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ON THE DRY AND WET SURFACE STRENGTHS OF COATED PAPER

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ABSTRACT

Lack of surface strength in coated paper can cause significant problems both in offset printing and in different converting operations. Several factors can influence this surface strength. The first part of this paper summarizes previous work concerning the relation between the mechanical properties of the coating film itself and the dry surface strength of coated paper. From studies including both clay and $CaCO_3$ pigments, it was concluded that both the in-plane mechanical properties of the coating films and the dry surface strength were to a large degree determined by the choice of pigments and the type of styrene-butadiene (SB) copolymer used as binder. The difference between clay-based and $CaCO_3$-based coatings was of special interest in this study. The second part of this paper describes a laboratory method for measuring the wet strength of coated paper. The method has been applied to paper coated with either clay or $CaCO_3$, the coatings being bonded with different amounts of SB. The fracture in the coating in the wet state is shallow and, contrary to the fracture in a dry coating, does not penetrate down to the base paper. The particles removed are also rather small, typically 10-30 μm in diameter. Paper coated with $CaCO_3$ had a higher wet surface strength than paper coated with clay. This may be due to a higher degree of adhesion between $CaCO_3$ and SB than between clay and SB, which would yield a higher water resistance.

INTRODUCTION

In offset printing of coated paper and also in various converting operations the coating itself is subjected to significant forces and deformation both in a dry and in a wet (moistened) state. The surface strength of coated paper (in both states) is thus an important quality parameter (1-3) in most situations. It is however difficult to assess with certainty the mechanism determining the coating rupture since the coated paper provides a complex system. There are a number of factors which might influence the mechanical performance of the coating on a base paper, e.g.

* The properties of the base paper
* The mechanical properties of the pigments and the binders constituting the coating
* The adhesion between binder, pigment particles and base paper
* The structure of the coating
* The process conditions during the coating operation

For example, the fact that the IGT-strength of a coated paper generally increases if the base paper is surface-sized prior to coating is an illustration of the importance of the base paper properties in this context. The failure mechanisms are not however necessarily the same in these two cases, which makes a comparison somewhat difficult. Another example is that a more intense drying during the coating process may increase the surface strength, which may be a result of changes in the binder distribution and reduced fiber swelling. The adhesion between binder, pigment particles and the base paper is obviously very important with regard to the mechanical performance of the coated paper, but it can also affect the printability of the paper (4).

It is certainly expected that the mechanical properties and the structure of the coating film itself will influence the surface strength (in both the dry and wet states) of the coated paper. The coating can be considered to be a composite material, consisting, to a first approximation, of pigment particles, binder (often a synthetic polymer) and voids. It can be expected that in addition to the properties of the pigments and the binders, the amount of binders used, the binder distribution, the size and the shape of the pigment particles and the adhesion between the pigment particles and the binder will also determine the mechanical properties of the coating film. It cannot a priori be assumed that the theories used to describe the mechanical performance of filled polymers (5,6) can be applied to coating films due to their low amount of polymeric binder and their non-homogeneous character. The prediction of the mechanical properties of the coating film itself is thus an extremely difficult task and the corresponding prediction of the dry and wet surface strengths of the coated paper even more so.

The purpose of the present communication is twofold. The first is to review earlier results (7) regarding how the binder and the pigment affect the properties of the coating film and to see whether these properties can, to some extent, be correlated with the dry surface strength of coated paper. The second is to describe a method for quantifying the surface strength of coated paper in the wet (moistened) state. To some extent, the ruptures in the wet and dry states are compared and the effects of binder content are investigated. Coatings based on both clay and calcium carbonate have been analysed using the proposed laboratory method. The purpose of this study has been to determine the load at which the rupture of the coated paper is initiated, i.e. when the first particles are removed from the coating.

MECHANICAL PROPERTIES OF COATINGS IN THE DRY STATE

Coatings in which clay or calcium carbonate has been used as pigment and carboxylated styrene-butadiene copolymers with different glass transition temperatures as

binders have been studied. The typical appearance of the fracture in the coating of the coated paper in the dry state (after testing in the IGT apparatus) is shown in Fig.1. A large piece, which may be of the order of 100 μm or more in diameter, is peeled off the coating. The fracture penetrates the coating down to the base paper and the fibers are clearly visible.

Fig 1—Scanning electron micrograph of a fracture in a coating (dry state). Note that the rupture goes through the coating down to the base paper.

The influence of binder choice on the properties of clay-based coatings.

An increase in the binder content improves the in-plane mechanical strength and the elongation at rupture of the clay-based coating film (7). This is to be expected since the increased binder level improves the stress transfer between the pigment particles. The binder thus takes an active part in this stress transfer. The glass transition temperature (T_g) of the binder also influences the mechanical properties of the coating. When a series of styrene-butadiene (SB) copolymers with T_g-values in the range -17 to 40°C were used as binders, the mechanical strength increased when SB-binders with higher T-values

were used (at constant binder levels) (7). The elongation at rupture of the film decreased with increasing T_g of the SB-binder used. When a binder with a T_g of -17°C was used, the in-plane ultimate elongation was ca 0.8% (10 parts of binder), whereas for binders with T_g -values exceeding room temperature the elongation was very low, below 0.1%. This is probably due to the brittleness of these binders.

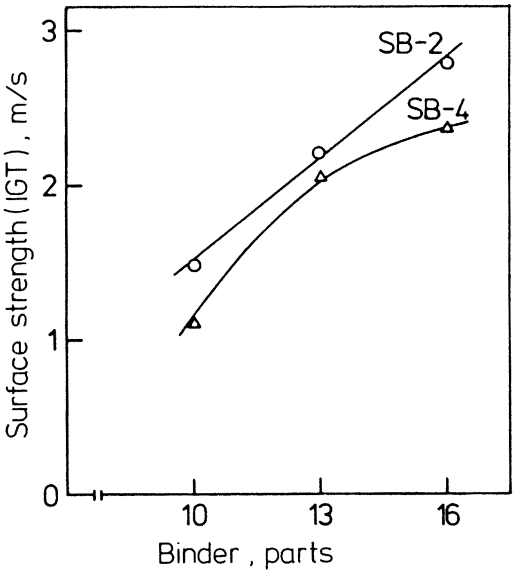

Fig 2—The dry surface strength (IGT-strength) of clay-coated papers vs the amount of SB-binder. Two SB binders with different T_g-values were used; 3°C for SB-2 and 25°C for SB-4.

Fig. 2 shows as a function of binder content the IGT-strength of paper coated with the same pigments and binders as discussed above. Two SB-binders were used here, one (SB-2) with a T_g of 3°C and one (SB-4) which softened at about 25°C. The dry surface strength (IGT-strength) increased with higher binder levels and was higher when a softer type of binder was used. This is not always true, but it holds in many situations. The behaviour shown in Fig. 2 is relatively well-known (8,9). There appears to be some kind of relation between the surface strength of the coated paper and the in-plane ductility, i.e. the elongation at rupture, of the coating film. For the

surface strength, the T_g -value is nevertheless not the only binder property which is important. The binder particle size, the degree of carboxylation and the amount of surfactants used may also influence the results (9,10).

The influence of pigment choice on the properties of SB-bonded coatings.

In a series of experiments, clay in the coatings was successively replaced by $CaCO_3$ while the same amount (10 parts) and type of SB-binder was used. Fig. 3 shows the in-plane mechanical strength of such coating films at different values of the clay/$CaCO_3$ -ratio. Values of the corresponding IGT-strength of the coated paper are also included in Fig.3. As can be seen, the in-plane strength of the coating films decreased with increasing amounts of $CaCO_3$, whereas the IGT-strength varied in the opposite manner. The elongation at rupture (not shown in Fig.3) decreased with increasing amounts of $CaCO_3$.

There are several possible reasons for the difference in mechanical behaviour between clay-based and $CaCO_3$-based coatings. First it should be remembered that when the IGT-strength is evaluated it is the out-of-plane properties of the structure which are of importance, whereas only the in-plane properties of the coating films were measured. There is also a difference in particle shape between clay particles and $CaCO_3$ particles. Clay particles are plate-like and more or less oriented parallel to the flow direction during the coating process. This gives better properties of such coatings in that direction (5) than the case when $CaCO_3$ particles, which have a more spherical shape, are used. In the transverse direction this is not necessarily true. An evaluation of the oxygen/carbon-ratio in the coating using ESCA (Electron Spectroscopy for Chemical Analysis) gave indications that the binder covered the $CaCO_3$ better than the clay particles (7). This indicates that for clay-based coatings the binder is more confined to regions (in the plane) between pigment particles, which can also partly account for the observed behaviour. In addition, the adhesion between $CaCO_3$ and SB appeared to be higher than between clay and SB (7), which may also be of importance in this context.

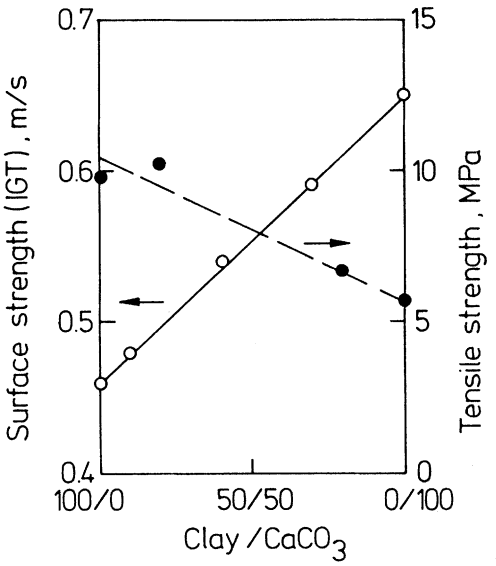

Fig 3—The in-plane mechanical strength of coating films ( ) based on blends of clay and $CaCO_3$ and the IGT strength of papers (o) coated with the corresponding blends. The SB-binder (10 parts) used has a T_g-value of 3°C.

Concluding Remarks Regarding the Dry Strength of Coated Paper

The effects of binder and pigment choice on the properties of the coating film itself and on the surface strength of coated papers are complex. It is probably even more complex than indicated here. There is some relation between the properties of the coating film and the dry surface strength of coated paper, but this relation is certainly not a straightforward one. The adhesion between the base paper and the binder may also have a strong bearing on the dry surface strength of the coated paper, and this certainly would make it difficult to find any direct correlation between the dry surface strength and the properties of the coating film. Measurements on coating films can however be valuable in the evaluation of the adhesion between pigments and binders, the binder distribution and a number of other factors which are important for the performance of the coated paper.

THE WET SURFACE STRENGTH OF COATED PAPER

In this part, a method to evaluate the wet surface strength of coated paper is described. A base paper with grammage of 70 g/m^2 and a Cobb $_{60}$-value of 30 g/m^2 has been used throughout this study. Both clay and $CaCO_3$ have been used as pigments. A carboxylated styrene-butadiene copolymer with a T_g-value of 3°C was used as binder together with 2 parts of carboxymethyl-cellulose.. A minor amount of a wet strength resin was also added to the coating color. The base papers were coated with a laboratory device and subsequently dried at 105°C for 30 minutes.

Measurement of the Wet Strength

The wet surface strength of the coated paper was measured at 23°C using a Prufbau-press. The coated paper was moistened with distilled water, which was transferred to the paper with a disc at a speed of 1 m/s. The amount of transferred water was ca 2 g/m^2. Two seconds after the wetting, a rubber disc covered with oil travelled over the surface of the coated paper at a constant speed. The viscosity of the oil was in this case 2.1 Pa.s, but oils with different viscosities can be used depending on the strength of the coated paper. After each such printing with oil the number of particles that adhered to the rubber disc was determined with the aid of a stereomicroscope. The printing operation was performed at a series of velocities.

Dynamic Mechanical Properties

The dynamic mechanical properties of the coatings (without the base paper) were measured as a function of time in a humid environment (90 % relative humidity, RH) at 23°C. The measurements were performed using a Torsional Braid Analyser operating at ca 1 Hz. Prior to the exposure to the humid atmosphere, the coatings were dried at 105°C for three hours.

RESULTS AND COMMENTS

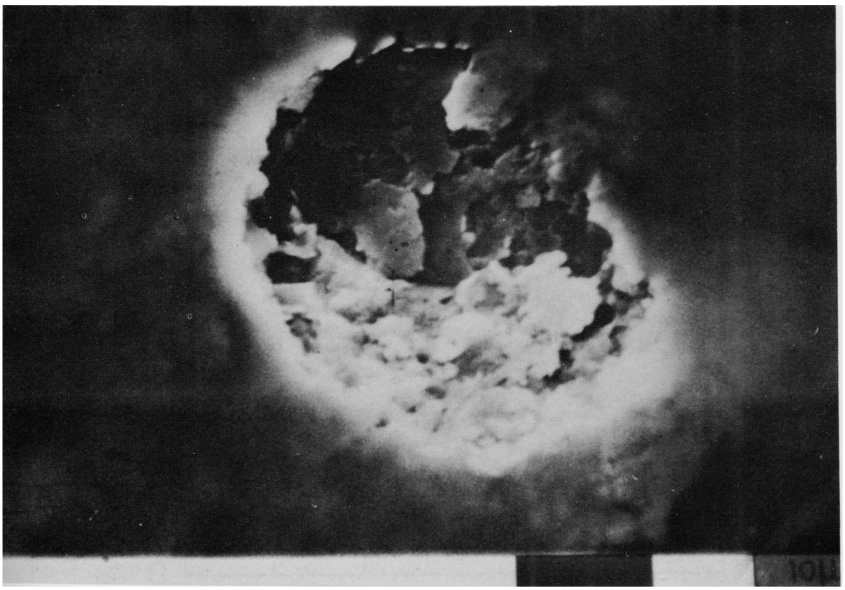

Fig 4—Scanning electron micrograph of a fracture in a coating (wet state) resulting from the Prufbau-test.

SEM-studies (Scanning Electron Microscopy) of the fracture in the coatings

Fig.4 shows a typical picture of the fracture in the coating in the wet state after testing in the Prufbau-press. A small piece of the coating, typically 5-30 μm in diameter, is torn from the coating and the rupture does not proceed down to the base paper. The piece removed from the coating may consist of an agglomerate of a few pigment particles. The appearance of the rupture is completely different from that observed in the dry state, cf. Fig. 1.

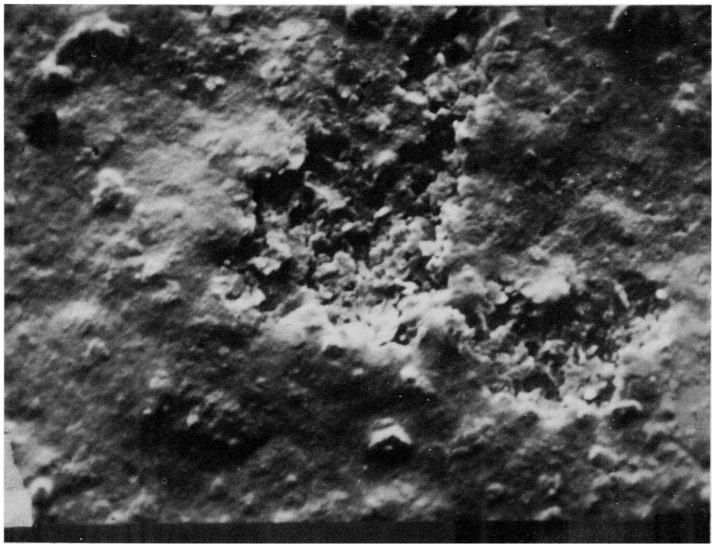

Fig 5—Scanning electron micrograph of a fracture which occurred during printing of the coated paper. The rupture is believed to be due to a lack of wet surface strength. Note the similarity with the appearance of the rupture in Fig 4.

Fig.5 shows another scanning electron micrograph of a rupture in a coated paper. In this case the fracture occurred during printing of the paper and it was believed that it was due to insufficient wet strength of the coated paper. The similarity in appearance between this fracture and that observed after the Prufbau-test (Fig.4) is obvious.

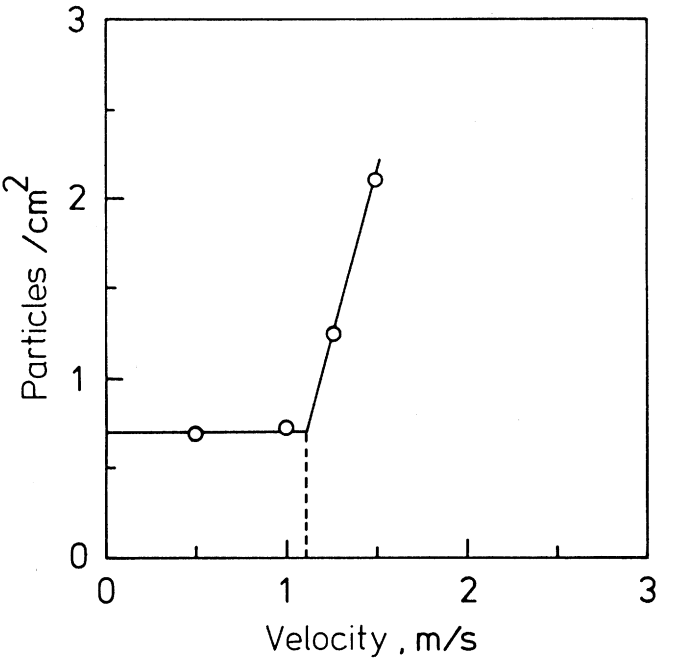

Fig 6—The number of particles/CM² removed from the coating vs the velocity of the rubber disc. At a certain critical speed the number of particles removed increases drastically.

Fig.6 shows how the number of particles/cm^2 that adhered to the rubber disc varies with velocity of the disc. The base paper was here coated with clay with 10 parts of SB as binder. Some particles are removed even at very low velocities, but at a certain critical speed the number of removed particles increases drastically, see Fig.6. This critical speed may thus be used as a measure of the wet surface strength of the coated paper.

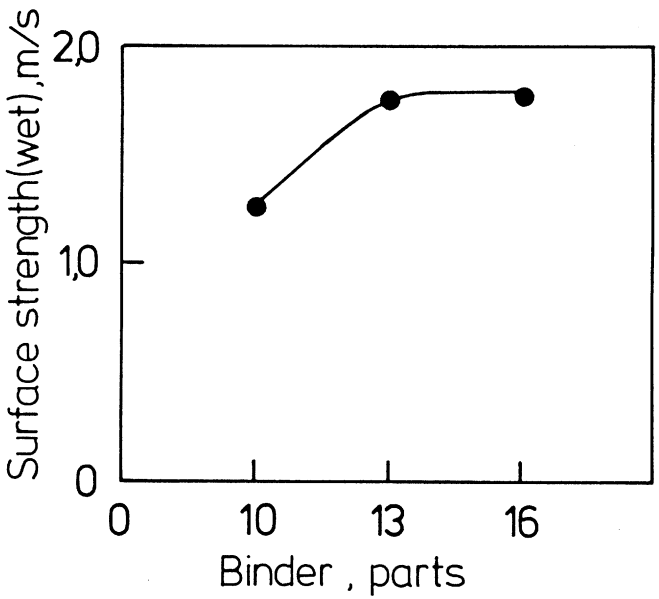

Fig 7—The critical speed (the wet surface strength) vs the amount of SB-binder. The papers were coated with clay pigments.

The effect of the SB-content on this wet surface strength (the critical speed) is shown in Fig. 7. As expected, an increase in the amount of binder increased the wet surface strength although there was a tendency for it to level out at higher SB-contents. Again, the pigment used in the coating was clay. It can be expected that the number of particles removed from the coating at velocities lower than the critical velocity may also provide information regarding how well individual pieces (particles) are anchored in the coating. To some extent this may be true, since the number of such particles decreases with increasing binder content as shown in Fig.8. However, more experimental work is certainly required to substantiate this point further.

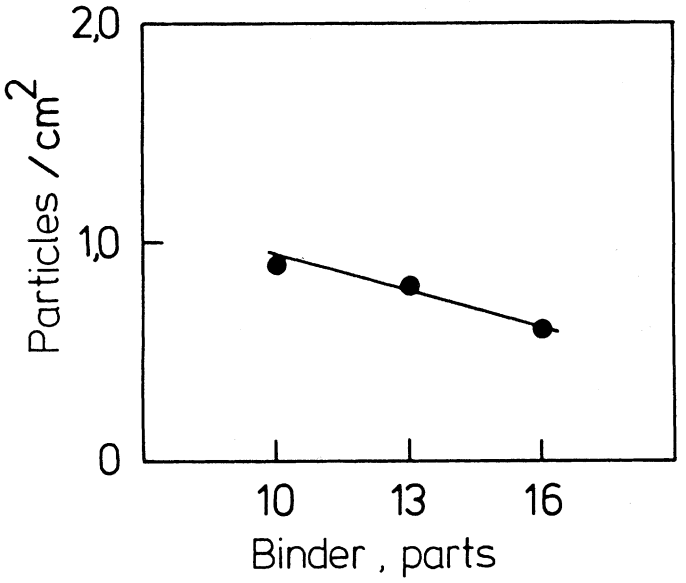

Fig 8—the number of particles/CM² removed from the clay based coatings vs the SB-content. The velocity of the rubber disc was lower than the critical one, corresponding to the horizontal portion in Fig 6.

The wet surface strength of paper coated with $CaCO_3$ and 10 parts of SB was also determined. In general, the wet surface strength of the $CaCO_3$-coated paper was found to be significantly higher than for clay-coated paper. This is in agreement with results from other types of wet pick resistance measurements (1). In itself this is not very surprising since earlier work has indicated that the SB-binder covers the $CaCO_3$ particles more than the clay pigments and that the adhesion between $CaCO_3$ and SB is higher than between clay and SB (7). The difference in particle shape between the two pigments may also be an additional cause for the difference in wet surface strength (7). If the adhesion is lower between clay and SB, the clay-coatings might be expected to be more sensitive to water exposure, since the interphase between the clay particles and the binder may be rather susceptible to moisture attack, which can lead to a deterioration in the strength characteristics.

This is analogous to the effect of moisture on the mechanical strength of filled plastics (5). The fact that clay is more hydrophilic than $CaCO_3$ (11) is also of importance in this context.

Effect of the Humidity of the Dynamic Mechanical Properties

In order further to study the effect of moisture on the mechanical behaviour of the coatings, dynamic mechanical testing was employed. The glass braids used in these experiments was impregnated with either clay-based or $CaCO_3$-based coating colours. After careful drying, the braids were exposed to a humid environment (90% RH) and the logarithmic decrement Δ was measured as a function of time during conditioning at this humidity. The logarithmic decrement, which is a measure of the mechanical losses, was chosen as a suitable parameter to follow the effect of the moisture since it is known that Δ is sensitive to changes in the structure.

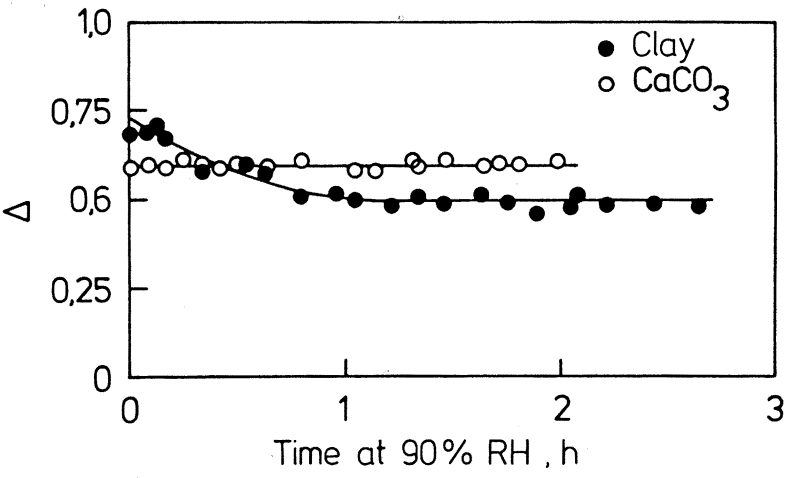

Fig 9—The logarithmic decrement for clay-based and $CaCO_3$-based coatings as a function of the time of conditioning at 90% RH at 23°.

Fig. 9 shows the variation of Δ with time of conditioning at 90% RH for clay and $CaCO_3$ coatings. The amount of SB in both cases was 10 parts per 100 parts of pigment. The $CaCO_3$-system appears to be virtually unaffected by the moisture, whereas the logarithmic decrement for the clay coatings decreases with time due to the effect of moisture. The observed behaviour is largely in agreement with the discussion in the preceding section, i.e. clay-based coatings are more water-sensitive than $CaCO_3$-coatings. From measurements of this kind it is not however possible to establish that it is the interphase between the pigment particles and the SB-binders that is primarily attacked by water, although, in this case, it is very probable.

For filled rubber, a lower value of the mechanical losses has been attributed to a lower degree of adhesion between the filler and the rubber (12). The same interpretation can perhaps be applied to coatings of the type discussed here and it would also fit the experimental observation. However, the interrelation between the dynamic mechanical losses and the adhesion between the phases cannot be considered to be fully understood at present and any detailed interpretation along these lines must be made with caution. More theoretical and experimental work on this subject would be most welcome.

Final Remarks Concerning the Wet Strength

The rupture in a wet coating differs considerably from that in a dry one. When tested in the wet state, smaller particles are removed from the coating and the rupture does not go through the entire coating down to the base paper. This implies that the properties (and amount) of the binder and the adhesion between the pigment and binder are likely to be primary factors in controlling the wet surface strength of coated paper. The nature of the interphase between the pigment and the binder and its stability against water is naturally very important in this context.

Some of the particles that were removed from the coating when measuring the wet surface strength were

analysed using the EDXA-unit (Energy Dispersive X-ray Analysis) of the scanning electron microscope. The results, which are only very preliminary in character, indicate that the composition of these particles is different from that of the coating itself. Work is now in progress at STFI to investigate this point further. It is at this stage not possible to give any definite statement concerning the general validity of the results or regarding the possible type of particles removed.

A laboratory method for evaluating the wet surface strength of coated paper has been proposed in this short communication. More systematic investigations regarding its applicability in different situations are currently being carried out in order to evaluate the usefulness of the method. Such studies are also expected to cast more light upon the mechanisms controlling the wet surface strength, including the effect of wet-strength resins, storage time, blends of clay and $CaCO_3$ etc. Perhaps, the most important test of the proposed method is to see whether it provides data which correlate with what today are claimed to be "wet surface strength problems" in practise. The results obtained from application studies so far indicate that this is the case. If so, the proposed method may be useful in isolating wet strength problems from other types of complications.

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Transcription of Discussion

On the Dry and Wet Surface Strengths of Coated Paper
by I. Pettersson, M. Rigdahl, I. Fineman and G. Engstrom

T. Krinkski Ralston Purina Co., St. Louis, USA

You mention in your paper that the sheets were dried at 105°C for 30 minutes. Do you think these drying conditions could contribute to possible excessive migration of latex through the coating surface?

Prof M. Rigdahl Yes, there always will be some influence by the heat treatment, that is true. However, this is a model experiment and I don't think the conclusions will be affected.

Prof. J. Kline Western Michigan University, Kalamazoo, USA

I am interested in your tests on the in-plane tensile strength measurements of the coated film and I am not sure how you would have done that measurement.

Rigdahl We coated films of varying thickness onto an aluminium sheet which had been laminated with polyethylene film. It is a very difficult procedure to perform accurately and requires a great deal of experience and expertise.

Kline I would question some of the explanations for the variation in strength on a couple of points, one of them being the difference between the structure of a film cast on polyethylene as opposed to a film cast on paper.

Rigdahl Yes, I am aware of what you are saying but what we are trying to do here is to indicate that surface strength is not the only important mechanical property of a coating.

I.K. Kartovaara FPPRI, Helsinki, Finland

It is known in papermaking that shives or coarse particles cause discontinuities in the network which can initiate rupture. Do you have any evidence that in your areas of rupture there was any difference in the particle size distribution compared with other regions?

Rigdahl If you examine the sample in an SEM you will see a range of particle sizes 1 micron up to 50 microns. We have not found any particular evidence to indicate that there is a concentration of large particles in these areas.

Kartovaara Have you measured the modulus of elasticity of those coating films and if so, does it follow the same pattern as tensile strength?

Rigdahl Yes, in most cases it does.

S.F. Loveday Townsend Hook, Snodland, England

In the litho printing process the first ink down is a water saturated ink on a dry paper. You have taken a dry ink on a saturated paper. Why is this?

Rigdahl We are trying to develop a method for looking at the onset of rupture in coating films in the wet state and of course we need more experience to see that the method reflects what one sees in production printing.

Chairman You mentioned that some of the material removed from the surface was of a different composition to the rest of the coating. What would be your explanation to this?

Rigdahl At this stage in our work I do not have an explanation to give you.

Chairman You showed in your model the platelets connected by polymer on the edges. Clay platelets in water have a quite different chemistry on the faces compared to the edges. Is your supposition that this is due to the different chemistry on the edge of the platelet?

Rigdahl No, I do not think that this is the major factor.

Prof. J. Marton Westvaco Corp. Laurel, USA

The strength of the coating is dependent on two other factors. One is the drying and the other is the interaction with the base material. So I feel in any work you do you should define a drying scheme which comes closest to reproducing real life conditions otherwise your conclusions may be a little different from practical reality.

Rigdahl At this stage I am not so much interested in what the paper does but rather how the mechanical properties of the coating affects the surface strength.

Marton In studies we have carried out in the past we have never seen a completely wetted particle such as you show in your model.

Rigdahl You should not regard the model as being too realistic but merely a device for stressing the possible differences between the clay pigments and the carbonate particles in this respect.