad (1)$$

$$d = \tan^{-1}(G''/G') \qquad (2)$$

where

$$g = g_0 \sin wt \quad \text{and} \quad t = t_0 \sin(wt + d) \qquad (3)$$

and where j is the imaginary number, $\mathrm{j} = \sqrt{-1}$.

Inertial Effects

In addition to the visco-elastic properties of coating colours arising from the mechanisms of interaction discussed above, it is also necessary to take account of the density difference between the solid phase material and that of the fluid medium in which it is suspended. This density mismatch for mineral pigments can be a factor between two and three times. In mineral processing, for example, the whole principle of size measurement and separation technology is based on this density difference separating the solid phase from the suspending fluid under the action of acceleration.

Under rapid changes of flow direction, or during high rates of acceleration/deceleration, the greater inertia of the solid particles tends to force the particles to cross the fluid streamlines or to lag behind the fluid flow. This means that the solid and liquid phases can become decoupled. The main coupling force between solid and fluid is derived from the viscosity of the fluid through Stokes' drag. If the inertia of the particles is sufficient to overcome the drag force, regions of increased solids concentration can occur. This, in turn, can manifest itself as a form of elastic behaviour as visco-elasticity is strongly related to particle concentration and particle crowding can lead to hysteresis in the stress-strain response of the colour, respectively. These inertial considerations are seen as complementary to the argument that some retained visco-elasticity exists in the coating colour in practice. Recognising the possibility of inertial effects may help to resolve the conflict between saying that the observed low strain (unsheared) elastic response is retained, whereas in the realistic situation on the coater, where some degree of pre-shearing has been experienced by the colour, all visco-elastic structure should have been destroyed!

"Relaxation-induced dilatancy"

Having described coating colour rheology in terms of interactions which act to compete against viscous flow under short-timescale stress/strain conditions, it has been proposed that, should the specific condition occur in which the solid and liquid media become partially separated whilst the elastic interactions remain dominant, a novel rheological behaviour may occur (44). We can imagine the effect in terms of the restoring action of the elastic solid-solid and solid-liquid interactional forces after partial separation has taken place, for example after filtration under a high pressure pulse, or by inertial up-concentration leading to stress hysteresis. We can represent this situation pictorially in Fig. 6. As the applied pressure pulse deforms the elastic structure, some of the free fluid phase is forced into the porous substrate and separated from the solid material of the coating colour. After the pulse, the relaxation behaviour is represented by a recovery of the elastic structure which is shown as having less water than before the pulse. The light-shading of the solid, as shown in the diagram, schematically represents the transient dilatant effect. The result being that the deformed internal structure, while returning to the pre-strained state by virtue of its stored energy after the pulse has subsided, partially reproduces the solid-solid and solid-liquid structure which existed prior to deformation but for which there is now insufficient free fluid to support flow under shear. This condition will be short-lived and lasting only over the timescale in which the elastic energy can be dissipated. By definition, therefore, this recently-proposed phenomenon, if realised in practice, will create a transient dilatancy - hence the description, *relaxation-induced dilatancy*.

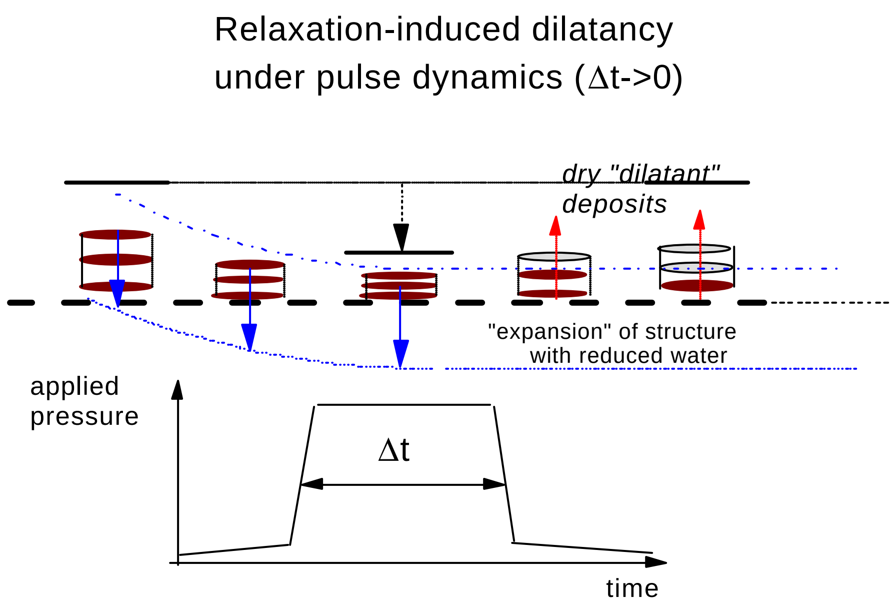

Fig. 6 Schematic representation of *relaxation-induced dilatancy* after pulse filtration of coating colours (reproduced from Gane 1997 (44)).

Kinetic Energy at the Nip Exit

The practical relationship between increased film thickness and the onset of misting is generally defined for coat weights above ~ 8 - 9 gm^{-2} when they are applied at speeds above ~ 1 000 - 1 100 mmin^{-1}. The kinetic energy imparted to the colour at the nip exit, as described by Gane et al. (29), is a controlling factor for the droplet or misting formation and is not only a function of speed but also of the geometry of the film split point. This geometry is important as it is affected by factors such as roll deformability, basepaper compressibility as well as the fluid layer thickness. To understand these factors better, let us consider first the simple case of non-deformable surfaces as shown in Fig. 7.

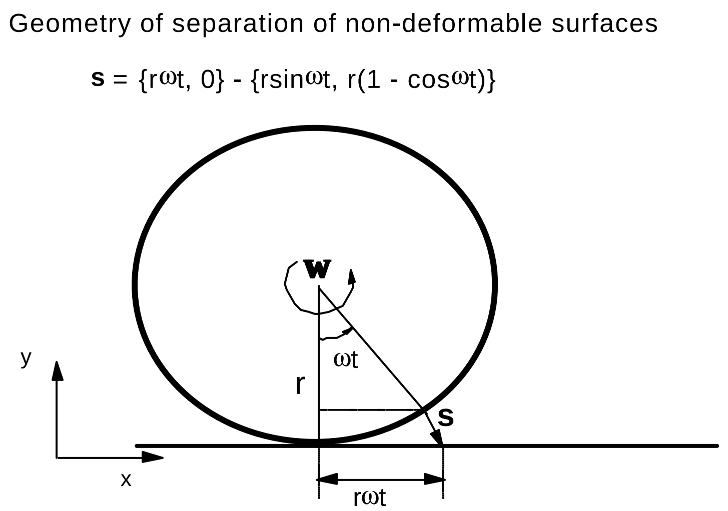

Fig. 7 Vector description of the separation length, **s**.

The kinetic energy of separation per unit mass in this simple system is given by,

$$(\mathrm{d}s/\mathrm{d}t)^2/2 = \omega^2\, r^2\, (1 - \cos\omega t) \qquad (4)$$

where, r is the radius of the applicator roll, ω the angular velocity and t the time to separation point. This function gives an increasing energy the further the film splits from the nip centre as shown in the dimensionless plot of Fig. 8.

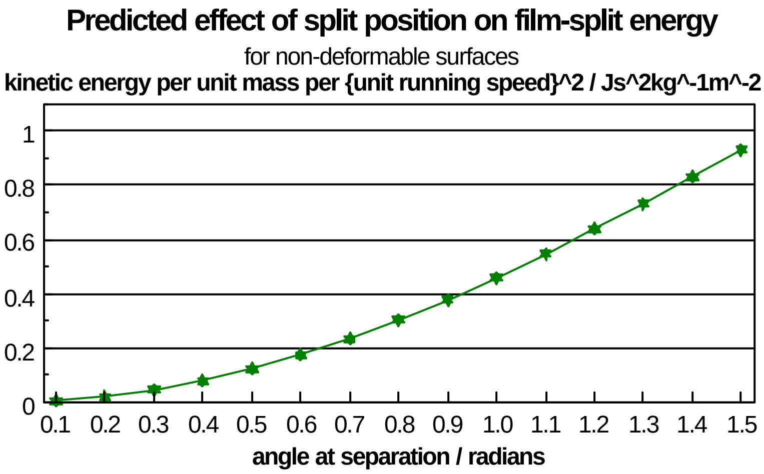

Fig. 8 Increase in kinetic energy factor as the point of separation moves from the centre point.

In the practical case of a deformable applicator roll and basepaper, the geometry changes. Effectively, the deformation of the nip boundary leads to a more rapid separation further from the nip centre. This higher separation rate at the split point is shown schematically in Fig. 9.

Geometry of separation with deformable backing roll and/or basepaper

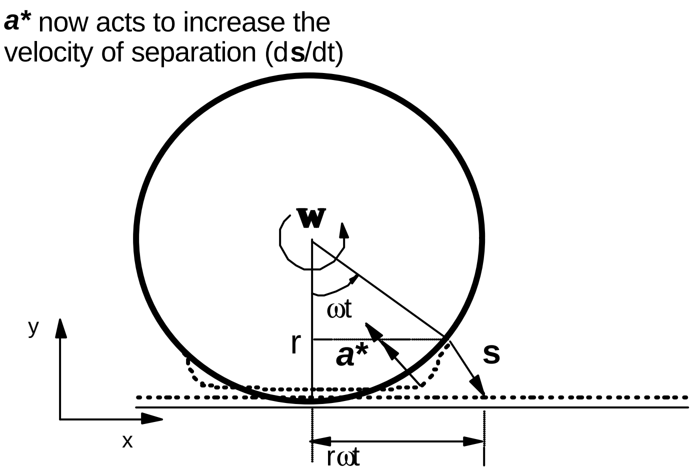

Fig. 9 Deformation increases the acceleration at the separation point.

So, when considering an increase in wet film thickness, we not only have an increase in kinetic energy as we move up the curve in Fig. 8 due to the delayed separation point but the geometry of the nip exit is also modified by the presence of the wet film. Should the film split occur under visco-elastic conditions or suffer from the proposed relaxation-induced dilatancy, then the curvature of the separation point will tend to take the form shown in Fig. 10. These effects of deforming the separation geometry, therefore, by either softening the nip or by increasing the film thickness will make misting worse unless the basepaper is also highly compressible and conforms to follow the exit geometry of the deformed roll.

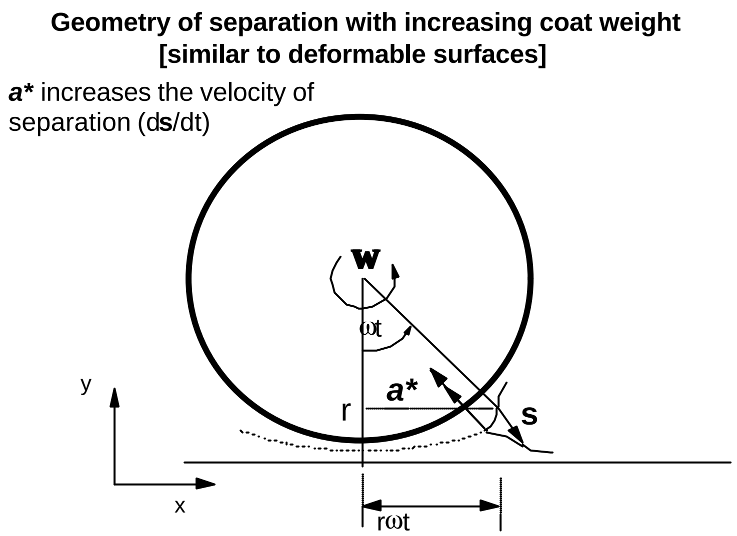

Fig. 10 The presence of the wet film is similar to deforming the backing roll.

Knowing the total kinetic energy of the system allows us to consider better the process of misting in respect of droplet formation. The formation of droplets requires that sufficient energy be given to the film split to overcome the surface tension force of the colour. This surface energy is difficult to define for a pigmented high solids coating colour as the system is not a simple liquid but a series of interfaces between liquid and solid and air. However, even if we cannot define the value of the surface energy realistically, it is the kinetic energy per unit length of meniscus that provides the important driving force for droplet formation. We must, therefore, consider the energy per unit length that the separation speed “pumps” into the colour. We may calculate this for our simple model of Fig. 8 by dividing equation (1) by the magnitude of *s*, thus,

$$(\mathrm{d}s/\mathrm{d}t)^2/(2s) = w^2 r \left\{(1 - \cos wt)/\sqrt{w^2 t^2 + 2(1 - wt\sin wt - \cos wt)}\right\} \qquad (5)$$

Interestingly, this is now a decreasing function the further the separation point is from the nip centre. This tells us that for a continuum purely viscous liquid, the longer the separation length can be made the better it will be in respect of misting. This is consistent with the accepted theory of increasing the meniscus curvature (i.e. length) by moving the split point back into the nip toward the origin for a given wet film thickness. If we now superpose the effect of the deformations of the exit geometry by the practical roll and basepaper compressibility, together with the volume effect of the coating colour, we have a series of plots that look like Fig. 11 in which the deformation leads to a delay in the point at which the energy per unit separation length curve begins. Also, the geometry at the start point will result in a higher energy and hence lead to worse misting. From these models, we can conclude that a combination of correct roll hardness to reduce deformation in relation to the basepaper and increased energy dissipation by the colour "rheology" are the key factors required leading to reduced misting.

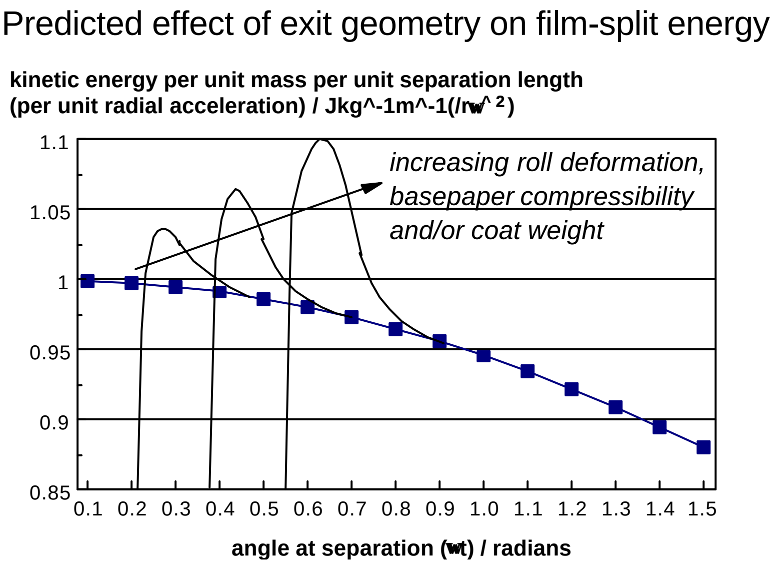

Fig. 11 Effective droplet forming energy as a function of split position.

So far, the issue of misting by this analysis has been considered as a classical problem arising from the creation of free surface generated in the fluid layer by the energy of separation between the applicator roll and paper surface at high speed and high film thickness. The problem arises, however, that the energy loss mechanism of "viscosity" control to reduce the misting can no longer be applied as it used to be in starch sizing. As discussed above, this is due to the pigmented, relatively high solids, coating colour undergoing both pulse filtration in the nip and experiencing high inertial forces at the nip exit. Although it is well recognised that there is a need for some filtration to form sufficient keying and coating weight control (52), the act of filtering under pulse dynamics can lead to dry build-up, an uneven film and coating surface, and difficulty in coat weight control from high solids return to the premetering unit. This effect can happen even more dramatically as the colour is diluted in the attempt to overcome the problem. When this effect is seen, the mechanism of relaxation-induced dilatancy can be suspected.

Fig. 12 illustrates the case of a pure starch solution which has visco-elastic properties. The penetration of the starch solution under the pressure pulse of the nip is partially restored by the elastic component of the rheology and acts to provide a surface film. This elastic component has also been suggested to be desirable for levelling of the film after the split has taken place (49). Under these conditions, no separation of the starch polymer from the solution occurs.

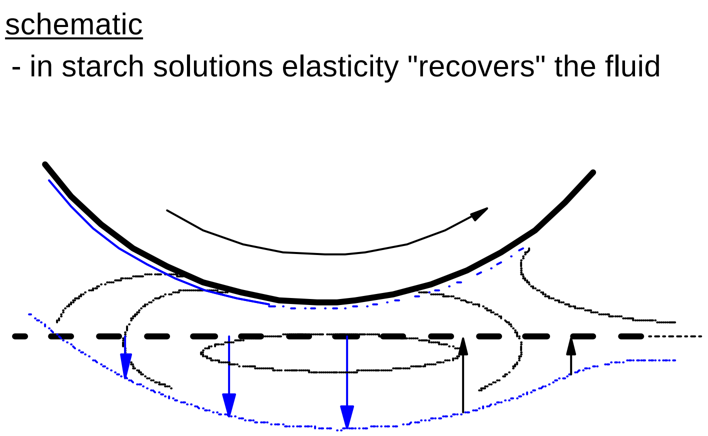

Fig. 12 Visco-elastic starch solutions in the sizepress.

In the case of pigmented coating colours, the action of the pressure pulse is known to lead to phase separation by pressure filtration of the free fluid phase from the remaining interactive solids and associated water. This can be expected to generate the conditions at the nip exit for the onset of relaxation-induced dilatancy, as shown in Fig. 13 (29). The critical factor, therefore, is the balance required between the desired level of dewatering for the formation of the filtercake whilst avoiding relaxation-induced dry deposits. It would be interesting to speculate on possible implications for extensional viscosity under such conditions of transient dilatancy. Furthermore, the negative pressure region at the nip exit may be invoked as a mechanism, once again, for inertial solid-liquid separation.

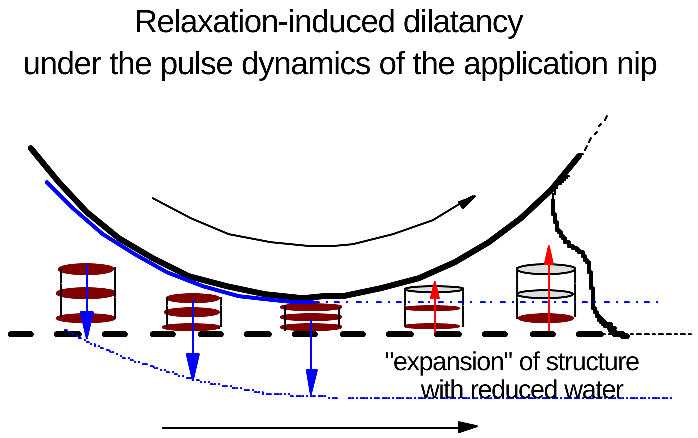

Fig. 13 Relaxation-induced dilatancy at the film split region of the nip (29).

Formulating for Improved Runnability of Pigmented Sizepress Coatings

Practical attempts to improve the runnability of pigmented sizepress coatings must take account of the two criteria described above, (i) reduction of the effective energy distribution that leads to misting, and (ii) the avoidance of those conditions which might lead to relaxation-induced dilatancy. To reduce misting there is a need to dissipate the energy of the film split through "viscosity" and a requirement to couple strongly the particle movements with that of the fluid flow.

It has been demonstrated that the structural orientation of pigments plays an important role in MSP coating (53). For example, in contrast with an optimised blade coating, platy clay formulations on the MSP have a disordered packing structure retained in the dry coating layer. The observation that platy clays run well in sizepress application systems (18, 26) is seen as arising from the strong cross-sectional coupling of the in-plane rotational axis of platelets with the flow, i.e. high aspect ratio pigments have an inherent energy loss mechanism and undergo less inertial up-concentration.

To enhance the anti-misting properties of blocky particles, such as natural ground calcium carbonate and fine US clays, to the level of platy particles it is necessary to increase the viscous drag between the fluid and the solid particles. However, as encountered in blade coating, attempts to use viscosifying agents in general usage today tend to generate water retention through interactive and associative forces. Fig. 14 shows a plot of the measured phase angle of a range of coating colour formulations, based on a fine ground natural calcium carbonate, as a function of classical water retention (54). The phase angle, d, which relates to the phase lag of the stress response of the colour to an applied oscillatory strain, as defined in equation (2), was measured at a controlled stress of 10 Pa using a 1 Hz oscillation frequency on a StressTech®[2] controlled stress rheometer. The water retention was measured using an EMCO® DPM27[3] ultra-sonic device by studying the time taken to reach the maximum rate of water absorption into a consistent basepaper chosen for this purpose. Clearly, the action of adding the various water retentive cobinders was to increase the water retention in a general correlation with increasing visco-elasticity as shown by the rapidly falling value of the phase angle.

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[2] StressTech® is a product name of RheoLogica Instruments AB, Lund, Sweden

[3] EMCO® GmbH, Leipzig, Germany.

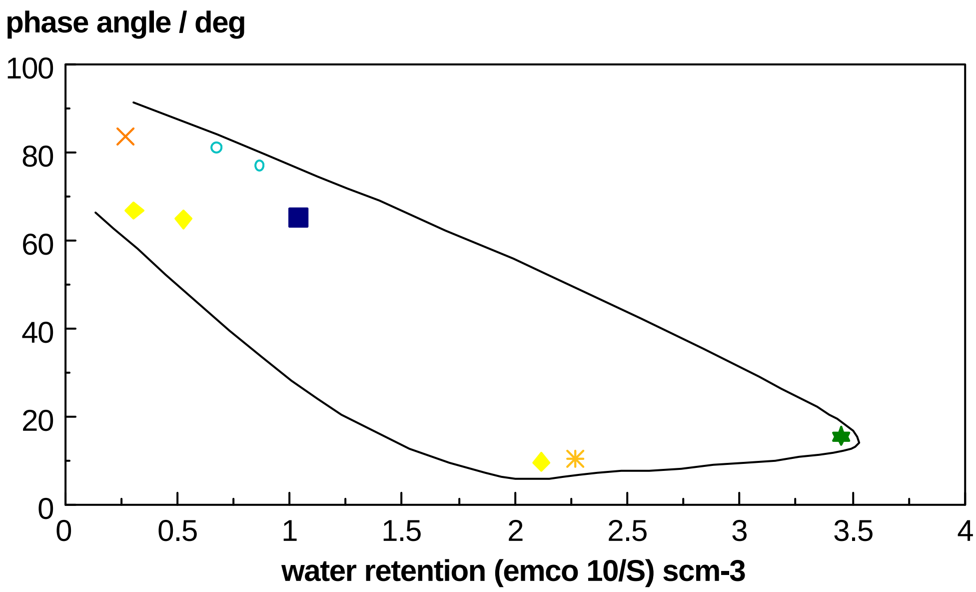

Fig. 14 Relationship between phase angle and water retention (symbols refer to the misting of the coating colours featured in Fig. 15).

These formulations are related to their respective runnabilities on a metered sizepress by the extensive pilot coating trial data used to construct the runnability contour map shown in Fig. 15 (29). A specially modified top-pan balance was used to collect the coating colour mist from the exit of a one-side coating nip at a speed of 1 500 $mmin^{-1}$ applying a coat weight of 8 gm^{-2} to a lightweight (~ 40 gm^{-2}) basepaper. Misting was then calculated as the mass of coating colour per second deposited on the pan. The plot shows contours of constant misting level over a map of the values of the viscous modulus, G'', and the respective water retention of the colours. Both the viscous modulus and the water retention were measured in the same way as described previously. The insertion of the dotted contours in Fig. 15 is naturally tentative and is simply an attempt to indicate general trends. This plot, however, suggests the existence of a potential optimum and has been a tool used successfully to predict MSP runnability and in developing formulations for reduced misting tendency.

Other workers, for example Salminen et al. (42), have also sought correlations between rheological parameters, water retention, and runnability. More fully, these findings (41) show that optimal combinations are required and not simply a general monotonic extrapolation of any single parameter or combination of such parameters. It must also be stressed that the proposed optimum (Fig. 15) is specific to the particular pigment and basepaper used. This is due to the variation of intrinsic rheology between pigment types and variations in filtration of different colours on different substrates. However, the implications illustrated by this set of experiments can be generalised in that the desired control of water retention should be coupled with a relatively high viscous modulus while limiting additional elasticity derived from colour interactions. Under these conditions high solids coatings can be realised.

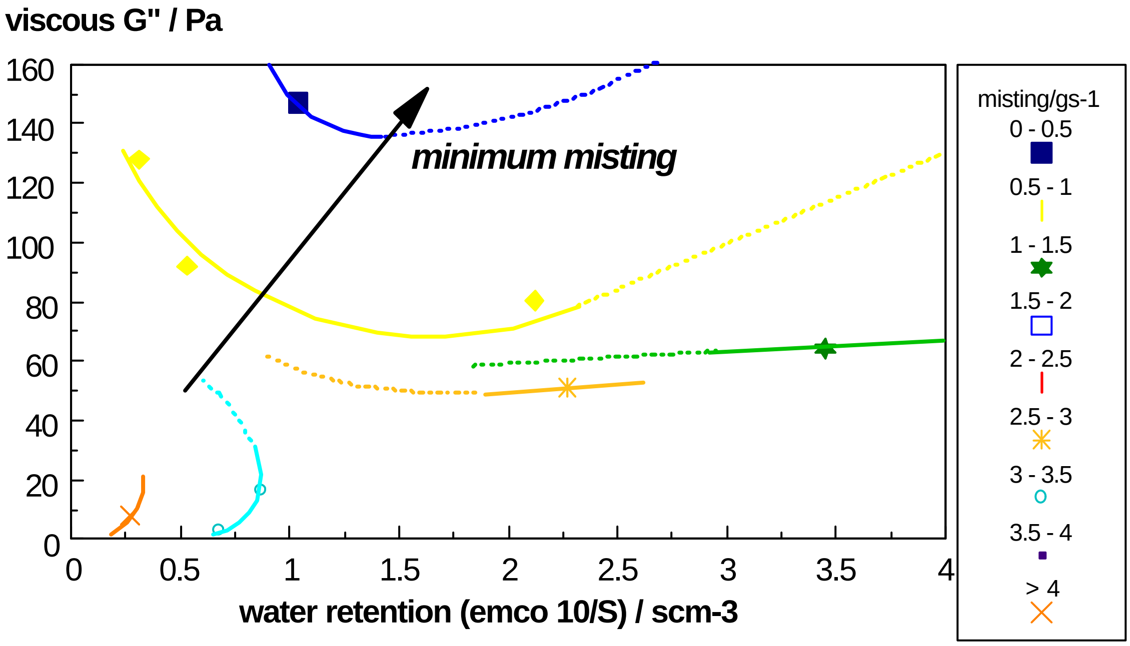

Fig. 15 Contours of constant misting as a function of G" and water retention (29).

The worst two misting formulations, in the left hand corner of the contour plot in Fig. 15, are good examples where simply attempting to achieve rapid dewatering with the aim of building a filtercake fails to correct misting. Further studies involving dilution of the colour, predictably, made misting worse (moving from the contour of open circles to the one with the cross). In the case of strongly elastic coating colours, dilution brought a further change. It was noted that a return of dry coating on the application roll after contact with the paper disturbed the metering of the fresh film onto the roll surface, giving skipping and some evidence of ribbing. Under these circumstances it is clear that a decoupling of the elastic and viscous components of colour rheology without losing water retention is the important goal.

We see, from this work, that development of formulations for the pigmented sizepress to be run at high speed follows broadly similar trends to those required for high speed blade coating (44) with the important exception of the highly critical dependency of the sizepress on the right level of dewatering to assist in reducing wet film thickness and in creating the desired level of coating pick-up. The criteria, therefore, can now be defined for the future development needs in this application also, namely, *highly interactive binders and cobinders should be avoided, rather a synergistic increase in viscous lubricity should be sought in combination with the right (usually low) level of water* *retention to reach an optimum in anti-misting and coat weight control* (29). How to achieve this is indicated after the following considerations.

Extensional viscosity

Fernando, reviewing misting mechanisms in architectural and industrial roll coatings (55-60) and spray atomisation processes (61-66), and applying these to the conditions prevalent on the MSP, supports the view given above that viscous forces play the dominant role in controlling the misting of non-Newtonian paper coatings and inks (67). However, in determining viscous forces, it is argued that extensional viscosity rather than shear viscosity should be used because of the deformation mode involved. For low viscosity Newtonian fluids, centrifugal forces become important at high application speeds (68).

The measurement of extensional viscosity in the case of paper coating colours is an area so far studied with little or no success. Application of the simple Trouton ratio (69) is difficult to justify due to the complex relationships of shear viscosity under the dynamics of the application (70). Assuming that model fluids will correctly mimic the effects of coating colours is unfounded as the measured effects from these model fluids are confirmable by uniaxial extensional measurements but those of coating colours are still unmeasurable (71-78). More recently, Kokko et al. (79), proposed a capillary method of determining an effective extensional response by using capillaries of two different lengths but of constant diameter. The information deduced comes only after analysis of the entry corrections derived from a range of fixed length capillary diameters. The cross-correlation between assuming corrections without extensional influence for the constant length capillaries and then its introduction when changing capillary length is tenuous and may suffer from the distortion arising from the relaxation lengths associated with visco-elastic interactions rather than purely extensional terms. However, there is an obvious residence time effect and this is important when considering shorter timescales in the MSP nip as speeds increase. Though extensional viscosity may not yet be directly measurable for coating colours, the search for methods to measure it is leading to support for transient phenomena.

A further recent comprehensive review of the published rheological criteria analysed surrounding the use of the MSP is given by Triantafillopoulos (80) in which can be found a wide-ranging reference list (39, 70, 81-110) including the finite element modelling work of Scriven et al. (32, 90-95) elucidating film-split patterning.

Building the filtercake

Trefz (52) has made one of the most coherent contributions to the mechanisms of MSP application and many of the concepts proposed have become current accepted practice. Despite some interpretational difficulties in respect to the absolute definition of the filtercake, its resistance to progressive dewatering beyond the immobilisation point being a gross oversimplification using time-independent parameters for the volume fraction of the colour, a, and a pore structure constant of the filtercake, k_m, and ignoring the inertial aspects of dewatering and visco-elasticity, the qualitative relationship is nonetheless valuable to discuss in order to develop our understanding:

$$V^* = [2\Delta P \Delta t / (\alpha k_m \eta)]^{0.5} \qquad (6)$$

where V^* is the volume of fluid phase lost per unit area through dewatering, ΔP is the applied pressure differential in the nip over residence time Δt for a colour of viscosity η. The inconsistency arises from the basic assumptions of continuity of rheological behaviour as solids increase because α, k_m and η all effectively increase and so, without further information on mechanisms, the filtercake asymptotically fails to form as solids rise and yet the separation between filtercake and fluid layers is fundamental to the concept and high solids is assumed to promote this. This means that in practice there must be an induced structure or discontinuity which carries the transition over the continuity expected from equation (6). This is yet more reason for developing analytical techniques in the future which can measure transient phenomena under pulse dewatering conditions. The equation (6) is more useful for visualising why low solids coating colours are problematical in respect to misting as it shows that at high speed insufficient dewatering occurs in the nip and the wet film thickness remains high when coat weights are high such that the chances for misting and film split phenomena are necessarily increased. This neatly summarises why those involved in developments of pigmented size press coatings who approached the issue from the point of low solids and progressively increased the solids (starch solutions gradually becoming pigmented) generally failed, whereas those who came from blade coating at high solids and progressively cautiously diluted succeeded – not all is yet understood about the physics of this transition and how to promote filtercake formation without the onset of detrimental rheologically-dilatant induced structures (44). This dichotomy between the accepted wisdom for starch and the practical findings for high solids colours is exemplified by Culp (111) who reported the case for starch that the best quality and evenness was achieved by having the film split in the middle of the starch film between the roll cover and the paper, i.e. actively combating dewatering/penetration. This is now completely superceded for pigmented colours by the practice of promoting dewatering to minimise the wet layer thickness and maximising the transfer ratio, T, as shown in Fig. 16:

$$T = 100\,[w/(s_c m)] \qquad (7)$$

where w is the coat weight on the paper expressed as gm^{-2}, s_c is the solids content in w/w% and m is the premetered film weight on the applicator roll surface also expressed as gm^{-2} (112). It is not obvious how the filtercake model can account for transfer ratio variation, especially when considering different types of pigments. For example, the high water retention intrinsic to broad size distribution platy clays operates against dewatering (18) but decreases the immobilisation solids of the coating (113) and increases the viscosity. Nevertheless, without correcting for these characteristics when using blocky pigments (29, 114), which in fact promote dewatering (18) and therefore should increase transfer ratio, either by increasing the solids or modifying the formulation (29, 112), the misting tendency of the blocky particles remains.

A straightforward relationship either via filtercake formation (40, 52) or transfer ratio (112) and misting is, therefore, not universal. We must also continue to question the long-held assumption that coating colours really behave thixotropically in application at high speed, as the concept of increasing fluidity of a colour, based on a reducing viscosity in the shear region approaching a nip, is completely contrary to the observation that the MSP applies a contour coat with only very little penetration into the basepaper surface voids.

Increasing the transfer ratio reduces misting

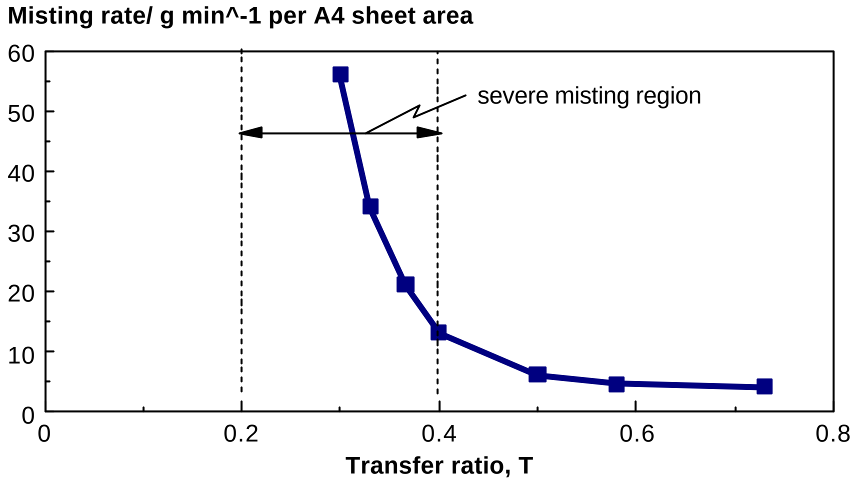

Fig. 16 Effect of transfer ratio on misting at 1 950 $mmin^{-1}$ (112).

Some indicators for formulating MSP pigmented coating colours

We have seen that viscous energy loss is identified as a means of reducing the impact of the film split and of counteracting the centrifugal forces which contribute to the misting tendency. The formation of a more concentrated layer next to the basepaper (the so-called filtercake) contributes to a visco-elastic layer which promotes separation of the film in the more purely viscous adjacent mobile layer. Achieving the balance between these factors depends on the pigment type in respect to morphology and water retention characteristics. When adopting blocky pigments with little viscous dissipation or intrinsic water retention, the formulation additives should provide for the viscous loss. These additives should avoid building visco elastic structures and should therefore be relatively non-interacting other than through physical packing criteria such as latex particle size - which in turn contributes to the volume fraction behaviour and as a consequence affects the viscous and high shear components of the colour rheology. Adsorption should be avoided, as also depletion flocculation/osmotic effects. Normally, the additives, therefore, should be further inert particles or emulsions, such as waxes or glycols for example, or they should be non-adsorbing low molecular weight species such as low molecular weight starch or the lowest available molecular weight CMC. The use of optical brighteners demands the support of an activating agent such as polyvinyl alcohol - once again this should be chosen to have low molecular weight and the effect on visco-elasticity should be thoroughly checked so that the best type can be identified. Synthetic thickeners are notorious for developing a “viscosifying efficiency” using small dosages. However, in general, they achieve this effect by building strong visco elastic structures. So, if synthetic thickeners are used, choose them for their apparent least thickening efficiency, i.e. choose relatively low molecular weight species that contribute to the viscous component of the rheology and not the elastic component.

The rheological properties of low structural viscosity work well in the actual nip of application to the paper, but there is always need for compromise in respect to coat weight control at the metering rod, pumping, cleanliness of the returning backing roll etc. Therefore, a strategy of seeking an optimum, as shown in Fig. 15, within the obvious constraints of the practical housekeeping on the machine, and not forgetting the end use character of the paper, is probably the best path available to follow today with the 'rule of thumb' that it is better to use more additive which thickens less than a small amount of a highly thickening agent.

SOME BASEPAPER CONSIDERATIONS

Interactions and surface roughness profile stability

Cross-sectioning studies combined with spatial wave analysis, first proposed by Gane et al. and Kent (4, 115) and then some ten years later repeated by Allem and Uesaka (116), showed the effect of coating-basepaper interaction. The basepaper roughening under the influence of moisture and hydraulic penetration as a function of the dwell time and dewatering characteristics was illustrated and shown to be of dominating importance with respect to modifications in coverage and final coated paper properties which was also supported in the meantime by Skowronski (117) and Gane et al. (118).

The use of the MSP as a precoater, eliminating the conventional dwell-time considerations discussed above, is gaining acceptance rapidly in the woodfree and board coating sectors. The contouring nature of the coat weight distribution provides for excellent coverage (25) and, provided the basepaper retains compressibility, the profile defects which are transmitted through to the topcoat can be compensated during the calendering process. Limitations arise when considering triple coating, in which case, if too much reliance is placed on the MSP coating to build coat weight, the rigidity or freezing of the base profile defects into the contoured coatings can no longer be compensated for during finishing. The combination of coater technologies is therefore of utmost importance. The MSP is used to best advantage on the first coat or, if the base is particularly rough, after blade or rod in the middle coat. Most modern installations of triple coated products run with the precoat relying on the MSP (119).

Runnability of the MSP, in respect to misting and patterning, is also severely limited when applying multilayer coatings (29). The closure of a precoated sheet makes the filtercake formation and dewatering phenomena necessary for good pickup and minimisation of the splitting wet layer difficult to achieve. This reduces the attractiveness of such technology for middle or topcoating considerations.

Absorption balance between the dewatering aspects of the coating colour and the absorptive rate and pore volume of the basepaper is critical. Today, as the acceptance of maximising filtercake formation grows, there is a danger that operators go too far in this direction, promoting highly porous bases and fast dewatering coating colours or colours operating very close to their immobilisation point. Such a situation is manifest by a dusting effect, in which dry coating colour spreads around the coating hall leaving a growing deposit of contaminating dust and a dry build-up can be seen in extreme cases on the applicator roll returning to the metering unit. This dry build-up can be indicative either of a separation occuring within the immobilised colour caused by too rapid dewatering, the existence of relaxation-induced dilatancy at the nip exit as a function of the coating colour solids-visco-elasticity relationship, or even by the forward carrying of relaxation-induced dilatancy at the exit of the metering rod. In all cases, the balance between wet misting and dry dusting must be carefully controlled, i.e. do not follow an over-enthusiastic reliance on just *one* model for anti-misting but consideration of the balance of all factors should be maintained.

In the woodcontaining sector, the attractive on-machine runnability aspects of the metered sizepress provide a strong stimulus for development in the LWC and LLWC coating areas. Once again, the quality of the basepaper in respect to uniformity and absorption criteria is crucial (120) and the roles of stone groundwood versus TMP continue to be a cause for debate.

CURRENT TRENDS

Light weight coated groundwood

Attempts to produce light weight rotogravure qualities are continually hampered, not only by basepaper quality and roughness development, relating to contour coating and basepaper relaxation, but by the inherent splitting and extensional geometry at the exit nip creating a disordering in the packing of conventional rotogravure pigments, especially those of high aspect ratio. While this assists anti-misting, it leads to a discontinuous surface on the micro-scale which in turn hinders the wetting by the solvent-based rotogravure ink on the timescale of contact in modern high speed presses.

The orientation of platy particles such as kaolin and talc can be observed by X-ray diffraction techniques, as outlined by Gane et al. (53), by comparing the in-plane (*001*) and almost perpendicular (*020*) Bragg reflexions. The rotogravure print quality is shown in Fig. 17 to be related to the orientation of the particles in which good missing dot performance and even dot gain demands in-plane orientation of the particles and *not* a disordered structure. Such disordering, unfortunately, is inherent to the MSP coater. Ordered coatings can only be achieved using in-plane shear such as from a blade application.

Sensitive correlation of rotogravure missing dot count with kaolin particle *mis*alignment as a function of solids content at fixed speed and blade *tip* geometry

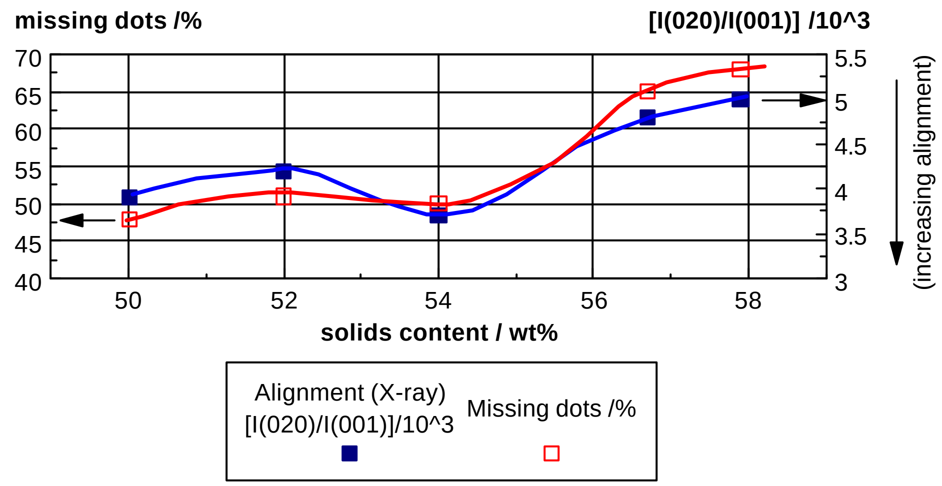

Fig. 17 Effect of particle orientaion on the rotogravure print quality (taken from Gane et al. (53)).

The orientational criteria, however, become less important as pigment aspect ratio decreases and the widespread use of electrostatic print assist, despite its tendency to reduce dot uniformity even on coated grades, indicates that, provided some compromise on quality can be tolerated, producers are willing to consider and to install the MSP for LWC with excursions into rotogravure production currently being witnessed in Europe.

Offset LWC qualities are more readily achieved using the metered sizepress and the increasing brightness demands in these grades with their inherently higher levels of low aspect ratio calcium carbonate and glossing clays makes them ideal candidates for this technology (110, 121, 122). The success of the identification of the FCO (film coated offset) grade as a market leader in a new genre is well documented (98, 103) and is testament to the potential in this application. Four units for production of LWC-FCO with MSP are in production in Europe and three are ready for start-up during 2000-2001 (123).

Mill	MSP application	Width /m	Speed /mmin^{-1}	Year	Prod.Cap. /kt
Running:					
Haindl Augsburg, Germany	C2S	3.6	1200	1993	100
Metsä Serla Kirkniemi, Finland	C1S + C1S	6.5	1200	1994	170
Papierfabrik Albbruck, Germany	C2S	3.3	850	1995	80
SCA Ortviken, Sweden	C1S + C1S	8.0	1200	1996	230
Under planning and start up:					
Perlen PM4 Switzerland	C2S	5.4	1500	2000	150
Cart. Burgo Verzuolo, Italy	C2S	10.5	1800	2001	400
Haindl Augsburg, Germany	C2S	9.6	1800	2000	400

Table 1 Current and projected LWC production using metered sizepress (taken from Åkesson (123)).

The leading manufacturers of MSP systems have installed and commissioned about 350 machines in the last few years and many can be seen in the lightweight coating and woodfree precoating applications. It is reported that at one pilot coater installation in Europe alone (VESTRA), since the MSP was commissioned at that site, 159 out of the past 541 trial days were used for MSP investigations, i.e. ~ 30 % (121). From these trials, running conditions have emerged with a line load of 15 kNm^{-1} for the highest speeds and with roll hardnesses of up to 90 P&J for softer normal rubber rolls with Polyurethane adopting harder options at between 30-35 P&J (121, 122, 124-130), thus supporting the trends previously discussed..

Newsprint

Economic factors place newsprint production in its present form increasingly under pressure to become cheaper and there is little room for development of conventional grades (131-141). However, coldset offset has potential for a variety of communications sectors and surface treated newsprint or even coated news can be derived from relatively simple MSP considerations (5). The four colour press is no longer only considered for advertising but is also becoming part of the news content pages. This is a trend caused by the need to remain attractive against the electronic media distribution of news and to attract advertising in high quality inserts and magazines. The increased costs of coating can be set off against the reduced consumption of ink and improved service life, improved print contrast and a more uniform impression. Recycled fibre can also be used readily in such grades due to the relatively stress-free application afforded by the MSP.

Recently, work has been reported by Paprican studying the application of surface treatment to a 46 % solids “wet web” at 600 mmin^{-1} by installing an experimental film applicator with an hydrophilic rubber covering within the press section at the fourth press, after the shoe-press, of the paper machine, including various starches and polymer additives (142). Starch application at 2 gm^{-2} improved strength and ink holdout and almost doubled the z-direction tensile strength as measured by Scott Bond on the calendered paper. Carboxymethylcellulose at 0.15 gm^{-2} had similar effects with improved linting tendency being observed. Pigment-starch, mixtures, based on calcium carbonate, could be applied up to 6-7 gm^{-2} with further strength improvements and a 3-point lift in brightness. The improved starch holdout was attributed to the filtercake formation of the immobilised pigment layer.

Coated InkJet and Digital papers

Copy papers form another commodity under increasing price competition. The high quality of uncoated copy grades today with ultrahigh brightness, bulk and stiffness can no longer be developed further along traditional lines. The door is open for an improved grade through the use of coating. A number of solutions are already becoming available, ranging from new forms of surface modified calcium carbonates and clays through to colloidal precipitated calcium carbonate, all targetted at full or part replacement of high cost precipitated silicas (143, 144) in inkjet applications. Commercial results from surface enhanced aluminosilicate and specially structure surface-modified calcium carbonates have been shown to reduce lateral ink spread and strikethrough.

Recent modelling and experimental observations by Gane, Schoelkopf et al. and Schoelkopf, Gane et al. (146, 147) have highlighted the possibility of developing rapid absorption properties with respect to water and low viscosity oils by concentrating the pore size distribution of porous media within the 0.05 to 0.1 µm region. This leads to a concentration of the otherwise differentiating preferred pathway dynamic of absorption caused by inertial retardation of short timescale imbibition into larger pores. Such a preferred pathway is shown in Fig. 18, where a Pore-Cor[4] model unit cell is used to describe a porous structure, typically found in a compressed calcium carbonate coating layer, with its associated wide range of pore sizes.

[4] Pore-Cor is a software program name of the Fluids Interaction Group, University of Plymouth, PL4 8AA, UK

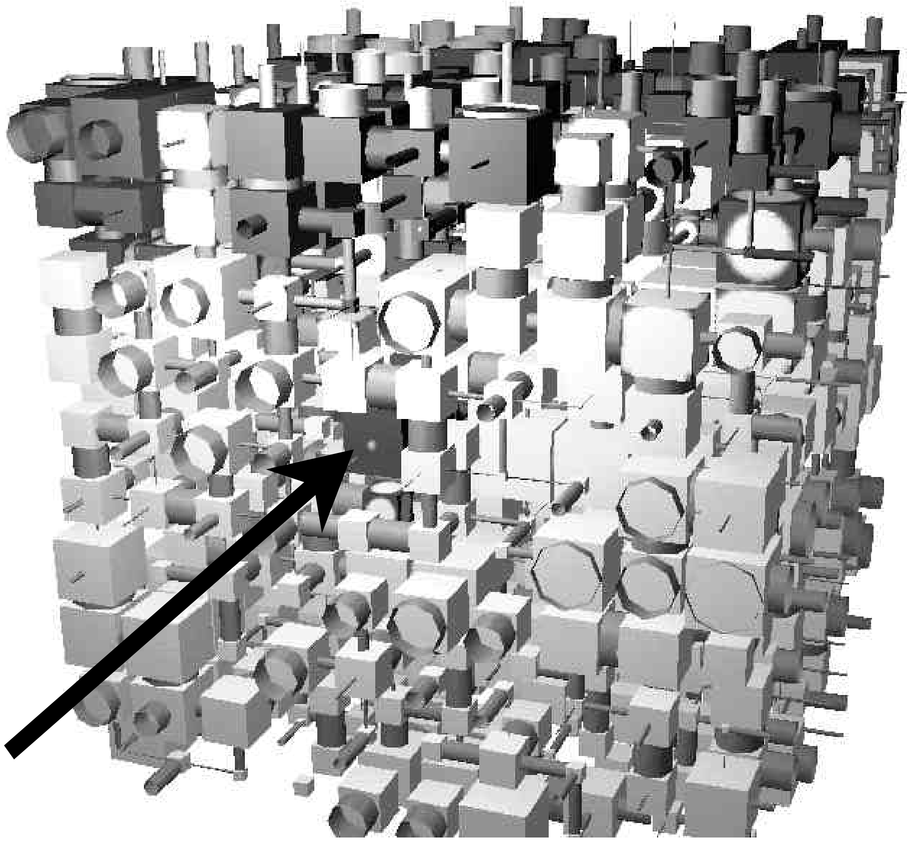

Fig. 18 Schematic of a Pore-Cor cell filling under inertially controlled exclusion for water and a high porosity structure (porosity $\boldsymbol{\Phi}$ = 28.02 %, pore row spacing Q = 1.26 µm)

We can see that the fluid has permeated deeply into the structure following a pathway defined by the wetting algorithm based on the Bosanquet equation (148),

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\pi r^2 \rho x \frac{\mathrm{d}x}{\mathrm{d}t}\right) + 8\pi \eta x \frac{\mathrm{d}x}{\mathrm{d}t} = P_e \pi r^2 + 2\pi r \gamma \cos\theta \qquad (8)$$

which was solved by Schoelkopf, Gane et al. (145) in the absence of any external pressure, (P_e = 0), to establish in particular a short time absorption with permeation linear with time t, acting through the shortest, finest capillaries before the laminar Poiseuille viscous drag can be established over these short distances; where r is the radius of the capillary, x is the distance permeated by the fluid of density, ρ, and viscosity, η. In larger pores, the fluid is momentarily retarded due to the mass which has to be accelerated according to Newton's Law and the permeation proceeds subsequently by the familiar $\sqrt{t}$ relationship of Lucas Washburn (149, 150).

The pigment design shown in Fig. 19, an example of a calcium carbonate pigment structure derived to develop internal pore volume and rapid absorbency, is based on the model and concentrates the pore size within the critical linear *t* absorption. This allows fluids to be captured preferentially into these structures rather than distributing them throughout $\sqrt{t}$ dependent structures.

Such a pigment with a designed surface area of $\geq$ 75 m^2g^{-1} also provides high adsorbency for polymers and dyes, and effects a strong toner adhesion in laser printing.

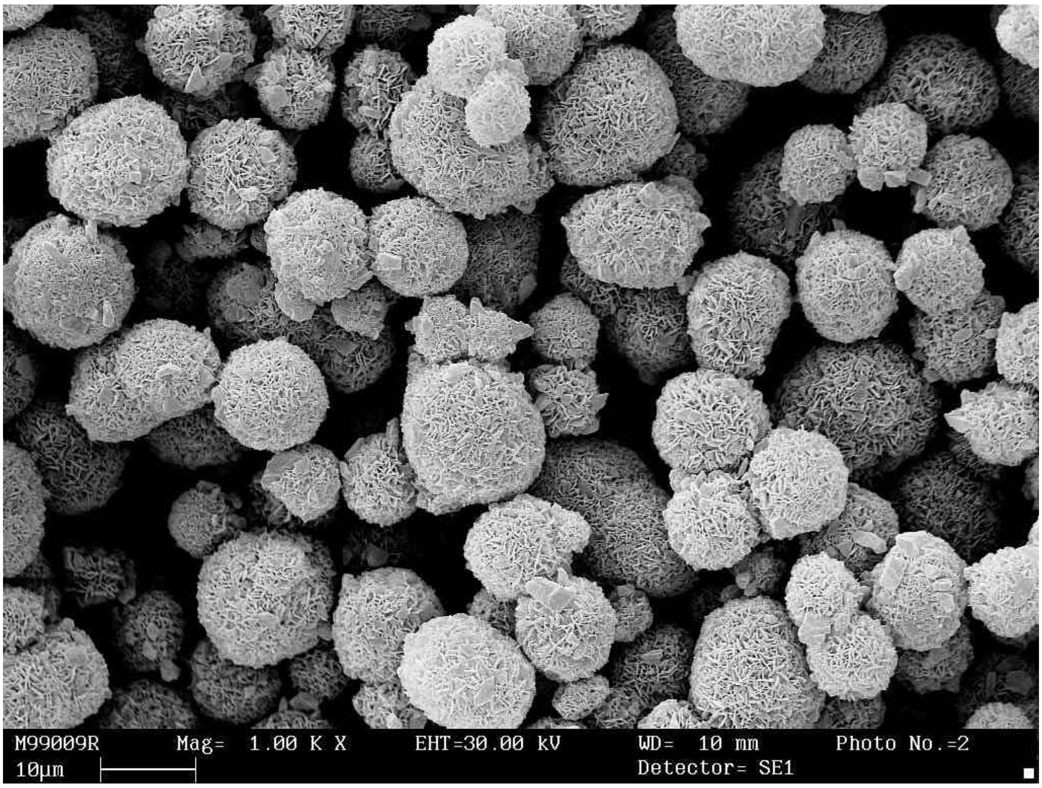

Fig. 19 Electron micrograph of modified natural ground calcium carbonate designed for maximum absorption rate based on the absorption studies of Gane, Schoelkopf, Matthews, Ridgway and Spielmann (145, 146).

These concepts may also be suitable for avoiding the use of internal sizing by using high surface area pigments as fillers and as coatings. The internal absorption capacity acts to capture ink and prevent strikethough - a role traditionally played by the internal sizing to stop wicking along fibres. Coating colour solids content today for some of these newly developing grades is relatively low: silicas today are coated at ~ 20-25 %w/w. With speciality binders and polymers, some of the newest proposals target ~ 50 %w/w, for which the MSP is ideally suited.

High surface area pigments suggested as fillers for MSP coating basepapers

Not only can we consider competitive absorption strategies in respect to printing but also in respect to promoting effective coating colour dewatering without impulse pressures by drawing the water phase into these filler structures if used to fill MSP coating basepapers. Such a strategy avoids the problems of impulse pressures leading to relaxation-induced dilatancy whilst still promoting the necessary filtercake formation for good coverage and MSP runnability. This concept is shown schematically in Fig. 20.

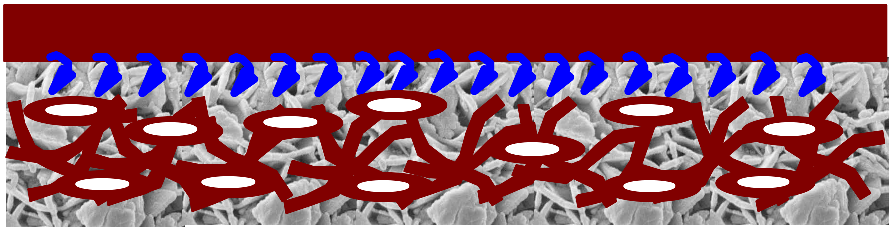

Fig. 20 Absorption following the inertial pathway model promoting immobilisation of a coating layer.

A future in post-coating treatment?

Surface chemistry plays a determining role in interactions with both existing and emerging printing technologies. To introduce novel surface chemistry, modifications in conventional suspensions are extremely difficult and moves against the already accepted optimisation of dispersions and rheological properties of coating colours. Why not use the MSP to apply solutions of chemicals and/or polymer dispersions directly onto a preformed coating layer? This could, for example, encompass the cationisation of anionically dispersed coatings, obviating the need to develop specialised cationically dispersed pigments and binders. Barrier layer coatings could be made from polymer films applied to conventional coated grades. The opportunities seem endless, the innovation amongst our scientific and engineering community needs to be awakened to take advantage of the tools for rapid change that this technology provides.

CONCLUSIONS

The metered sizepress is seen as a dominant coating technology for surface treatment of a wide variety of basepapers. Development potential continues to be strong based on the theoretical and practical issues reviewed in this article and can be divided into the following *categories*.

Runnability of high solids pigmented coating colours on the metered sizepress depends on a complex balance between rheology and water retention. A simple mechanism of filtercake formation is difficult to control as coating weight increases. The problems of misting and film uniformity cannot be solved in the same way as for starch sizing. It is suggested that the reason for this derives from the complex nature of the interactions in the coating colour suspension. A novel rheological phenomenon is considered as a possible limiting factor in this process. Examples of pigmented metered sizepress coating show that the pulse dynamics acting on coating colours play an important role in film splitting phenomena and the formation of deposits after pulse dewatering of visco-elastic coating colours. This rheological phenomenon has been defined as 'relaxation-induced dilatancy'. To avoid deposits and misting it is necessary to run with the promotion of controlled dewatering and a high viscous component (loss modulus, G'') whilst minimising elasticity (storage modulus, G'). This requires the use of thickeners and additives which, contrary to today's blade coating practice, develop water retention control without forming additional strongly elastic interactions in the coating colour. The predominance of low molecular weight starch and other polymer, glycol and wax additives in metered sizepress formulations has been a natural consequence of these theoretical considerations.

The *basepaper* uniformity is of prime importance as the metered sizepress applies a contoured coating preserving the roughness profile and relaxation characteristics of the basepaper.

Metered sizepress coatings are now firmly established in most of the standard *offset coating grade applications* either within multi-coating woodfree grades or for lightweight woodcontaining grades. Limitations are still seen for traditionally formulated rotogravure coatings due to the retention of the basepaper roughness profile and the disordering of high aspect ratio pigments. Surface microroughness features can reduce gloss and printability potential.

New *upgrading* of hitherto uncoated papers will be the future growth for metered sizepress outside the traditional coated grades. Newsprint surface treated and full coated, inkjet and digital printing papers are among the most likely to develop rapidly.

Finally, the *future* is virtually unlimited when consideration is given to yet untried concepts. One is suggested here: the modification of surface chemistry, structure, adsorption and absorbency by post-coating surface treatment of specialised pigments and chemicals using the metered sizepress.

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