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A REVIEW OF THE INFLUENCE OF PIGMENTS ON PAPERMAKING AND COATING

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INTRODUCTION

Much of the scientific study of papermaking is concerned with the properties and behaviour of the cellulose fibres that form the basic structure of all grades of paper and board. This is entirely understandable because the fibres are the major constituent and their spatial arrangement, bonding, mechanical, physical and chemical properties are fundamental to the properties of the finished product. In addition, the nature of the papermaking process, involving low solids contents in water, rapid drainage and thin layer structures, and the complexity of the structural and chemical properties of the fibres combine to create interesting and challenging scientific problems.

However, whenever paper or board is to be printed on or to be used for writing or copying, the papermaker will have undoubtedly added some form of filling or coating pigment to enhance the quality of the image produced. The amount added will vary from less than 5 wt%, in the case of some newsprint grades, to as much as 50 wt% for some high quality multiple-coated grades for offset printing. The type of pigment added will also vary from relatively low-cost, natural mineral products to complex, synthetic inorganic or organic products. The way in which

these pigments interact with the fibre and other components in the system is of fundamental importance, and therefore of great interest to the papermaker. In addition the problems are just as challenging as those presented by the fibre.

The scientific principles surrounding the chemical and physical properties of these pigments and their production have, of course, been studied extensively. The purpose of this review is not to catalogue the pigments currently used in papermaking and discuss their properties and effects on a separate basis, but rather to draw together those properties which influence the production and properties of paper and board and highlight the common themes that apply to all pigments. There are several excellent reviews [1-3] which give much more detail about individual pigments. There are also excellent reviews discussing the use of pigments for filling [4-6] and for coating [7,8] to which the reader is referred for further detail.

In reviewing the effect of pigments on papermaking, including coating and the effect on the properties of the finished sheet it becomes obvious that some of the more critical properties, such as particle packing or surface interactions, are important in more than one area and this creates some difficulty in structuring the discussion. The layout adopted has been to address the fundamental physical properties and chemical properties separately, and present the aspects which apply generally before referring to the effects more specifically related to coating or filling. Inevitably there are overlaps which are unavoidable.

To avoid any confusion the term pigment is used throughout to cover both filling and coating, but the term filler is used for filling applications only. No distinction is made between terms on the basis of particle size or the complexity of the particles. In the past fillers have been considered as cheap, mineral products, however, with the increasing use of complex particles (e.g. some PCC's and synthetic pigments) in many filling applications, this generalisation is no longer possible.

THE PHYSICAL PROPERTIES OF PIGMENTS - THE BASIC PRINCIPLES

That the physical properties of pigments are of fundamental importance is clearly illustrated by Table 1 which describes in general terms some of the major effects

Examples of the Effects of the Physical Properties of Pigments on the Properties of Paper

			Efi	ect on:		
	Rheological	Mechanical	Optical	Bulk and Air	Optical	Printing
Pigment	Properties	Properties of	Properties of	Permeability of	Properties of	Properties of
Change:	of Slurries	Filled Paper	Filled Paper	Filled Paper	Coated Paper	Coated paper
Mean particle size	0	-ve	+/-ve	-ve	+/-ve	+/-ve
decreasing						
Particles become	-ve	0	0	-ve	0	+ve
more platey						
Particle size	-ve	+ve	+ve	0	+ve	+/-ve
distribution						
becomes steeper	1					

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Dimensional Relationships of Particles

	Spheres	Discs	Rods
Characteristic size	diameter:d	disc diameter:d	rod length:d
Surface area/unit mass	$6.\frac{1}{d}$	$\left(\frac{2(a+2)}{\rho}\right)\cdot\frac{1}{d}$	$\left(\frac{2(2a+1)}{\rho}\right) \cdot \frac{1}{d}$
Particle number/unit mass	$\left(\frac{6}{\rho\pi}\right)\cdot \frac{1}{d^3}$	$\left(\frac{4a}{\rho\pi}\right)\cdot\frac{1}{d^3}$	$\left(\frac{4a^2}{\rho\pi}\right)\cdot\frac{1}{d^3}$

where a is the aspect ratio (ratio of disc diameter to disc thickness or ratio of rod length to rod diameter) and ρ is the specific gravity.

Shape Factors for Particles of e.s.d. = d as Measured by Sedimentation

	Sphere	disc (r = 20)	rods (r = 20)
Actual size	d	2.96 d	8.5 d
Surface area/unit mass	S	2.48 S	1.6 S
Particle numbers/unit mass	N	0.51 N	0.43 S

brought about by changes in pigment particle size, shape and size distribution. Other properties which are important include refractive index, density and intraparticle void structure.

Particle Size and Shape

Initially, the dimensional relationships between particle size, surface area and numbers must be recognised. These are shown in Table 2. This is relevant because the effects of pigments on, for example, the physical structure of paper and board or the rheological properties of coating colours could be related to particle numbers and/or dimensions whereas the effects on chemical properties such as sizing or on the action of process additives are more likely to be related to surface area.

The next problem is the influence of shape, whilst ground natural calcium carbonates have blocky particles which may be assumed to be near spherical, many pigments have particles which are clearly nowhere near spherical, for example kaolin and talc are platy, halloysite and aragonite are needle-like. The relationships shown in Table 2 contain constants related to shape rather than size: the so-called shape factors. For practical purposes these shape factors need to be coupled with the method of size measurement. Apart from microscopic examination, particle size can be measured by a variety of techniques [9] based on phenomena such as sedimentation, light scattering power, translatory and rotary diffusion or conductivity changes. In most cases the experimental data are interpreted using theory that assumes that the particles are spherical and the results are quoted in terms of 'equivalent spherical diameter' (e.s.d.). This gives a good description of blocky particles, but can be misleading for other shapes. Table 3 gives the shape factors [10] relating the characteristics of model disc and needle-shaped particles to spherical particles for the most common commercially used measurement technique: sedimentation from a dispersion in water. Clearly, there can be quite significant differences in size, surface area and particle numbers between blocky particles and strongly anisotropic particles measured as having equivalent size by sedimentation. Similarly relationships have been derived [11] for other size measurement techniques.

Particle Size Distribution

The particle size distribution (p.s.d.) of a pigment is important for two reasons. Firstly, if the pigment particles are well spaced, for example when used as a filler in an uncalendered paper, they could act more or less as individual particles. This means that their overall effect could be approximately a linear summation of the effects of the individual particles. Many paper properties could then be estimated from a knowledge of the particle size distribution and the behaviour of particles in relevant size fractions. Secondly, when the pigment particles are not well spaced, for example as a filler in a supercalendered paper or as a constituent in high solids coating colours or ,indeed, as a constituent in a dried coating, packing effects and the void space between particles could be as relevant as individual particle sizes. Narrow size distributions give poor packing, which has the advantage of creating void space in dried structures and hence could enhance properties such as light scattering power, but which could be detrimental to properties such as the viscosity of coating colours.

Particle Void Volume

Some pigments, for example calcined kaolins, scalenohedral PCC, precipitated silicates and fumed silica, have particles which consists of rigid aggregates of small 'primary' particles. These aggregates contain considerable void volume and this again influences the effects generated by the pigment. The void volume could bring considerable benefits such as absorption of printing inks (improving inkholdout) and increased light scattering power. Obviously the aggregates must survive the papermaking process for these benefits to be gained. The void volume also reduces the apparent density of the pigment particles so that they could have a significantly greater structural effect in a paper or board than might be assumed from simplistic estimates of particle size from sedimentation measurements made assuming the particles are solid. This could be detrimental in that strength, for example, may be greatly reduced and arguably beneficial as bulk may be increased.

PHYSICAL PROPERTIES OF PIGMENTS-SOME PRACTICAL EXAMPLES

Table 4 lists some typical pigments used today. They are described in terms of (where known) their p.s.d. as measured by sedimentation, 'particle shape', solid material density, intra-particle void volume, surface area and refractive index. Fig. 1, (a)-(j) [5] shows scanning electron micrographs of selected examples to illustrate actual shapes of particles. The relative differences seen between the particles of blocky pigments, chalk and marble, and those of platy pigments, kaolin and talc, are easily inferred from the p.s.d., surface area and the relationships illustrated in Table 3. For the more complex aggregated particles it is more difficult, some pigments have relatively blocky aggregates, for example the scalenohedral PCC. Other pigments such as the urea-formaldehyde have more anisotropic aggregates. There is insufficient information in macroscopic measurements to describe these differences. However, clearly they all have significantly larger actual particle sizes than may at first seem when sedimentation p.s.d., data alone are considered.

Most of the commonly used pigments have very similar densities and refractive indices, in fact only titanium dioxide stands out in having a high refractive index and it is this which gives titanium dioxide its unique light scattering power.

PHYSICAL PROPERTIES OF PIGMENTS-EFFECTS WHEN USED FOR FILLING

Structure, Strength and Bulk

Table 4 and Fig. 1 show that the pigments (also referred to as fillers in this section) contain particles which vary in size from, at the largest, equivalent to that of the width of typical wood fibres to, at the smallest equivalent to that of the width of fibrils. The surface area is typically such that, at normal filler contents, a substantial area of the fibre could be in contact with filler. For example, a blocky filler at a filler content of about 25 wt% (total sheet weight) and with a surface area of $6 \text{ m}^2/\text{g}$ could be considered to cover about 30 % of the surface of fibres which have a surface area of $1 \text{ m}^2/\text{g}$.

		Refractive	Index		1.57	1.57	1.57	1.59	1.58	1.58	1.58	1.58	1.58		1.59	1.57	2.55	1.56	1.58	1.45	1.57
		Surface Area	m ² /g ⁻¹ N ₂	BET	22	14	7	17	3	15	13	2	6		L	12	10	50	22	100	L .
	Internal	Void	Volume	cm ³ /g			,	1.0	1				0.7					6.0	2.7	2.5	•
		ISO	B'ness		86	88	82	96	84	94	95	95	96		83	86	- 16	96	8	8	95
Ę			-0.5		08	40	15	15	10	65	45	20	17		-	S	40	20		22	30
ce wt.%			-		63	90	25	70	25	82	65	35	50		2	30	94	35		30	60
rticle Siz			-7		98	80	40	90	45	95	8	99	80		17	60	96	50		40	90
Pau			01 +		0	0	10	1	5	0	0	1	•		30	10	0	20		9	0
		Specific	Gravity		2.6	2.6	2.6	2.7	2.7	2.7	2.7	2.7	2.7		2.7	2.7	3.9	2.5	1.5	2.4	2.4
	Electron	Micrograph	Fig. 1				8	f	۹			c	P		e		k	q	j		60
		Pigment			Ultra-fine kaolin	Fine kaolin	Coarse kaolin	Calcined kaolin	Chalk	Ultra-fine ground marble	Fine ground marble	Coarse ground marble	Scalenohedral precipitated	calcium carbonate (PCC)	Coarse talc	Fine talc	Anatase TiO ₂	Synthetic Alumino-Silicate	Urea-formaldehyde	Fumed silica	Aluminium trihydrate

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b







Figure 1 — Micrographs of pigments — see Table 4













Figure 1 (continued) — Micrographs of pigments — see Table 4

From a geometrical viewpoint, therefore, it is unlikely that the filler could influence the distribution of fibres in the x-y plane, but it is highly likely that the filler could influence contacts between fibres in the z-direction or perhaps impede fluid flow through the sheet. In fact optical and electron micrograph studies confirm this, and show that the filler is also strongly associated with any fibre fines and fibrillation which may be present [5]. On this basis it is easy to understand that finer fillers have a greater effect on the physical properties of the sheet than coarse fillers[12]. Fig. 2 [13] shows the effects of a wide range of narrow p.s.d. kaolin and calcium carbonate based fillers on the burst strength of a typical fine paper furnish at 20 wt% filler content, clearly the filler must significantly reduce fibre-bonding area and the finer the filler the greater the reduction. But as is shown by Fig. 3 the dependence on size is not simply related to surface area, or particle numbers. When the effect on sheet bulk is also considered it becomes apparent that actual particle dimensions and the packing arrangement of particles in filler/filler or filler/fibre-fines flocs are critical to the overall structural effects [2,5]. The filler particles separate fibres and hence reduce bonding. At the same time the volume of the fibre network (i.e. sheet bulk per unit fibre mass) is increased to an extent dependent on the area reduction in bonding and the distance of fibre separation [5].



Fig.2 Sheet Burst Strength at 20wt% Filler



If the discussion is extended to include aggregated filler particles, the importance of particle structure because clear. Fig. 4 & 5 [14] show that strong or rigid aggregates have much greater influence on strength and bulk than weaker aggregates. Again this is accounted for by particle dimensions and packing, the weaker aggregates collapse as the sheet dries becoming more dense and hence disrupting the fibre network less.

TABLE 5 Fillers in Uncalendered Fine Paper

If the pigment particles are independent of each other then properties such as the sheet Burst Strength or the Apparent Light Scattering Coefficient of the filler should be given by linear, weighted sums of the effects of narrow p.s.d. fillers:-

$$B_L = \sum_{i=1}^{l=n} w_i B_{L_i}$$
, $S_L = \sum_{i=1}^{l=n} w_i S_{L_i}$

where B_t and S_t are the Burst Strength* and Apparent light scattering coefficient respectively for a filler calculated at loading L, w_i is the amount of size fraction i in the filler, and B_{Li} and S_{Li} are the respective paper properties given by size fraction i at loading L.

_	_	_	-	_	-		-	-	-		
	SL	Estimate	m ² /kg	168	169	139	151	149			
		Actual SL Coefficient	m²/kg	167	167	132	148	148			
	Br	Estimate	%	40	37	42	40	43			
	Actual BL %	at 20 wt.%	loading	40	38	42	40	48			
			<0.5	10	23	13	17	4		25	j35
/ hm			0.5-1	20	20	12	15	14		35	250
omponent			1-2	30	30	20	23	24		40	190
urrow size c			2-4	30	20	25	25	33	50	45	130
itent of na			4-7	~	4	17	12	20	% loadin	50	60
Cor			7-12	2	3	8	5	S	fillers at 2(54	50
			>12	0	0	5	3	0	row size	56	35
		Test	Filler	_	2	3	4	5	Properties for nar	Burst strength %	Light scattering coefficient m ² /kg (457 nm)

Burst Strength quoted as % of unfilled sheet strength.
 Data for ground limestone fillers in a 40:60 Softwood:Hardwood Kraft furnish (400 CSF).

Table 5 tests the independence of pigment particles in an open sheet structure (uncalendered fine paper) and confirms that, at least for fillers in these systems, the strength properties of fillers with different p.s.d.'s can be estimated from the effects of narrow p.s.d. fillers (derived from similar material) by simple weighted, linear summation. This is interesting because, as implied above, the particles appear to act relatively independently. At first this seems to contradict the hypothesis that the packing of particles in flocs is an important feature, which would suggest that fillers with broad p.s.d.'s and more efficient packing would have proportionally less affect on sheet properties, but it is more likely to imply that (unless deliberately formed by flocculation with a polymeric flocculant) homogeneous, closely-packed filler flocs do not occur in these systems and the filler is part of looser flocs intimately mixed with fibre fibrillation and fines. This is supported by the optical properties of the system as discussed below. In highly filled systems with limited amounts of fibre fibrillation such as the super calendered magazine papers the situation may be different but there are insufficient published data for analysis.

Retention

In most modern papermaking systems retention is strongly influenced by chemical interactions which are discussed below. However, particle size, shape and surface area remain important. Simple physical entrapment favours the retention of coarse particles (and platy particles [15]), so that for fast machines with pulp chemical environments that impede the effectiveness of retention aids, so that physical entrapment dominates, the filler p.s.d. in the papermaking system can be quite different to that in the sheet [16]. When flocculation by polymeric retention aids is the dominant retention mechanism, surface area becomes critical at high loading levels because, as indicated above, the filler particles occupy a large proportion of the available attachment sites on the fibres. Lagmuir type adsorption models have been used quite successfully to describe retention behaviour under these circumstances [17-20]. However, surface area as measured by gas-phase adsorption (typically N₂ BET) may not give a reliable measure of 'surface coverage'. Given the different size and shape of fibre components and filler particles [5], some form of shape factor may be required to allow for the physical anisotropy of the papermaking system.



The general principles apply to all pigments and explain why the structured pigments such as silica, synthetic alumino-silicates, some PCC's and calcined clay give high bulk and relatively poor strength and why the various studies of polymer-flocculated fillers have shown improvements in strength but probably with no benefits in terms of bulk.

Air Permeability

Fillers also affect the air permeability of the sheet through their effect on sheet structure and on the air permeability of the filler/fibre fibrillation/fines flocs in which they are contained within the sheet. The former effect increases the air permeability of the sheet (compared with unfilled sheets at the same total sheet weight) whereas the latter generally reduces permeability. As expected from the use of permeability measurements in general [21] as a means of estimating the surface area of particulate systems, there is a strong relationship between the surface area of a filler and air permeability. Typically fillers with surface areas greater than about 5 m^2/g invariably reduce permeability, fillers with lower surface area can increase permeability [22-24].

Optical Properties - Light Scattering

The physical properties of the filler affect the optical properties of the sheet through the light scattering behaviour and several studies [13,25-29] have drawn attention to the relationship between particle size and light scattering. Most of these studies have shown a maximum light scattering power at about 0.5 micron diameter for fillers derived from the most commonly used materials, kaolin, talc and calcium carbonate. Fig.6 shows some of these data. This is also discussed below in relation to refractive index. The form of the relationship is in qualitative agreement with the Mie theory [30], which refers to single spherical particles. However, further analysis of the relationship generally involves some sweeping assumptions. In the first instance [25,31] the various constituents of the sheet interfere with each other optically so that it is difficult to separate the light scattering arising from individual particles from that arising from the void structure between particles. Generally speaking, from a semi-quantitative view of the structure of the sheet obtained from microscopic studies of cross-sections [5]. it may be accepted that light scattering in an uncalendered sheet with a density less than say 0.8 g/cm³ arises mainly from particles (filler and fibre), and this is supported to a large extent by the analysis in table 5. For a more compact structure such as a supercalendered paper with a density of greater than about 0.9g/cm³, or indeed a coating layer, the light scattering arises mainly from the void structure [31], and for structures of intermediate density no simple rule can be applied. Secondly, for a filler the interactions between the pigment particles and the fibre, fibrillation and fibre fines, e.g. reduction in bonded area and the encapsulation of filler particles in loose flocs with fibre fibrils and fines, create

additional light scattering features [32-36] which are often included as part of the 'apparent' light scattering effect of the filler. Indeed, in an early observation [37] of these interactions it was concluded that the filler particles themselves did not scatter light and that all of the light scattering attributed to the filler actually arises from fibre or fibrillation surfaces. This was, however, an over simplification arising from the coarse p.s.d. of the filler used in the studies, which naturally led to poor scattering from the pigment particles.



The model proposed by Kubelka-Munk [38] offers a reasonably precise description of the optical properties of paper and board [39] and is commonly used to separate the light scattering and absorption coefficients of individual components in the sheet, although other analytical, seemingly more appropriate, models have been developed based on the reflective properties of structures containing discreet layers [40,41]. Nevertheless, the models all allow a separation of light scattering effects, which increase both opacity and brightness, from light absorption effects, which increase opacity but decrease brightness. In using the Kubelka-Munk model it is normal to assume that the light scattering and light absorption coefficients of the sheet are weighted, linear summations of those of the individual components [42,43]. Therefore, for a filled sheet an equation of the form:-

$$(S,K)_{sheet} = (S,K)_{unfilled sheet}(1-L) + (S,K)_{filler}L,$$
 (equ.1),

Apparent Light Scattering Coefficient of Pigments as Fillers

Apparent Light Scattering of Filler at	10 wt.% Loading	$(457 \text{ nm}) \text{ m}^2/\text{kg}$	160	130	110	120	20	ed 120	140	120	200	150	340	290	290		250
Fibre Environment			Bleached Softwood Sulphite (300 CSF) Uncalendered	" " (600 CSF) "	" " " (300 CSF) Calendered	Groundwood (Softwood) Uncalendered	Groundwood (Softwood) Supercalendered	Bleached Eucalyptus Sulphate (400 CSF) Uncalender	Bleached Softwood Sulphite (300 CSF) Uncalendered	Bleached Softwood Sulphite (300 CSF) Calendered	Bleached Softwood Sulphite (300 CSF) Uncalendered	" " " Calendered	Bleached Softwood Sulphite (300 CSF)				
Filler			Kaolin (50 wt.% -2 μm)	=	=	=	=	=	Chalk (45 wt.% -2 µm)	=	Kaolin (80 wt.% -2 μm)	=	Calcined kaolin	Scalenohedral PCC	Synthetic Alumino-	Silicate	Silica

where $(S,K)_{sheet}$ is the light scattering (S) or absorption(K) coefficient of the filled sheet, $(S,K)_{unfilled sheet}$ are similar coefficients for a fibre-only sheet, $(S,K)_{filler}$ are 'apparent' coefficients for the filler and L is the filler loading, is used to estimate the apparent(but not measurable) properties of the filler given the measurable properties of the filled and unfilled sheets.

Table 6 give some typical results for S_{filler} calculated for various filled sheets. The sensitivity of S_{filler} to the physical environment of the filler particles is clearly shown. The extent to which interaction between the filler and fibre adds to S_{filler} depends on the fibre type and treatment, sheet forming conditions, wet pressing and calendering conditions. Techniques to quantify the effects and relate them to other sheet properties such as tensile or burst strength have been described [36], and for well fibrillated pulp systems the contribution to the apparent filler light scattering coefficient may be as much as 40% [34].

The results, in Table 6, include pigments such as calcined kaolins and scalenohedral PCC's which have a certain amount of internal void volume and this also enhances the apparent light scattering coefficient. That the enhancement is due to internal void volume can be demonstrated by mercury porosimetry measurements [44,45]. The table also includes data for fillers flocculated with polymers, and which show a reduction in light scattering coefficient compared to the untreated filler. This is due to the reduction in interaction with the fibre rather than a significant optical crowding effect [36], this is discussed further below.

Further evidence of the relative balance between particles and voids as light scattering elements in the sheet can be obtained from the relationship between the light scattering coefficient and the wavelength of illumination. This gives an estimate of the characteristic size of the light scattering elements [25]. For a typical fine paper furnish the characteristic size for the fibre related scattering elements is about 2 microns [46] and for the fillers with solid particles in uncalendered sheets the characteristic size is very similar to the size expected from sedimentation p.s.d. data. For fillers with internal void volume the characteristic size is close to the diameter of the internal voids as estimated from porosimetry. For coating layers the characteristic size correlates well with the mean void diameter for the layer as a whole, again as estimated from this type of analysis support the semi-quantitative view expressed above on the

Characteristic Size of Light Scattering Elements

			Pigment	
			Internal	
		Mean Filler	Void/Size	Characteristic
Pigment	Environment	Size d ₅₀ µm	щ	Size µm
Kaolin 1	Uncalendered fine paper firmish	0.8		0.9
Kaolin 2		0.7	I	0.8
Kaolin 3	=	0.3	1	0.4
Kaolin 4	=	0.2	1	0.3
Calcined		1.5	0.6	0.7
kaolin				
			Coating Void	
			Size µm	
Kaolin [47]	+5 pts latex binder (freeze-			
	dried or air dried)			
	density g/cm^3 - 0.89	0.4	0.25	0.23
	1.45	0.4	0.10	0.08
	1.56	0.4	0.12	0.12

approximate relationship between sheet density and the nature of the major light scattering elements.

Refractive Index

Table 4 gives the refractive indices of common pigments. Refractive index differences at interfaces e.g. pigment-cellulose, pigment-air, pigment-binder etc. determine the optimum size of scattering units [48] and the magnitude of scattering coefficients [49]. Increasing the difference increases the scattering coefficient and reduces the optimum size. The similarity between the refractive indices of most pigments and cellulose means that close contact between pigment particles and fibres may be expected to significantly reduce the apparent light scattering coefficient. This is important to the understanding of interactions in the sheet. For example, the fact that the apparent scattering coefficient of many fillers are relatively large implies that any form of close interaction (e.g. hydrogenbonding), which could have a significant beneficial impact on sheet strength, does not actually occur and, conversely, if it could be created then the potential increase in strength would be offset by a dramatic loss in light scattering. The extremely flexible, platy particles of smectite actually do make sufficiently close contact with fibres to eliminate light scattering [50] with the expected improvement in sheet strength, but there are few other published examples.

Titanium dioxide deserves special mention as it is the only regularly used pigment with a refractive index significantly greater than that of cellulose or indeed water. This obviously explains its remarkable optical benefits. It also explains the great sensitivity of its optical properties to homogeneous aggregation [51,52,1]. Other pigments do not demonstrate this phenomenon to any great extent [6], losses in optical properties for most pigments through homogeneous aggregation may be shown to be a consequence of less interruption of fibre bonded area as stated above. For titanium dioxide, however, close association of pigment particles leads to a noticeable optical crowding effect (the average refractive index of the environment is increased), which reduces the light scattering power. For other pigments with refractive indices close to that of cellulose, the optical crowding is probably also present, but it has no relative effect because the optical environment of pigment particles in homogeneous aggregates is little different from that in heterogeneous aggregates with fibrils or fibre fines or indeed from that of particles loosely associated with fibre surfaces. Similar arguments explain the benefits of using secondary pigments to 'extend' titanium dioxide. Fig. 7 shows the apparent light scattering coefficient of titanium dioxide as a component in a mixture of fillers in fine paper as a function of titanium dioxide content in the sheet. It is interesting to note that the light scattering coefficient of titanium dioxide is determined by the amount of titanium dioxide present and is independent of the amount of other pigments present. Alternatively the fibre is as effective an extender for titanium dioxide as other pigments. This supports the discussion above.



The refractive index differences at interfaces and the average refractive indices of environments in the sheet is also important to phenomena such as the wet opacity of label papers and the light scattering properties of coatings with high binder contents.

Printing

Pigments as fillers affect printing properties by changing the rate at which the ink penetrates the sheet and the depth to which it penetrates. If the ink stays on the sheet surface with a controlled amount of spreading, a well defined image is formed, print density is high and ink-strike through is reduced. In supercalendered sheets, platy pigments that give low air permeability and presumably low liquid permeability, give good print properties [53]. In newsprint sheets, pigments with intra-particle void volume reduce ink-strike-through or penetration into the sheets [22,54-58]. Presumably, the pigment absorbs the ink, or ink vehicle preventing deep penetration, and this is supported by the strong correlation between ink-strike-through and total void volume of the pigment [59].

PHYSICAL PROPERTIES OF PIGMENTS- EFFECTS WHEN USED FOR COATING

Rheology and De-watering

Coatings are invariably applied as slurries of pigments, various chemical binders and 'flow modifiers' in water at high solids (coating colours). The rheological properties of these slurries are often critical in determining not only the 'runnability' of the coating colour but also the properties of the final dried coating. The so- called de-watering property, which whilst not strictly rheological, is included here because it is also has a profound effect on coating application and final properties. This is understandable because the coating is applied to an absorbent base sheet. The dynamics of coating is too deep a topic to be discussed in detail here but is reviewed elsewhere [7,8,60]. However it is possible to highlight some general principles. Chemical interactions, particularly between the pigment and the flow modifiers or soluble binders, are important and this subject is discussed below. In terms of the physical properties of the coating colour perhaps the most important aspects are particle packing and particle anisotropy. Measurements of sediment volume of pigments have been used to gain some insight into the relationship between packing and rheology [61,62]. The viscosity curve as a function of shear rate for most coating colours is as shown in Fig. 8 [63]. An initial shear thinning region is followed by a region of more or less stable (or Newtonian) behaviour after which the viscosity can rise rapidly (dilatancy). There is some evidence that a second high shear thinning region exists [64,65]. There are no simple expressions to describe the whole curve. The initial shear thinning region represents a combination of a breakdown of weak particle interactions, which exist even though the particles are highly charged through the addition of chemical dispersants, and alignment of particles and flow modifier molecules with the direction of flow [66,67]. The region of stable viscosity is perhaps the easiest to model and is relevant to activities such as pumping and roll-applications where near laminar flow may be assumed and shear rates are 10^2 -10⁴. The most successful analytical expressions are based on Einstein's equation [68]. These once again only strictly apply to spherical or near spherical particle systems and describe viscosity in terms of the volume fraction of particles in the colour and the maximum packing fraction achievable. Examples are Krieger and Dougherty's equation [69] or (below) Mooney's equation [70]:-

$$\eta_{rel} = \eta_o \exp\left[\frac{k\phi}{1-\phi/P_f}\right], \qquad (equ. 2),$$

where η_{rel} is the relative viscosity, η_o is the viscosity of the aqueous phase of the colour, k is a shape factor (2.5 for spheres), ϕ is the volume fraction of particles and P_f is the maximum packing fraction of the particles.



The maximum packing fraction can be calculated from the particle size distribution [71,72] and Fig. 9 shows measured viscosity compared with predicted viscosity for a very simple coating colour containing a ground calcium carbonate pigment, a styrene-butadiene latex and a CMC (carboxymethyl cellulose) flow modifier. The latex particles are included in the total volume fraction of particles and the effect of the flow modifier is included in the viscosity of the aqueous phase. The theory fits well for this system and it can be seen from the form of Mooney's equation that reducing the maximum packing fraction by, say, using a pigment with a steeper p.s.d. will increase the viscosity. This is observed in practice. In general, the observation can be extended to other, non-spherical pigments [73]. Intuitively, anisotropy reduces the maximum packing

Viscosity mPas.	$\begin{array}{c c} \hline @ \\ 10 & \hline \\ 1000 & \sec^{-1} \end{array}$		320 30	400 204	350 250	100 25	160 34	170 dilatent	
	Slurry Solids Content 3	wt.%	11	71	63	71	68	50	
imentation)		10 wt.% <	0.1	0.12	0.15	0.1	0.2	0.25	
ize (µm) (sed		50 wt.% <	0.3	0.6	0.8	0.5	0.7	0.6	
Particle Si		10 wt.%	0.8	2.3	5.0	1.5	1.5	2.0	
		psd	broad	broad	broad	steep	broad	steep	
	Asnect	Ratio	8	25	40	4>	\$	aggregates	
		Pigment	Kaolin			Calcium carbonate		Calcined a	clay

TABLE 8

Viscosity of Pigment Slurries

fraction and hence increases viscosity. Obviously, strong aggregation of pigment particles to form a relatively narrow size distribution of larger particles occupying a relatively high apparent volume also increases viscosity. Table 8 gives some viscosity information for various pigment-only slurries and confirm that steep p.s.d. and extremely platey pigments have relatively poor viscosity. The aspect ratio's were estimated from electron micrographs. The onset of dilatancy or the region in which viscosity increases rapidly is extremely important because it could well relate to runnability problems in high speed coating operations where shear rates up to 10^6 have been estimated [74]. Various attempts have been made to link dilatancy to pigment particle characteristics. The simplest observation is that the factors which increase the Newtonian viscosity often increase the tendency to dilatancy. More recently the power of computers has allowed numerical simulations of the flow of particulate systems [75-77] and phenomena such as shear induced aggregation have been predicted. However, the modelling is still restricted to very simple shape and size distributions.



A strong note of caution is that the viscosities of particulate systems as measured by conventional cone and plate or capillary viscometers may not be actually relevant to the short time scale and flow patterns experienced by the colour in some situations, for example in the region of the blade of a blade-coater [63,78,79]. Several studies have been made [80-82] in an attempt to assess the significance of viscoelasticity or the development of forces perpendicular to the plane of shear to paper coating. Again, however, direct experimental evidence to confirm the exact relevance of such phenomena to commercial practice is difficult to obtain [64]

De-watering refers to loss of the aqueous phase of the coating colour into the base sheet. During the application of the coating, the solid fraction of the coating layer and of the coating colour in the applicator head increases, and hence viscosity increases. This could be a major cause of runnability problems. Furthermore the rate of de-watering influences the time taken by the coating layer to immobilise [83,84], or cease to flow into the porous surface of the base sheet. This influences the extent to which the coating covers the surface, which is of course of critical importance to the properties of the finished coating in terms, for example, of uniformity and ink reception.

Returning to the comparative sizes of fibres and pigment particles and to the spatial structure of the sheet, it can be appreciated that 'holes' and 'pores' between fibres in the immediate surface layer are typically 1-10 times the diameter of normal coating pigment particles, so provided the coating colour remains fluid, the whole colour can flow into the surface. The fibres themselves act like 'sponge-filters': the aqueous phase of the coating is drawn or forced into their internal structure through relatively small fissures in their surfaces, but the pigment particles are barred because they are now relatively too large. Alternatively the aqueous phase may 'wet' the fibre surfaces, again without the pigment particles or it has been suggested that water molecules may diffuse into the fibre structure [85]. From a modelling point of view, the surface of the sheet can be considered [86] as a network of 'macro' and 'micro' pores. The whole colour can flow along the macro-pores, but only the aqueous phase can flow along the micro-pores. The Lucas-Washburn equations can be used to describe this flow:-

$$\frac{dl}{dt} = \frac{2.r.\gamma.\cos\theta + P.r^2}{8\eta.l}, \qquad (\text{equ. 3}),$$

where, $\frac{dl}{dt}$ is the linear flow rate, η is the viscosity of the whole colour or just the aqueous phase, γ is the surface tension, θ is the contact angle, *r* is the macro or micro pore radius respectively and *P* is the applied pressure [87,88].

The de-watering rate is thus determined partly by the viscosity of the aqueous phase and partly by the capillary network of the system. So-called water retention aids are added to increase the aqueous phase viscosity and hence reduce de-watering [89]. The internal capillary network of the colour (i.e. the space around the particles) creates a viscous drag which also reduces de-watering and which is not accounted for by the equation above [86]. The shape and p.s.d. of the pigment particles have a major influence on this drag. Coarse, blocky particles with a narrow p.s.d. generally produce an open, relatively isotropic pore network, whereas very platy particles with a broad p.s.d. can present a particularly closed network if the particles are aligned perpendicularly to the direction of fluid flow. Hence, if the particles are aligned parallel to the sheet or fibre surfaces by flow in the applicator system, the flow of the aqueous phase out of the colour is reduced [90,63].

Optical Properties and Bulk

Bulk is obviously directly related to void volume. As implied in the discussion above on the effects of pigments as fillers, the light scattering properties of coatings are determined not only by the volume, but also by the dimensions of the void structure [47,91,92]. This structure is created to a certain extent by the pigment particles and once again features such as particle size, shape and p.s.d.. are important. However, of these the p.s.d. is probably the most critical. Steep or narrow p.s.d.'s lead to poor packing and hence increase pore volume. The particle size influences the dimensions of the voids rather than the volume, void dimensions need to be in the range 0.3-0.7 microns [25] and this is given generally by particles in the size range 0.3-2.0 microns. The influence of particle shape is less clear [47]. However, mixtures of pigments with different particle shapes can produce synergistic increases in bulk or void volume [62,93]. Void volume can also be increased by rigid aggregation of the pigment (i.e. creating particles with a fixed, internal void volume) and this is demonstrated for example by calcined kaolins [93] and PCC [44].

Gloss

Paper gloss is strongly influenced by the size and shape of the pigment particles rather than the steepness of the p.s.d., particularly at relatively high coatweights (> about 12 g/m² per side). Gloss has been shown to be related to the microtexture of the surface [94] and at high coatweights this is determined primarily by the pigment particle size and, for anisotropic pigments, by their orientation:-

$$\log_e \frac{I'}{I} = -16.\pi^2 \cdot \sigma \cdot \frac{\cos^2 \vartheta}{\lambda^2}, \qquad (\text{equ. 4})$$

where I and I' are the incident and reflected light intensities respectively, σ is the standard deviation of surface step heights about a mean plane, λ is the wavelength of incident light and ϑ is the incident angle.

Fig. 10 shows the relationship between surface microtexture (or roughness) and gloss for kaolin and ground calcium carbonate pigments. Fig. 11 shows how this relates to the particle size and shape [95]. The coatings were applied to a smooth non-absorbent base, to eliminate effects caused by deformation of the base, and the pigments had relatively narrow p.s.d.'s. The kaolin particles are aligned to a certain extent by the coating process, as shown by XRD studies [45,96], and, when aligned, the texture created by the kaolin particles is a function of particle thickness rather than diameter. Other studies have shown similar particle shape related effects[97].



For low coatweights (< about 7 g/m^2) applied to absorbent sheets, where the base sheet surface can be deformed by swelling of the fibres as the coating colour dewaters, the ability of the coating to adequately cover the surface has a dominating effect [98,99]. In these circumstances a complex combination exists of coverage

created by rapid de-watering, coverage created by particle aggregation and coverage created by the natural dimensions of large particles.

Many sheets are filled as well as coated. The closing up of the pore structure of the sheet by the filler has a beneficial effect on coating coverage [100,101] as may be expected, and improves the gloss of lightly coated sheets. Heavily calendered magazine papers are sometimes highly glossy with no coating at all. In this case the gloss is generated in the same way as for a coated paper except that the surface texture is made optically smooth by the alignment and packing of the filler particles in the sheet voids close to the surface.

Printing

In the discussion of the effect of pigments as fillers on the printing properties of paper or board attention was drawn to ink spreading and penetration. For coating there are additional considerations: the coating can reduce the flexibility of the surface so that ink transfer can be a problem and the permeability of the surface can be sufficiently low to give problems with ink drying (and other porosity related problems, such as mottle). Rotogravure printing requires a relatively smooth and flexible surface to give good ink transfer with low permeability to minimise penetration [102]. Coarse, very platy coating pigments with relatively steep p.s.d.'s seem to be favoured [103], although a degree of compressible structure introduced into the coating by chemical flocculants has also been claimed to be successful [104]. For offset printing the control of the absorption properties of the coating is more important than optimising ink transfer, which seems to be less of a problem than for rotogravure printing. Hence in the design of coating pigments for offset printing more emphasis is placed on high gloss, controlled pore structures and surface strength (i.e. surface area and particle packing characteristics are selected for minimal binder demand as well as maximum light scattering). However the commercial importance of many developments has restricted the depth of published analysis [105]. References to tortuosity and the transport of liquids along interconnected but complex pore systems [106,107] demonstrate the difficulty of controlling the structure to give optimum print properties and show how different particle shapes may be expected to influence transport. There is evidence, for example, that the 'steps' in pore diameter created by angular, blocky pigments may impede transport. Conversely the tortuous pores created by platy pigments may also be expected to impede transport.

THE CHEMICAL PROPERTIES OF PIGMENTS-GENERAL PRINCIPLES

In the same way as the physical properties of pigments influence sheet-making and final properties so do the chemical properties and again there are some general principles. The bulk chemical content alone of the pigment determines properties such as solubility, light absorption, refractive index, and hardness. The surface chemistry of the pigment determines properties such as adsorption, surface charge, contact angles with liquids and surface energy including acid-base interactions. These distinctions serve merely to separate those properties which are dependent on surface area from those which are independent of surface area. Obviously, in the absence of large amounts of surface contaminants the bulk chemistry also determines surface interactions. Surface contamination and the interactions between pigment surfaces and chemical additives in the papermaking and coating processes are often the most seriously overlooked chemical aspects of the use of pigments. For example, many studies of the electrophoretic mobility of pigment particles are made in model suspensions that bear little resemblance to the environment found in real papermaking systems or that ignore surface changes arising as a result of the processing carried out to produce and deliver the pigment.

Surface Energy, Contact Angle and Adsorption Properties

The determination of the surface energy of a solid is difficult [108]. However, for the purpose of the use of pigments in paper and board, surface energy can be estimated from the work of adhesion (W_a) between the solid surface and various liquids and which can be obtained from adsorption [109] experiments. This approach is consistent with the need to understand the interaction between pigment surfaces and water, ink vehicles, polymeric binders and surface coatings. Work of adhesion is also related to contact angle (between a liquid and a solid surface) by the Young-Dupre equation.

$$W_a = \gamma_1 (1 + \cos\theta).$$

Contact angle is highly relevant to wetting processes such as printing as can be seen from the form of the Lucas-Washburn equation given above. Ink cannot wet or penetrate the surface if the contact angle is greater than 90° . Contact angles on

Pigment	µeq/g polydadmac	µeq/g polyvinylsulphate	-
Chalk (untreated)	3.9	1.3	
Kaolin (untreated)	7.5	1.2	
Kaolin + 0.5 wt.% Alum	7.5	4.7	
Kaolin + 1.0 wt.% Alum	9.0	7.5	-
Kaolin + 1.5 wt.% Alum	8.6	9.0	
Kaolin + 0.15 wt.% cationic	4.5	5.6	-
polymer			_

Polymer Adsorption Measurements

particulate substances are, however, difficult to measure directly. A method relevant to paper using the Bristow wheel has been proposed [110].

Work of adhesion is generally considered [111] to be a sum of various components representing dispersion forces, acidity and basicity. Dipole interactions and hydrogen bonding have also been considered [112].

$$W_a = W_a^d + W_a^d + W_a^b + \dots,$$

where the superscripts d, a and b refer to dispersion forces, acidity and basicity respectively. Each component can be related to the surface tensions of the solid and the liquid using the relationships,

$$W_a^d = 2\sqrt{\gamma_1^d}\gamma_s^d, \quad W_a^a = 2\sqrt{\gamma_1^b}\gamma_s^a, \quad W_a^b = 2\sqrt{\gamma_1^a}\gamma_s^b \text{ etc.}, \quad (\text{equ. 5})$$

where γ_1 and γ_s represent surface tension components for the solid and liquid respectively.

Unfortunately the published data [112-115] for pigments so far are sparse and show poor absolute agreement, presumably because of unknown differences between the histories of the samples used. Studies using calcium carbonate, kaolin and silica [112,113], however, show how the basicity of the calcium carbonate surface, for example, restricts the adsorption of basic substances; and show how pre-treatment of the surface, for example by adsorbing aluminium ions onto a silica surface to increase acidity, can enhance the ability of the surface to compete with the acidity or basicity of the solvent. The results also confirm the amphoteric nature of kaolin surfaces. The surface acidity and basicity can also be estimated from measurements of the adsorption of charged polymers from solution [116], table 11 gives some typical data. Again it is shown that the surfaces of pigments can have acidic and basic sites. For retention studies, polymer adsorption measurements may be quite relevant as they can be used to show how polymers can compete with other adsorbates. For example the adsorption of polydadmac is not restricted by the presence of alum, whereas as may be expected the adsorption of polyvinyl sulphate is enhanced. The adsorption of the polydadmac is, however, restricted by the presence of other cationic polymers. Some pigments, in particular talc, are quite hydrophobic indicating low surface basicity and acidity. In papermaking terms, this gives

Light Absorption Coefficients

	Light Absorption Coefficient
Pigment	m ² /kg (457 nm)
Talc	2.0 - 4.0
Kaolin	2.0 - 4.0
Calcined kaolin	1.2 - 1.7
Marble	0.3 - 0-7
Chalk	2.0 - 4.0
Anatase	<0.2
Aluminium Trihydrate	<0.2
Silica	<0.2

benefits in terms of allowing the surface to adsorb unwanted resins and pitches, but has disadvantages in reducing the interaction between the pigment and the fibre and hence increasing the dusting at the paper surface [117,22]. Future analysis of the results of wetting and adsorption experiments to separate the various components of adhesion will give valuable insight into the interaction between pigments and other components used either in papermaking and coating or in subsequent use such as printing [118,110].

Light Absorption

Table 9 gives some light absorption coefficients for common pigments. For most of these pigments, the light absorption coefficient of the pure, base material is very low and absorption is due to organic and transition metal impurities present either as particulate, surface or bulk structure contaminants. Whichever is the case the effect is such that the total light absorption of a sheet is remarkably close to the weighted, linear sum of the components (see equ.1) and, unlike the light scattering coefficient, is almost entirely independent of environment and structure. Light absorption, depending on the source of colour, varies with the wavelength of light (giving pigments a natural shade). More importantly it also extends into the ultra-violent (and infra-red) region, and this can have a deleterious effect on the performance of fluorescing agents, which absorb in the UV region and fluoresce in the visible region. This effect is critical for pigments such as titanium dioxide, which have relatively low absorption over the visible region but absorb strongly in the UV [1].

Hardness

Hardness is relevant only for its effect on abrasion. Moh's hardness scale rates pigments between values of 1 for talc and about 8 for quartz. Most common pigments lie in the range 3-5. In practice significant quantities of hard impurities such as quartz are detrimental, but, as with many other properties, pigment particle size and shape dominate if differences in hardness are less than about 3 Moh's units [119].

Solubility

Solubility is a concern for some pigments and in particular for gypsum and calcium carbonate. Gypsum or hydrated calcium sulphate, has a solubility of about 2 g./dm³. This implies that at equilibrium any papermaking system containing gypsum, also contains significant quantities of calcium and sulphate ions which obviously strongly influence the aqueous chemistry. A further difficulty occurs in high solids coating colours where the conventional 'high surface charge' approach to fluidity and stability cannot be used and a 'steric stabilisation' approach is required. Solubility has restricted the use of gypsum in paper despite its relative abundance. Calcium carbonate presents a further difficulty in that the solubility is pH dependent. For practical purposes, calcium carbonate is not used at a pH below about 7.0 when the equilibrium calcium ion content becomes appreciable. In the pH region 8-10 however solubility is not a major factor.

SURFACE CHEMISTRY IN AQUEOUS SYSTEMS-EFFECTS WHEN USED FOR FILLING

The surface chemistry in aqueous solution of pigments used as fillers has a profound effect on retention and on the influence of chemicals either present as impurities or added to perform a function during or after papermaking. Surface potentials and interactions in solution are modified by the adsorption of various materials, and the amounts required to produce a certain change in, for example, particle mobility or hydrophobicity will be linearly related to the surface area of the system. The surface area of the pigment is an important part of this.

Particle Mobility, Surface Charge and Retention

The electrophoretic mobility is the velocity of the particle in a known liquid under the influence of a unit electric field gradient. Electrophoretic mobility is a measurable phenomenon and this is usually converted to a surface potential, the zeta-potential, by use of the Helmholtz-Smoluchowski equation, which corrects for the influence of the viscosity and dielectric constant of the solution and the permittivity of free space. The equation is only quantitatively correct if the particle size is significantly greater than the thickness of the electrical double layer [120], however, in a similar way to the estimation of particle size or pore

Zeta Potentials of Fibres and Pigments

Zeta Potential (mV)	-20	+22	-35	+15	-15		-20	0	+12	-15	-30	-10	-20	6-	-28	-48	+25	+4	-15	+5	0	-40	<i>ii</i> +	-13
Ha	5	9	9	9	9		6	~	8.5	~	,	4	9	4	9	6.4	4	9	6	9	v	5	9	9
Ref.	(124)	(126)	(127)	(124)	(125)		(128)	(128)	(129)	(129)	(123)	(130)		(131)		(132)	(131)		(131)	(125)	(133)	(134)	(125)	(125)
Environment (where known)	20 ppm in 10 ⁻³ mol dm ⁻³ NaCl.	+0.5 wt.% PEI (on kaolin) + H ₂ SO ₄ to pH 6.	20 ppm in 0.2 x 10 ⁻⁶ mol dm ⁻³ sodium lignosulphate + H_2SO_4 to pH 6.	20 ppm in 0.6 x 10 ⁻⁴ mol dm ⁻³ Al ₂ (S ₂ O ₄) ₃ + NaOH to pH 6	In presence of pulp fines + H ₂ SO ₄ to pH 6		200 ppm in distilled water	200 ppm in distilled water	1000 ppm in distilled water + 10 ppm Ca ²⁺	1000 ppm in distilled water with pulp fines +30 ppm Ca ²⁺	NaTPP 10 ⁻⁴ mol dm ⁻³	Distilled water + H ₂ SO ₄ or NaOH to required pH		Distilled water + H ₂ SO ₄ or NaOH to required pH		Deionised water	Distilled water + H ₂ SO ₄ or NaOH to required pH		In presence of pulp fines + H ₂ SO ₄ to pH 6	In presence of pulp fines $+7 \times 10^{-5} \text{ Al}_2(\text{SO}_4)_3$	+1 wt.% PEI (or anatase) + H ₂ SO ₄ to pH 6	Distilled water	Distilled wataer + H ₂ SO ₄ to pH 6	In presence of pulp fines + H ₂ SO ₄ to pH 6.
Pigment	Kaolin:					Calcium Carbonate:	Chalk	Marble	PCC	PCC	Marble	Talc		Titanium dioxide		Anatase	Rutile		Anatase			Silica	Hydrated aluminium oxide	

diameter, it gives a reasonable measure of the surface potential. Table 10 gives some results for typical pigments and pulp fibres. Whilst the mobility may be a measurable phenomenon through which to monitor zeta- potential, the interest for papermaking is in the use of zeta-potential as a means of predicting particle interactions leading to coagulation or flocculation.

It is generally accepted that a zeta-potential of at least 20 mV is required to prevent the coagulation of like-charged particles [121] and that a zeta-potential of about 40 mV is required to prevent flocculation by non-ionic polymers or polymers of similar charge to the particles [122]. From table 10 it can be assumed that under normal conditions, most common pigments will coagulate readily with fibres and fibre fines and that most water soluble polymers that interact with the surface will promote flocculation. The zeta-potential is influenced by the adsorption of so-called charge determining species, these may be simple ions such as Ca²⁺ for calcium carbonate particles [123] or H⁺ for kaolin [124] or more complex ions such as the inorganic poly-ions (e.g. hydroxy-aluminium polymers (cationic) or poly-phosphates (anionic)) or synthetic poly-ions (e.g. poly-amines (cationic) or polyacrylates (anionic). In fact most papermaking systems [125] contain a mix of charge determining material that defines the zeta-potential of most of the particulate matter present, be it pigment or fibre, and as may be seen from table 10 the zeta potential of most untreated pigments in the presence of pulp fines is about -15 mV. Retention in general becomes a problem when the amount of charge-determining material present is so great that the zeta-potential is excessive. Alternatively retention of the pigment, specifically, can be a problem if the pigment has been pre-treated with a large amount of a charge determining material, and this occurs for example when pigment dispersions designed to be stable in a coating formulation are used as fillers [135]. Interestingly adding a large amount of cationic polymer to the filler before addition to the papermaking system has a minor benefit only on retention [136,137]. At first this seems strange as the (now) cationic filler particles should be strongly attracted to the fibre surfaces. However, simple coagulation in this way is not sufficient to retain fillers in the high shear environment of a modern paper machine and other retention mechanisms are required. Whilst surface charge is undeniably important a further and more complex consideration is the adsorption and conformation polymeric retention aids. A wide literature exists on the effectiveness of retention aids and the mechanisms of retention [138,139], and the details are outside the scope of this review. However, bridging between particles by long chain polymers is recognised as an important feature of many

retention systems. This requires strong anchoring points on the particle surfaces and a more or less linear polymer stretching away from the particle surface. This presents a difficulty as the ends of the polymer need to interact strongly with the particle surfaces whilst the centre part of the polymer must contain a sufficient number of mutually repulsive groups to straighten the chain. These groups should not necessarily interact strongly with the particle surface as this would collapse

not necessarily interact strongly with the particle surface as this would collapse the polymer on to the surface. This is very difficult to achieve through polymer design. A compromise is, however, reached through the so-called patch-charge mechanism [140] in which patches of intense charge are created on the particle surface by adsorption of a highly charged species, such as a short-chain polymer, and these areas are used as anchor points for a homogeneously charged polymer of opposite charge to the patch. The charged groups of the polymer keep the polymer straight and, provided the patches are small and the remaining particle. surface does not interact strongly with the polymer, the polymer can 'bridge' to patches on other particles. For many pigments this idealised mechanism is possible through the natural characteristics of their particle surfaces (discussed above). For example kaolin particles generally have strong negative charge on the surface of the plates, but have positive charges at the edges [141]. Similarly, calcium carbonate particles can adsorb a small amount of negative species even when the overall surface charge is negative. In fact this heterogeneity of the surface charge is probably one of the most important aspects of pigment when used as fillers, underlining the importance of the surface energy and polymer adsorption studies. Ensuring that the zeta potential of the pigment is reasonably close to zero probably enhances this aspect.

Filler Pre-flocculation

In the discussion of the physical properties of fillers, reference was made to the different effects of rigid and weak aggregates. Rigid aggregates are formed by chemical structuring such as the calcination of kaolin [142], precipitation of a cementitious additive [143] or crystal growth habits [29]. Weak aggregates are generally formed by polymer flocculation, generally by the polymer bridging mechanisms referred to above. There are numerous patented processes and references in the literature [144,145]. Control of floc size and structure is an important issue [146,147] as the principle aim is to decrease the influence of the filler on sheet strength without introducing clearly visible flocs. The order of addition of polymeric retention aid and its effect on paper properties is discussed

in the literature and some of the phenomena observed are attributed to preflocculation of the filler [148].

Adsorption of Chemicals by Pigments

Filler particles adsorb process chemicals such as retention aids and substantive chemicals such as sizes, dyes and flourescent agents. This can have a two-fold effect. Firstly the functional effect of the chemical may be changed. For example, the effectiveness of sizing chemicals is reduced because the filler introduces an increased area of hydrophilic surface [5,149]. Secondly, the retention or position of the chemical may be affected by the influence of the filler on other components of the system. Retention is perhaps the major issue: many chemical additives require a polymeric retention aid, which can be adsorbed by the filler. Again the effectiveness of sizing chemicals can be used as an example [135]. Pre-treatment of the filler with charge or hydrophobicity determining species can be used as a means of avoiding some of these effects [150].

Pigments appear to affect the yields of flotation de-inking processes. This is believed to be a result of adsorption of chemicals in the system by the pigment [151-154]. There is also some evidence that adsorption of wood-chemicals by certain pigments with intra-particle void volume increases the surface friction of the sheet [155].

SURFACE CHEMISTRY IN AQUEOUS SYSTEMS- EFFECTS WHEN USED FOR COATING

Coating colours are a mix of pigments, binders (soluble or particulate or both together), flow modifiers and other chemicals such as dyes or flourescent agents. Generally the pigment is dispersed using anionic polymers, and the mechanism of stabilisation is partly high anionic charge and partly steric [156,157]. The high solids contents of the slurries, with solid volume concentrations of around 50% and weight concentrations up to 78% for some pigment-only slurries, requires a strong element of steric stabilisation [158]. It is common practice to ensure maximum stability of the pigment-only slurry before other coating components are added. Recently, several studies [159-163] have considered the interactions between the pigment and the soluble binders or flow modifiers, which are generally anionic or non-ionic. These studies have shown differences between

calcium carbonates and kaolins which can be related back to the different basic and acidic natures of the surfaces. Essentially there is greater evidence of interaction between kaolins and additives such as carboxymethyl cellulose than there is for interactions in calcium carbonate containing systems. This interaction leads to structure formation in the colour which may influence runnability of the coater or the final nature of the coating.

Earlier studies looked at the influence of adding cationic polymers to these strongly negatively charged systems. This clearly causes considerable interaction, which has a significant effect on the final coating [86,104]. There are benefits in terms of coverage, optical properties and rotogravure printability (as referred to above). These are all consistent with a more open and fast draining system created by partial flocculation of the coating colour.

Fully cationic-charge stabilised coating colours have also been considered [164,165], but the benefits reported are more easily explained by partial flocculation rather than any specific interactions between a cationic coating and an anionic base paper. This is a result of the difficulty in creating sufficient cationic charge in the system to fully stabilise the colour.

SUMMARY

There are several key properties that underlie the effects of pigments on papermaking and paper or board properties. These are:-

Particle size, shape and particle size distribution, Intra-particle void volume, void shape and size, Particle packing and inter-particle void volume, shape and size, Surface area, Bulk chemistry and refractive index, hardness etc.,

Surface energy and adsorption behaviour,

Electrophoretic properties in aqueous environments.

Many are interlinked, for example particle packing is related to particle size distribution and shape or electrophoretic properties are influenced by adsorption of charged species. They are also interlinked with the properties of the fibres and hence the whole sheet. However, the nature and magnitude of any effect of a pigment on the sheet can be explained by one or a combination of these properties and, similarly, differences between pigments can be explained. For example, the excellent optical properties of a precipitated alumino-silicate pigment compared with those of a ground calcium carbonate are mainly due to the presence of intra-particle void volume. The fact that a fumed silica may have greater intra-particle void volume than the precipitated alumino-silicate but may give inferior optical properties will arise because the characteristic void size of the silica is too small for optimal light scattering. Many other examples could be given to demonstrate the relationships.

As the sheet density increases, for example with heavy calendering or within a coating layer, so the importance of packing and the nature of the void space between particles increases.

The scientific progress required lies in areas such as the development of simple means to characterise pigment properties in more detail, including particle shape and structure and surface chemical properties. This will lead to greater understanding and control of end-use properties such as response to printing inks. Other areas include the development of a better understanding of sheet structures containing pigments, the rheological properties of coating colours and the importance of void structure to liquid flow. These areas and others are being actively studied and significant progress can be expected over the next few years.

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Transcription of Discussion

Review Paper: The Influence of Pigments on Papermaking and Coating

Dr Richard Bown, Research & Technology Director, ECC, UK

Sven Lohmander, Research Engineer, STFI, Sweden

In your paper you have a table where you examine the influence of the aspect ratio on the viscosity of some pigment only slurries. You write that you have measured the aspect ratio from electron micrographs, and so I assume that you have a number based aspect ratio, is that correct?

Richard Bown

Yes that is so.

Sven Lohmander

Do you not think that it is more relevant to use the mass or volume based aspect ratio which is the aspect ratio of the large particles if you want to examine the effect on the rheology?

Richard Bown

You are correct, the reason that I put that table in is to demonstrate how broad changes in shape influence rheology in a broad way. So really the difference between number shape factors and mass shape factors are not that critical in that comparison but you are correct.

Sven Lohmander

I just wanted to say that there could be quite a large difference between the number based and the mass based aspect ratio.

Richard Bown

That is correct, but for these samples the differences are not actually that great. Your question, however, emphasises my point that we must be careful to describe the pigment properly.

Juha Mentu, Microbiologist/Laboratory Manager, Enso Group Oy, Finland

I would just stress a point of view as a microbiologist because my experience is that the mill environment is different compared with that of laboratory trials, that's because the very heavy extra cellular polysaccharide production, slime and biofilm formation by microbes in the system which causes, for example, aggregation of mineral particles, discolouring etc. Have you studied these also in a mill environment?

Richard Bown

In terms of the effect that environment has on the surface chemistry, no. In terms of the structure of the paper, yes. You can look at the structure of the finished paper in the sheet and the general concepts I've been talking about generally apply quite well. The impression I have about the effect of dissolved substances in the aqueous system is that they absorb on all surfaces so that the pigment would look very much like the fibre. This is in fact shown by the data in the literature on surface charge.