 Calcium carbonate fillers in rosin-sized papers

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Calcium Carbonate Fillers
in Rosin-Sized Papers

by

Rebecca Louise Hooper

A Doctoral Thesis
Submitted in partial fulfilment of the requirements
for the award of
Doctor of Philosophy
of Loughborough University of Technology
December 1993

Supervisors:  Prof. M. J. Jaycock
              Roe Lee Paper Chemicals Co. Ltd.
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              Department of Chemistry

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Declaration of Originality

The work presented in this thesis was conducted by the author between October 1990 and May 1993, and it has not been submitted wholly or in part, to this or any other University for a higher degree.

Rebecca L. Hooper
December 1993
I humbly beg, Sir, that you will honour this book, by taking it - (not under your protection, - for it must protect itself, but) - into the country with you; where, if I am ever told, it has made you smile, or can conceive it has beguiled you one moments pain - I shall think myself as happy as a minister of the state; - perhaps much happier than any one (one only excepted) that I have read or heard of.

Laurence Sterne, 1760
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Appendix 1
Summary

Calcium carbonate is one of the preferred fillers for the paper industry. This research compared the physical and chemical properties of calcium carbonates produced by different methods and their use with a novel rosin sizing system. The effectiveness of a polymeric retention agent, which flocculates particles during paper production, has also been examined.

Particle and surface characteristics of these fillers have been examined using: dye adsorption from solution, Fourier transform infrared spectroscopy (FTIR), using diffuse reflectance to examine surfaces (DRIFT), laser diffraction particle size analysis, nitrogen gas adsorption, scanning electron microscopy (SEM), x-ray photon spectroscopy (XPS) and x-ray powder diffraction.

Paper was prepared on a small laboratory machine and the Adirondack handsheet machine. A series of sheets, designed to reveal trends in the effects of the size and filler levels, were produced for testing. The behaviour of the paper was assessed using the Cobb test, to quantify water repellency, and the ash test, to determine the amount of filler remaining in the finished sheet.

The research provided information about the particle and aggregate sizes of the fillers, their crystal structure and their surface charges. The results of the adsorption work on the fillers were used to compare two theories describing dye adsorption from solution. The evidence suggested that dye molecules adsorb at angles to the surface determined by the number of adsorption sites available. The Cobb and ash test results suggested that the PCC fillers required more rosin emulsion to produce paper with an acceptable Cobb value because of the increased surface area of these sheets.
Chapter 1
Introduction
1.1 Introduction

Rosin size is one of the preferred sizing agents for the paper industry, and used in conjunction with papermaker's alum, can be used without other retention aids. Until recently the major fillers used in the paper industry were naturally-occurring clay and calcium carbonate, with titanium dioxide added in small quantities. Developments in the manufacture of precipitated calcium carbonates (PCCs), have made it possible to produce an inexpensive filler with relevant properties similar to titanium dioxide. Unfortunately, the new fillers have proved difficult to use at high loadings with rosin emulsions.

This work examines these PCC fillers, their natural counterpart, ground chalk, and their role in papermaking. The effect of a polymeric retention aid upon paper produced using the fillers, was also examined.

Without a knowledge of papermaking and its requirements this work cannot be placed in context, for this reason the second chapter of this thesis discusses all aspects of papermaking at the laboratory and industrial scale. As industrial papermaking is a complicated procedure, the simpler laboratory papermaking processes are examined first.

Paper normally is made from cellulose fibres derived from wood with the addition of fillers, pigments and sizing agents. Fillers such as chalk and clay reduce the amount of fibre needed in the sheet and increase sheet opacity. Pigments enhance the paper in some way, i.e. titanium dioxide is an optical brightener, sizing agents impart some degree of water repellency to the sheet. The level of addition of fillers, pigments and sizing agents depends on the intended use of the paper, e.g. kitchen paper is less water repellent than writing paper, airmail paper is light and contains less filler than photocopier paper.
Cellulose pulp is usually produced from wood, which has its bark removed and is broken into chips. There are two basic methods of pulping, the chips are mechanically ground into individual fibres or chemically broken down. Chemical pulping is the most common form producing high quality pulps when combined with bleaching.

The process of beating refers to the fibrillating of pulp fibres. Fibrillating enhances inter-fibre bonding and affects the properties of the finished paper. The beaten pulp is a suspension of cellulose fibres in water to which papermaking additives are added. Paper is formed on a wire mesh that allows the water to drain through and retains the fibres. Fillers and sizing agents are retained in the fibre mat by colloidal and mechanical retention mechanisms, retention agents are added to enhance these mechanisms. The paper is pressed between rollers to compact the sheet and to remove some of the remaining water. Finally the paper is dried at elevated temperatures.

Swales (1992) determined the zeta potentials of the rosin sizes he produced, to predict their behaviour in novel sizing systems. The theory describing the zeta potential and a discussion of the sizing system used throughout this research are both included in Chapter 3. This sizing system, or Neusize™ process, enables calcium carbonate fillers to be used in conjunction with rosin size and papermaker's alum, a method usually considered to be too acidic and needing constant pH adjustment. This chapter details the desirable optical properties of a papermaking filler (i.e. high opacity, low absorptivity, high refractive index compared to air), and compares the properties of common fillers. A discussion of the uses of retention agents which flocculate particles in the papermaking system is included.

The materials used in this work are listed in section 4.1, section 4.1.1 is a discussion of precipitated calcium carbonate production. The techniques used to
examine the fillers are discussed in the later sections of Chapter 4, they are scanning electron microscopy, x-ray powder diffraction, laser diffraction particle size measurement, Fourier transform infrared spectroscopy using diffuse reflectance to examine surfaces, x-ray photon spectroscopy and pH measurement. Gas adsorption and adsorption from solution are discussed in detail. The Cobb test (Cobb 1934), used to quantify the water repellency of paper and the ash test, to determine the filler content, are described at the end of the chapter.

Chapter 5 has been split into two sections for convenience. The first section presents and discusses the results of the examination of the particle and surface characteristics of the fillers. The second discusses the results of the tests carried out on paper containing the fillers and the effects of retention agent addition. The final chapter draws conclusions from the previous discussion.
Chapter 2
Papermaking
2.1 **Introduction to Papermaking**

A discussion of most aspects of papermaking and paper can be found in Casey (1980). Papermaking can be split into several simple sub-divisions.

2.1.1 **Beating**

This term refers to the flattening and fibrillating of pulp fibres. Pulp is beaten to form a suspension of pulp fibres in water. The resulting increase in surface area increases inter-fibre bonding. The stock is then treated with additives for paper production and referred to as the furnish.

Beating affects the physical properties of the finished sheet and may affect the passage of the pulp stock through the papermachine. The larger surface area available for bonding increases the retention of size, fillers and some dyes.

The drainage time of water from the stock is an indication of how quickly the paper can be formed on the paper machine. Drainage time is increased with increased beating. This may be advantageous leading to a slower draining stock producing a more even distribution of fibres and fillers during sheet formation, however slower drainage slows the speed of the paper machine. Beating improves sheet formation and burst strength, the load necessary to rupture a sheet deformed by a sphere, but can lower tear resistance, the work done in tearing a sheet of paper a fixed distance.

The amount of beating varies according to the type of fibre and the specifications of the finished paper e.g. grease proof paper requires well beaten, but long, uncut pulp fibres.
2.1.2 **Formation and Drainage**

This refers to the formation of paper on the wire mesh of the papermachine. The furnish is distributed over the mesh and allowed to drain, unsatisfactory formation is due to fibre flocculation or "clumping" often associated with poor distribution and drainage. The fibres and fillers remaining on the wire form the sheet.

2.1.3 **Pressing and Drying**

Most of the remaining water is removed by squeezing it out of the sheet under pressure and by drying at elevated temperatures. The final sheet usually contains 5% moisture.

2.2 **Laboratory Scale Papermaking**

2.2.1 **Handsheet Machines**

Laboratory papermachines produce small sheets of paper, called handsheets, for testing. The complete papermaking process can be examined using a small scale laboratory machine and models, applicable to an industrial scale machine, proposed. Two types of handsheet machine were used in this work. Both are described in the following section.
2.2.2 Glass Handsheet Machine

A 2% mixture of the dry pulp in water is beaten in a litre Kenwood blender for at least thirty minutes. The blender blades are blunted, which ensures that the pulp is fibrillated and cutting reduced.

The untreated suspension, or thickstock is then mixed with the required fillers. Magnetic stirrers are ideal for this purpose as they evenly distribute the filler without beating the pulp any further. An aliquot of thickstock is treated with sizing agents if required.

The upper chamber of this machine is shown in Fig. 2.2.2. The chamber is filled with water and the treated thickstock is dispersed in this using a specifically designed mixer. This distribution is called the thinstock. Any retention agents are added as the thickstock is dispersed. The drainage tap, tap B, is opened and the sheet is retained on the wire as the water drains through. Some of the additives, fillers and small fibres are lost through the mesh as drainage begins but are retained when the fibre and filler mat is formed. These lost particles are called the fines. The fines fraction of the furnish is arbitrarily defined as the particles that can pass through a 75μm hole (200 mesh). The fraction retained is called the fibre fraction. The sheets are formed under vacuum using a Buchner flask. The aluminium vane reduces turbulence beneath the sheet and prevents removal of fibres and fillers from the bottom of the sheet or "scouring". The wire is removed from the machine with the sheet attached.

The sheet is pressed from the wire onto a stainless steel plate using a rubber roller. The wire and plate are held between two paper blotters. Pressing compacts the sheet evenly and a large amount of the water remaining in the sheet is pressed out and absorbed by the blotters. It also produces a glazed side, due to the steel plate, and a rougher, wire side to the sheet. The sheets are dried in an
Fig. 2.2.2 Glass Handsheet Machine

- Wire
- Buttress Joints
- Rubber Rings
- Aluminium Vane
oven at 105°C for at least 10 minutes until they can easily be removed from the stainless steel plates.

This machine produces circles of paper, two inches in diameter. It does not closely mimic the industrial process but results are used to determine relevant experiments that can be carried out on a more appropriate machine.

2.2.3 Adirondack Handsheet Machine

A schematic diagram of this machine is shown in Fig. 2.2.3(a). It is designed to closely emulate conditions on an industrial paper machine. The Deckle box is sealed with the forming wire in place. Valve B is closed and valve A opened. Water is pumped in to fill the upper half of the box. The treated stock is dispersed in this water and allowed to drain under vacuum through valve B.

The machine is designed so that the drained water, white water, can be recycled if desired. This is standard practice in the majority of industrial mills in an attempt to achieve maximum retention of all additives and the fines fraction, and to reduce water consumption and effluent volume.

The wire is removed and placed in a felt wallet. This is fed under a stainless steel press roll at pressure. After pressing the sheet contains 50-60% water. On an industrial scale it is far more cost effective to remove some of the water in the press section than to remove all of the water in the drying section. The reduction in water content increases the strength of the wet sheet (wet strength) so it can be peeled from the wire by hand and fed onto the drum dryer.

The dryer consists of a continuous felt band in contact with an electrically heated drying roll. The sheet is fed between these two surfaces. It travels around with the drying roll and is removed at the front of the dryer. The dryer lowers the moisture content of the paper from 50-60% to 4-8%, evenly distributed
Fig. 2.2.3(a) Schematic Diagram of the Adirondack Handsheet Machine
throughout the paper.

2.3 Industrial Scale Paper Production

2.3.1 Beating and Refining

These two terms refer to the beating of the pulp to increase the surface area of the fibres. Beating is a batch process and refining a continuous one, carried out by several refiners in series or parallel. A common beater is pictured in Fig. 2.3.1(a), this type of beater was used to prepare the pulp for papermaking on the Adirondack handsheet machine.

Many papermaking additives are added to the stock after beating when mixing is most rapid i.e. in the machine chest which contains a stirrer. A schematic diagram of the entry system for thickstock on a papermachine is shown in Fig. 2.3.1(b).

2.3.2 Industrial Papermachine

A schematic diagram of a common papermachine is shown in Fig. 2.3.2. The processes carried out on a papermachine can be subdivided into four.

(a) Formation and Drainage

(b) Pressing

(c) Drying and Calendering

(d) Reeling and Winding

Formation, drainage and pressing are referred to as the wet-end of the system, drying, calendering and reeling are the dry end.
Fig. 2.3.1(a) Schematic Diagram of a Beater
Fig. 2.3.1(b) Approach Flow System Schematic Diagram
Fig. 2.3.2  Schematic Diagram of a Papermachine
2.3.3 Formation and Drainage

The pulp suspension is distributed on a constantly moving wire mesh, water drains through and the paper is retained on the mesh. The consistency of the stock, i.e. the amount of pulp fibres and fillers in the water suspension depends on the specifications of final product. Thin tissue paper needs only 0.2-0.5% consistency but paper for corrugated board is often made with stock of 0.7-1.0% consistency.

A detailed diagram of the wire section of a Fourdrinier papermachine is shown in Fig. 2.3.3. The table rolls support the wire and foils wipe the bottom of the wire to remove large quantities of water. The baffles prevent water from the rolls returning to the sheet and can be used as foils. The water content of the paper must be reduced so that it can support itself when it is removed from the wire to enter the press section. The consistency at this point must be between 20-30% or the sheet will not have sufficient wet-web strength and will break. The suction boxes at the end of the wire aid drainage and increase the consistency of the sheet.

The couch roll maintains a constant vacuum to aid drainage. The lump breaker roll is a soft rubber roll designed to compact the sheet and remove any lumps that might cause the paper to break in the presses.

2.3.4 Pressing

The main objectives of pressing are to continue the water removal process and to compact the sheet so that fewer breaks can occur. The surface also becomes less fibrous so the dryers remain clean and efficient.

There are two types of pressing used, depending on the type of paper being produced.
Fig. 2.3.3  Wire Section of a Papermachine
(a) **Pressure-Controlled Pressing**

Increases in pressure can increase sheet dryness or can be used to increase the speed of the sheet through the press section without loss of sheet dryness. This type of control is ideal for lightweight papers, i.e. tissue and newspaper, where there is little resistance to the movement of water.

(b) **Flow-Controlled Pressing**

Here, the time the sheet spends in the press section determines its dryness. The fibre network exerts resistance to the passage of water so that pressure controlled pressing is ineffective. This type of pressing is used for heavy papers and is frequently found in automated mills.

There are many different arrangements of press rolls possible, often they are stacked to occupy less space. A simple arrangement, the suction transfer press, is shown in Fig. 2.3.4.

2.3.5 **Drying and Calendering**

(a) **Drying**

The most common method for drying paper is to feed both sides around several steam heated cylinders. The water in the sheet evaporates into the surrounding air. The paper is held to the cylinder by continuous felts driven by the cylinders. In most modern mills the felt is made of a strong, open, plastic mesh, although cotton felts are still used. A large drying section is shown in Fig. 2.3.5(a). For such a machine a hood over the dryers aids uniform drying and regulates humidity.
Fig. 2.3.4  Suction Transfer Press
Fig. 2.3.5(a) Drying Section of a Papermachine
(b) **Calendering**

This literally means to press with a roll. In fact, the paper is passed through a stack of heavy rolls under high pressure. All rolls, except the bottom one, are driven by the paper movement. Such a stack is called a machine calender and one is shown in Fig. 2.3.5(b). Calendering is used to improve sheet printing properties.

The calender rolls are usually found after the drying section and the operation is called on-machine calendering. If the stack is positioned between two dryers it is called a breaker stack. Calendering is most effective when the moisture content of the paper is above normal, the sheet is softer and the fibres more flexible so that they slip against each other and the sheet more readily pressed.

Machine calenders are made up of two to ten chilled, cast iron rolls in a stack. Gloss calendering is the most common form, the paper is pressed by a soft roll onto a very smooth, steel roll. Matt calendering produces a smooth sheet with little increase in gloss. Calendering can control porosity and smoothness, important properties for printing papers, it is also used to control calliper.

2.3.6 **Reeling and Winding**

After calendering the paper is reeled up, as shown in Fig. 2.3.5(b). The reels are removed from the machine and taken to be wound. Winding cuts the paper into the desired reel widths for dispatch.

2.4 **Pulping**

This is essentially the separation of wood fibres from other plant material. There are several types of pulping, i.e. mechanical, chemical, semichemical and
N.B.: Calendar rolls may be steam heated & reel drum water-cooled.

Fig. 2.3.5(b) Calender Stack and Paper Winding
thermomechanical. Both the type of wood and the type of pulping affects the properties of the finished sheet. The pulp used throughout this work was manufactured chemically by the sulphate or kraft process. Only this type of pulping is discussed. Hard and softwood pulps are discussed below.

2.4.1 Hard and Softwoods

Softwood, such as pine, is less dense than hardwood from deciduous trees, and has longer fibres. Reputedly, softwood pulps produce stronger papers than hardwoods, due to their longer fibres.

This assumption is true for tear strength but tensile strength depends on inter fibre bonding. Tensile strength refers to the breaking load per unit width of a sheet 200mm long and 25mm wide. The load is increased at a uniform rate until the paper breaks. Unbeaten, long, softwood fibres produce low tensile strength paper.

Blends of hard and softwood pulps are used by most mills. The addition of short, hardwood fibres increases the surface smoothness and printing qualities of the paper.

2.5 The Kraft Process

This is an alkaline process that uses sodium hydroxide and sodium sulphide as "cooking ingredients". Cooking refers to the heating together of chipped wood and the chemicals above. Cooking removes the lignin cellulose inter-fibre bonding material.

The pulp produced is considered to be of superior quality to that from other methods and has high strength. Any wood can be used and cooking times
are short. The pulp is ideal for making paper bags and brown wrapping paper because it is dark but must be bleached before printing papers can be produced. The process is shown schematically in Fig. 2.5. The most important parts of this process are discussed below. By-products of the process are alkali lignin, turpentine and tall oil.

2.5.1 Digester

This is where the wood chips are cooked with solutions of the sodium chemicals, called white liquor. The digesters are run between 160-180°C. Two types of digester exist, batch digesters which treat isolated loads of wood chips and continuous digesters which process a constant stream of raw material.

These digesters yield the same quantity and quality of pulp. If pulp specifications are constantly changing, batch digesters are used. Continuous digesters are ideal for unchanging pulp requirements. The mixture of cooking chemicals and lignin that leaves the digester is called black liquor.

2.5.2 After Cooking

The blow tank separates the cooked wood chips into individual fibres. The knotter separates out large impurities and uncooked wood by coarse screening. Washing removes soluble solids. Inefficient washing can lead to difficult pH control on stock preparation and foaming problems on the papermachine. Screening and cleaning removes incompletely cooked wood, fibre bundles, bark, grit, scale and other impurities. Separation relies on the differences in size, shape, specific gravity and surface area compared to individual pulp fibres.
Fig. 2.5  Flow Diagram of the Kraft Process
2.5.3 **Liquor Recovery**

This process regenerates the sodium hydroxide and sulphide consumed by cooking, generates heat which supplies the digester and destroys organic pollutants. It makes the whole kraft process more cost effective.

The main steps are shown in Fig. 2.5. The liquor is concentrated to high solids content by evaporation. The concentrated liquor is burnt in a regenerating furnace to produce sodium carbonate. This passes into a lime kiln where it reacts to produce sodium hydroxide. The calcium carbonate precipitated is burnt to regenerate calcium hydroxide. Obviously some sodium is lost, mainly at the washers.

2.5.4 **Tall Oil**

Tall oil is an important by-product of the kraft process, its major constituents are rosin or resin acids and fatty acids. These acids are saponified during cooking to form tall oil soaps which float to the surface of the black liquor during evaporation. They must be removed to reduce foaming in the later stages of processing. Crude tall oil is used in the production of linoleum and as a surface active agent. The rosin acids are used to produce rosin sizes for the paper industry. Unsaturated fatty acids are used in soaps and as alkyd resins in paints and varnishes.

2.5.5 **Bleaching**

Bleaching of kraft pulp is essential to obtain the high brightness required for top grades of paper. It involves the removal of the residual lignin in the pulp
and is considered part of the pulping process.

Bleaching takes place in several stages. During acid stages, an oxidizing agent is added, the alkaline stage extracts the oxidation products. Some oxidizing agents, e.g. hypochlorite, can be added under alkaline conditions combining oxidation and extraction.

Bleaching of kraft pulp commonly includes acidic chlorination, alkaline extraction, hypochlorite and chlorine dioxide bleaching. Due to environmental concerns, chlorine bleaching is gradually being replaced by chlorine free bleaching.
Chapter 3

Theory of Colloids, Sizing and Fillers
3.1 **Lyophobic Colloid Stability**

Colloids are particles with dimensions of 0.1 to 10μm dispersed in a medium, if the medium is aqueous they are called lyophobic. The size range of colloidal particles given above is not an absolute limit, stable colloids with one or two particle dimensions below 0.1μm or above 10μm are known. Everett (1988) has discussed the basic principles of colloid stability, of which Verwey and Overbeek (1948) gave a thorough and definitive account.

Colloids are made up of small particles separated by a fluid medium. If the medium is inert the particles will flocculate to reduce the total free energy of the system. Intermolecular forces are due to the attraction of instantaneous dipoles, van der Waals'-London forces (London 1930), which are responsible for the attraction of colloidal particles. Each spontaneous dipole induces a similar dipole in the molecules surrounding it. The spontaneous dipoles of the molecules within the colloidal particle at any one moment, combine to produce an overall attractive force. Since a large number of dipoles are involved, a long range attractive force, that extends into the dispersion medium, is produced. When thermal motion brings colloidal particles into range of the attractive forces, flocculation occurs. In an aqueous medium, repulsive forces can exist that prevent flocculation and keep the colloids stable. If these forces are electrostatic they can be explained in terms of the ionic double layer surrounding colloidal particles.

3.1.1 **The Ionic Double Layer**

In aqueous media, colloidal particles carry an electrical charge at their surface created by two main mechanisms, the ionization of surface groups and the adsorption of ions from solution onto the particle surface (Everett 1988). The
effect of electrolyte addition on colloid stability and the electrophoresis of colloidal particles gives evidence for this. The surface charge is equal and opposite to the charge of the intervening medium and the system is electrically neutral overall. This surface charge leads to an uneven distribution of counter-ions, relative to the bulk of the dispersion medium, in proximity to the surface, known as the ionic double layer.

Helmholtz (1879) proposed the first model for the ionic double layer. He envisaged a fixed layer of counter-ions at the particle surface neutralizing the surface charge. Gouy (1910, 1917) and Chapman (1913) accounted for the thermal motion of ions in solution by postulating a diffuse double layer in which the potential falls away exponentially with distance from the surface, for a flat double layer. The thickness of the double layer, $1/\kappa$, is defined as the distance from the surface that the potential falls to $1/e$ of its surface value and is dependent on the ionic concentration of the solution. A more concentrated solution will reduce the potential over a shorter distance.

Stern (1924) extended this model to account for the finite size of ions, this model proposes a layer of finite sized ions adsorbed at particle surface (the Stern layer), then a diffuse double layer. A schematic diagram of a flat ionic double layer is shown in Fig. 3.1, where $\delta$ is the Stern layer thickness, $\Psi_0$ is the surface potential, $\Psi_\delta$ is the potential at the edge Stern Layer. The surface potential is assumed to fall off linearly in the Stern layer then exponentially in the aqueous phase.

Verwey and Overbeek (1948) describe the potential, $\Psi_x$, at a point, x, from the surface, with the equation,

$$e^{\Psi_x/2} = \frac{e^{\Psi_0/2} + 1 + (e^{\Psi_0/2} - 1)e^{\delta}}{e^{\Psi_0/2} + 1 - (e^{\Psi_0/2} - 1)e^{\delta}}$$

$$- (3.1)$$
Fig 3.1 Schematic Diagram of the Flat Ionic Double Layer
where the symbols have the same meanings as above and $e$ is the elementary charge on an electron, $v$ is the valencies of the ions, assuming $v_+ = v_- = v$, $k$ is the Boltzmann constant, $T$ is temperature, $n$ is the number of ions per cm$^3$ in the bulk of the medium, where $\Psi_X = 0$ and $\varepsilon$ is the dielectric constant of the medium.

As colloidal particles move through the dispersion medium they carry with them a static layer of fluid inside a boundary layer. The outer edge of this layer is referred to the plane of shear and the potential at this distance from the surface is the zeta, $\zeta$, potential. The theory of a flat double layer can be used to predict the interactions of colloidal particles if the double layer thickness, $1/\kappa$, is much less than the particle radius. Verwey and Overbeek (1948) thoroughly discuss the interaction of two spherical double layers.

When similar colloidal particles approach one another their ionic double layers interact and repulsion occurs. If the potential energy of repulsion forms a sufficient barrier to flocculation the colloid is stable, otherwise flocs of lower surface free energy are formed. Addition of an electrolyte to the aqueous medium can cause a layer of ions to adsorb onto the surface of the colloidal particle. This could enhance colloid stability by increasing the potential energy of repulsion or reduce this and cause flocculation of the particles, depending on the relative charge of the adsorbing ions.
3.1.2 Significance of Zeta Potential

As colloidal particles are charged they will move under the influence of an electric field. The boundary layer remains stationary relative to the particle. The viscous forces due to the intervening medium oppose this motion and at a steady state these forces will be equal.

Electro-kinetic phenomena allow the zeta potential to be measured. Swales (1992), using the steady state described above, determined zeta potentials to model the Neusize™ process used throughout this research. There is no evidence that the zeta potential is exactly the potential at this plane as it is calculated using the viscosity and dielectric constants of the medium which are bulk properties. Zeta potential measurements are used as an indication of surface potential and to predict colloid behaviour.

3.2 Sizing

Sizing refers to the water repellency of paper or the process of imparting this property. It is split into two sub-divisions, surface and internal sizing. Surface sizing involves the addition of film forming substances, i.e. starches, waxes, etc., to a preformed fibre web. Internal sizing refers to the addition of wet-end chemicals to enhance sizing of the sheet. Internal sizing was used throughout this work and is discussed in this section. The most common internal sizing agents are rosin emulsions and alkyl ketene dimer (AKD) emulsions.
3.2.1 Rosin Emulsions

Rosin is produced from three sources, gum rosin from living pine trees, wood rosin from aged pine stumps and tall oil rosin, a by-product of the kraft process, see section 2.5.4. The major component in all these rosins is the family of resin or rosin acids, a member of which is shown in Fig. 3.2(a). The sizing ability of rosin is thought to be improved by reacting the molecule with a dienophile to produce a tricarboxylic acid, Fig. 3.2(b), a process called fortification. Swales (1992) found that if the rosin is not sintered on the paper, fortified rosin is a more effective sizing agent. With sintering, both forms of rosin had similar sizing properties.

Rosin emulsions are the most commonly used form of rosin size because of their high free acid content, between 75-100%. Other forms such as low viscosity liquids and dry rosin, a water soluble powder, have been used in the past but contain little acid and are known as rosin soaps.

The first commercial rosin emulsion was "Bewoid" size (Weiger 1932 and 1935). The product contained 90% free rosin acid in rosin soap stabilized by 2% casein, by weight of rosin. To achieve this unsaponified rosin is mechanically dispersed in the presence of 2% sodium hydroxide and casein. Although new products have been patented, they are mainly based on this original emulsion. The product Neusize™ is produced in a similar fashion. Rosin is melted under agitation and sodium hydroxide is slowly added to saponify some of the acid. A water in oil emulsion is initially formed, stabilized by casein, and is diluted, when inversion occurs, to form an oil in water emulsion. The product was supplied at 30% solids by Roe Lee Paper Chemicals Co. Ltd.
Fig. 3.2(a)  Member of Rosin Acid Family, Tetrahydroabietic Acid

Fig. 3.2(b)  Fortified Tetrahydroabietic Acid
3.2.2 Papermaker's Alum

"Papermaker's alum" is in fact an hydrated salt of aluminium sulphate, \( \text{Al}_2(\text{SO}_4)_3\cdot18\text{H}_2\text{O} \), commercially available as a 47% solution. It is used as a retention agent in conjunction with rosin size. The hydrated aluminium cation \([\text{Al(H}_2\text{O})_3]^{3+}\) is believed to act as a bridge between the anionic cellulose and anionic rosin size.

3.2.3 Reverse Sizing

This method of sizing with rosin emulsions is the most frequently encountered in the paper industry. The required amount of alum is mixed with the thickstock and then the size is added. The optimum pH for this method of sizing is 4 to 6.5. At higher pH's the alum forms aluminium hydroxide and aluminate ions. These low pH values eliminate the use of calcium carbonate as a filler. The carbonate, added to the thickstock before the alum, is decomposed by the acidic alum and the carbon dioxide released can cause foaming problems and calcium sulphate deposition. Paper containing calcium carbonate is usually sized with AKD at pH values above 7.

3.2.4 The Neusize Process

This sizing method was developed by Barlow, Jaycock and Street in 1986 (Pat. Pending) and studied by Swales (1992). It is now the sizing method of approximately twenty paper mills and has been used throughout this research. The alum and size are premixed to form an unstable cationic suspension which flocculates with cellulose on addition to the thickstock. This whole process, after
the alum and size mixture has been added to the thickstock, takes place at neutral or alkaline pH which has enabled calcium carbonate to be used as a filler.

3.2.5 Alkyl Ketene Dimer

AKD is generally used as the sizing agent when paper is produced under alkaline conditions, e.g. when it contains calcium carbonate as a filler. Covalent bonds are thought to be formed between the size and cellulose so that the need for alum as a retention agent is eliminated and the system can be run at higher pH values. The exact nature and degree of the reaction between the cellulose and the AKD is still a matter of dispute.

3.3 Papermaking Fillers and Pigments

The addition of fillers is frequently a part of the papermaking process. Historically, they were added to low grade papers to reduce the amount of fibre necessary, now they are also included to enhance the optical and printing properties of paper. Fillers have a higher affinity for printing inks than cellulose fibres and the fine pore structure created increases the rate of absorption of oil from the ink. Pigments are more expensive than fillers and are added to the paper in smaller quantities to specifically enhance the properties of the sheet. For the purposes of this discussion the term fillers will be used to describe both fillers and pigments. Usually fillers are added to the thickstock, as a dispersion in water, before all other chemicals.
3.3.1 Optical Properties of Fillers and Pigments

When light strikes the paper surface part of it is specularly reflected, where the angle of incidence equals the angle of reflection, part is refracted and part absorbed. At each fibre or filler particle surface, the same phenomena occur. The portion of light transmitted through a fibre is split between internal reflection, refraction through air or filler, and absorption. This process, called scattering in this discussion, continues until all the light emerges as diffusely transmitted or reflected light, or is absorbed. The amount of scattering depends on the refractive indices of the paper components and the number of times light passes between them. The refractive index of a medium is the ratio of the velocity of light in the medium to the velocity of light in a vacuum. Light passing through objects of the same refractive index, two touching fibres or filler particles, is not refracted.

Reflectance is measured in two ways, specular reflectance, called gloss, and diffuse reflectance, called brightness. During brightness measurements the sample is usually illuminated at 45º to the normal with readings taken parallel to the normal, sometimes readings are taken at 90º to the incident beam. Within the paper industry, brightness is measured at 457nm, the wavelength most sensitive to the colour changes that occur when the pulp is bleached, and a wavelength easily achieved using a mercury lamp (Hg green line). Pulp brightness is the most important factor affecting paper brightness. A highly bleached pulp produces brighter sheets than one of a medium bleaching. Titanium dioxide and calcium carbonate are highly reflective fillers that can be used to increase the brightness of an unbleached pulp to that of a medium bleached pulp.

The reflectance, or brightness, of paper is measured with a sheet of the paper against a backing material. \( R_0 \), backed by a black cavity, \( R_R \), by a white
body of reflectance $R'$, a paper pad of "infinite" thickness. When no change in reflectance occurs on doubling pad thickness, the pad is termed infinitely thick. $R_\infty$ is the most common measurement and is referred to as papermaker's brightness.

Opacity is a measure of the light transmitted through paper. Since light at a fibre surface is reflected, transmitted or absorbed, reflection can be used as an indirect measure of transmission. It allows brightness and opacity to be determined on the same apparatus, reducing capital costs. Opacity is usually measured by the "contrast ratio", the ratio of diffuse reflection of a sheet backed by a black cavity, where transmitted light is absorbed, and a white body, where light is reflected back into the sheet. $R_\gamma/R_\infty$ is called "printing opacity" and is the most common contrast ratio calculated.

The opacity of paper is described by the Kubelka-Munk theory (Davis 1940). Two optical constants are defined by the theory, the specific scattering coefficient, $S$, and the specific absorption coefficient, $K$. $S$ is the limiting value of light energy scattered backwards per unit thickness as thickness becomes small, $K$ is the limiting value of light energy absorbed per unit thickness as the thickness becomes small. It is common practice to express these constants in terms of weight rather than thickness, which can be measured more precisely than thickness, is not affected by calendering and is how most papermaking constants are expressed. The symbols for the constants based on weight are $s$ and $k$. The scattering and absorption power are $sW$ and $kW$ respectively, $W$ is the basis weight of the paper in grams per square metre.

Steele (1935) and Judd (1938) have published the derivation of the Kubelka-Munk equation, shown here,

$$R_\infty = 1 + (k/s) -[(k/s)^2 + (k/s)]^{0.5} - (3.2)$$
This is transformed to become,

\[
\frac{k}{s} = \frac{[1 - R_\infty]^2}{2R_\infty} \quad \text{(3.3)}
\]

where \( R_\infty \) is the reflectance of a paper pad, if measured at 457nm it is papermaker's brightness.

Tables giving values of \( sW \) corresponding to known values of \( R_\infty \) allow \( s \) and \( k \) to be calculated. Kubelka (1948) showed that \( R_0 \), the reflectance of a sheet of paper backed by a black cavity, and \( R_\infty \) could be used to determine \( sW \) with hyperbolic functions.

If the coefficients of the individual components in the paper are known, the overall coefficient of the paper can be calculated, as shown,

\[
s_{\text{paper}} = (1 - y)s_{\text{pulp}} + y s_{\text{filler}}
\]

\[
k_{\text{paper}} = (1 - y)k_{\text{pulp}} + y k_{\text{filler}}
\]

where \( y \) is the fractional content of filler. Comparing the \( s \) or \( k \) values of filled and unfilled paper determines the \( s \) or \( k \) value of the filler.

Since \( s \) is dependent on the basis weight of the sheet, the larger the filler fraction the higher the scattering power of the paper. The increased scatter is due to the difference in refractive index between fibres, filler and air, and an increase in the number of scattering surfaces due to the small particle size of fillers. Fillers with high \( k \) values are undesirable with white paper because although they increase sheet opacity they also reduce brightness.

3.3.2 Properties of Common Fillers

An ideal filler has a high refractive index, greater than water and air, a small
particle size, low solubility in water, is white and inexpensive. The three most common fillers are calcium carbonate, clay and titanium dioxide. Table 3.3.2(a) shows the refractive indices of air, cellulose and common fillers. These are generalized figures used for reference purposes, actual values will vary for each individual variety of clay and calcium carbonate filler.

Table 3.3.2(a)
Refractive Indices of Paper Components

<table>
<thead>
<tr>
<th>Material</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1.00</td>
</tr>
<tr>
<td>Cellulose</td>
<td>1.53</td>
</tr>
<tr>
<td>Clay</td>
<td>1.55</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>1.56</td>
</tr>
<tr>
<td>Titanium Dioxide</td>
<td></td>
</tr>
<tr>
<td>Anatase</td>
<td>2.55</td>
</tr>
<tr>
<td>Rutile</td>
<td>2.70</td>
</tr>
</tbody>
</table>

The small difference between the refractive index of air, cellulose, clay and calcium carbonate shows that these fillers rely on the increase in the number of filler-air interfaces to increase opacity. At a low level of addition, titanium dioxide has a larger effect on opacity than other fillers. If filler loadings are too high the filler particles will be in optical contact and the effective scattering power of the filler is reduced. This factor means that in practice clay is better at opacifying paper than calcium carbonate. Any substance that flocculates filler particles will reduce paper opacity. All these factors must be optimized when determining filler loading.
Table 3.3.2(b) shows the specific scattering coefficients of pulp and fillers.

Titanium dioxide fulfils all the required filler specifications except cost. It is widely used as white pigment in the paint industry and is expensive. Usually it is used in conjunction with other, less expensive fillers or to produce special orders. Clay is an inexpensive filler often combined with titanium dioxide to produce printing paper. Precipitated calcium carbonates have high brightness and have been suggested as an alternative to titanium dioxide for use with AKD size or Neusize™.

Table 3.3.2(b)

Specific Scattering Coefficients of Paper Components

<table>
<thead>
<tr>
<th>Material</th>
<th>$s/\text{gm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Pulp</td>
<td>20 - 40</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td></td>
</tr>
<tr>
<td>Precipitated</td>
<td>170 - 210</td>
</tr>
<tr>
<td>Ground</td>
<td>100 - 120</td>
</tr>
<tr>
<td>Clay</td>
<td>120 - 150</td>
</tr>
<tr>
<td>Titanium Dioxide</td>
<td></td>
</tr>
<tr>
<td>Anatase</td>
<td>400 - 550</td>
</tr>
<tr>
<td>Rutile</td>
<td>530 - 700</td>
</tr>
</tbody>
</table>

3.4 **Fines Retention**

The fines fraction of a papermaking furnish is arbitrarily defined as the part that passes through a 200 mesh (75 μm hole sieve). The portion retained is the fibre fraction. Fines are made up of filler particles, fibre fragments, size, alum and
other additives. It is desirable to maximize the retention of the fines fraction when the sheet is initially formed (first pass retention), and economics dictate that any fines passing through the sheet are recycled in the backwater whenever possible.

Fines are retained by two mechanisms, mechanical entrapment and colloidal attraction. As the fibre web is formed on the wire, particles too large to pass through the web are mechanically retained. The flocculation of fillers, fibres and size using alum and other retention agents gives evidence for a colloidal retention mechanism.

3.4.1 Retention Agents

Any additive that has a flocculating effect on the paper furnish will aid retention. Polymeric polyelectrolytes enhance retention by two colloidal mechanisms.

(a) Patch Model Mechanism

This model was described by Gregory (1973). Discrete patches of polymer are adsorbed on the particle surface, producing uneven surface charge, as shown in Fig. 3.4.1(a). This leads to another attractive force between colloid particles, in addition to van der Waals'-London forces, and when attractive forces outweigh repulsive forces, flocculation occurs.

(b) Polymer Bridging Mechanism

The polymer adsorbs on the surface of the particle in a series of loops. Large loops extend beyond the Stern layer of counter-ions, as shown in Fig. 3.4.1(b), and adsorb onto other particle surfaces, causing flocculation. High molecular weight, cationic polyacrylamides are commonly used in the paper
Fig. 3.4.1(a) Schematic Diagram of Patch Model Mechanism

Fig 3.4.1(b) Schematic Diagram of Bridging Mechanism
industry to retain fines in this manner. The resulting flocs are resistant to the hydrodynamic forces present during papermaking. Ruehrwein and Ward (1952) first described this mechanism.
Chapter 4

Materials, Instrumentation and Experimental
4.1 **Materials**

**Fillers**

The following precipitated calcium carbonates (PCCs) were provided as dry powders by Pfizer Speciality Minerals\(^{+}\).

- Albacar HO
- Albacar PO
- Albacar LO
- Albafil

The data sheets associated with these products are shown in Appendix I.

Young's PCC, specially prepared by Prof. P.A. Young\(^*\) as a 12% slurry.

Snowcal 60, ground chalk, produced by ICI as a dry powder.

\( ^{+} \) Now Speciality Minerals Inc.

\( ^* \) Prof. Peter A. Young of Longcliffe Quarries Ltd., Brassington, Derbyshire DE4 4BZ

**Paper Chemicals and Pulp**

- Neusize\(^{TM}\) emulsion, provided by Roe Lee Paper Chemicals Co. Ltd., at 30% solids.

- Papermaker's Alum, provided by Roe Lee Paper Chemicals Co. Ltd., as a 47% solution.

- Percol 63, a high molecular weight, cationic, polyacrylamide, retention agent, produced by Allied Colloids Ltd. as granules. The data sheet for this product is included in Appendix I.

Baycell kraft pulp.
Chemicals

Buffer tablets, pH 4 (phthalate) and 7 (phosphate), purchased from Fisons Scientific.

Calcium carbonate, specified laboratory reagent, purchased from Fisons Scientific.

Calcium hydroxide, specified laboratory reagent, purchased from Fisons Scientific.

Heptane, fraction from petroleum, specified laboratory reagent, purchased from Fisons Scientific, dried with No. 3A molecular sieve, nominal pore size 3Å, purchased from Fisons Scientific.

Methylene Blue, conforms to BP 1973, dye content 96.101%, purchased from Fisons Scientific.

Nitrogen gas, supplied by BOC gas cylinders.

Orange II, C.I. 15510, certified by Biological Stain Commission, dye content 95%, purchased from Aldrich Chemicals, recrystallized from 1:1 ethanol:water mixture before use.

Paranitrophenol, specified laboratory reagent, minimum 97% paranitrophenol, purchased from Fisons Scientific.

Potassium bromide, Analar grade, containing 99.5% potassium bromide, purchased from Fisons Scientific, ground to small particle size with an agate mortar.

Sodium hydroxide, specified laboratory reagent, purchased from Fisons Scientific.

Stearic (octadecanoic) acid, Analar grade, purchased from BDH, containing 99.5% stearic acid.

Except for papermaking with the Adirondack handsheet machine and
unless otherwise stated, all water used was doubly distilled.

4.1.1 Calcium Carbonate Fillers

Two forms of calcium carbonate are used as papermaking fillers. Natural, ground chalk or limestone and a manufactured variety called precipitated calcium carbonate (PCC).

Chalk is milled from natural deposits. The brand Snowcal 60 has been passed through a 60 mesh ensuring a maximum particle size of 250 μm. A large quantity of the sample was obtained at the beginning of this research to ensure no errors could arise due to differences between chalk from various quarries.

Pfizer's PCCs are produced by a two step process. Calcium oxide is initially reacted with water to form calcium hydroxide. In the second step the hydroxide is reacted with carbon dioxide. Control of the process conditions allows the product to have the specific properties required for a papermaking filler.

Prof. Young's PCC production method is awaiting patent and very little is known about the manufacturing process. A sample of the slurry provided was filtered through fibre glass filters, washed with ethanol and dried in air.

4.2 Scanning Electron Microscope (SEM)

At the top of the electron-optical column is the electron gun containing a tungsten filament. Thermionic emission electrons are produced when the gun filament is heated to 2700K. Electron recapture is prevented by a high voltage between the filament and an earthed anode disc, the electrons are accelerated away. Images of the sample surface are formed by scanning the electron beam over a series of small areas of the sample surface. The smaller overall area
scanned, the larger the magnification of the final image on a fluorescent screen. Mechanically moving the sample allows different parts of the surface to be scanned.

4.2.1 **Electron and Sample Interactions**

(a) **Unscattered Electrons**

High energy electrons may pass unaffected through the sample and cannot be used to form an image.

(b) **Elastic Scatter**

When an electron passes close to the nucleus of a sample atom it is attracted to the nucleus by its positive charge. The electron changes direction without energy loss. The scatter angle of the electron depends on how close it passed to the nucleus. Elastic scatter is most likely to occur when low energy electrons strike thick samples of high molecular weight. For most image formation, backscattered electrons, ($\text{bse, electron deflection} > 90^\circ$), are detected.

(c) **Inelastic Scatter**

There are many types of inelastic scatter but in all cases the incident electron interacts with the electrons of the sample atoms and loses kinetic energy. Secondary electron emission is used to form images of the surface.

Incident electrons remove loosely bound electrons in outer orbits of atoms. If the atoms are close to sample surface their electrons are not recaptured but emitted as secondary electrons.
4.2.2 Detectors

(a) Scintillator/Photomultiplier Electron Detector

The Everhard-Thornley Detector

This detector is found on many instruments and measures the emission of electrons by converting electrons to photons by scintillation and back to electrons in a photomultiplier tube. The final image is formed from this current.

(b) Solid State Electron Detector

This detector uses backscattered electrons to form the final image. When high energy scattered electrons strike a semiconductor, secondary electron emission occurs creating a free electron and an electron vacancy and a small current is generated. A sensitive amplifier is necessary to increase the signal for image formation. These detectors are slow to respond and are less common.

4.2.3 Electrical Charging

Most samples are non-conductive and surplus electrons from the SEM beam will accumulate on the surface over a period of time. The negative charge built up repels the approaching electrons and affects imaging. A thin layer of gold or carbon uniformly evaporated onto the surface is used to conduct the electrons away and also prevents the sample heating up. Lawes (1987) is a theoretical and practical guide to SEM.
4.2.4 Sample Preparation

An ISI SS40 scanning electron microscope was used throughout this work. The Pfizer calcium carbonate samples and the ground chalk were diluted to produce very weak slurries in ethanol to prevent particle flocculation. The slurry was sprayed onto a conventional glass coverslip as an aerosol. The ethanol evaporates in air when sprayed and the particles are unaffected by the aggregation that can occur during drying. The dried sample of Young's PCC was treated in an identical manner, the original 12% slurry was diluted with ethanol before spraying.

The coverslips were glued to aluminium stubs designed to be inserted in the SEM sample holder and were coated in a 10nm film of gold. A polymeric glue, soluble in water was used.

Samples of paper were prepared to expose a clean break in the paper to the electron beam. When paper is cut with scissors some folding of the cellulose fibres across the cut occurs. To prevent this the sheet was soaked in water for 10 minutes and frozen in liquid nitrogen. When the frozen sheet is broken the fibres along a breaking line snap without folding. These samples were glued directly onto the sample stub before coating with gold. The paper was produced using the laboratory glass handsheet machine described in section 2.4.2.

4.3 X-ray Powder Diffraction

Diffraction occurs when the incident radiation is of the same order of magnitude as the scattering object, x-rays with wavelengths 0.07 to 0.2nm are used to produce diffraction patterns with crystals. According to Bragg's law for x-ray diffraction by a crystalline material,
2d\sin\theta = \nu \quad - (4.1)

where \( d \) is the distance between two crystal planes, \( \theta \) is half the diffraction or scattering angle, \( 2\theta \) and \( \nu \) is the wavelength of the incident radiation. X-ray powder diffraction scans and detects monochromatic x-rays through a range of scattering angles. The diffraction angle where peaks in the intensity of the detected signal occur are used to calculate the \( d \) spacings of the sample. Comparing these values against a database, the powder diffraction file, that contains the \( d \) spacings of the different crystal structures of common substances, the compound and its crystalline form can be identified. Monochromatic x-rays are produced with a copper filter, 0.15405\,nm wavelength, for x-ray powder diffraction.

4.4 **Particle Size Measurement**

Light diffraction is one of the most widely used techniques for particle size measurement, in the range 1 to 1000\,\mu\text{m} diameter. A light source, often a laser, is directed at a narrow sample cell through which the sample, dispersed in a fluid medium, flows at right angles to the direction of the beam. The particle diffracts the light and a diffraction pattern for each particle is formed. The diffraction pattern depends on the particle size and so the final, composite diffraction pattern of all the particles in the sample is used to produce a particle size distribution.

4.4.1 **Polarized Intensity Differential Scattering (PIDS)**

PIDS is a technique used for sizing particles with diameters less than a micron and to enhance the distributions produced by diffraction methods. Diffraction patterns of particles less than 1\,\mu\text{m} in diameter are difficult to
distinguish. If a particle has a diameter close to the wavelength of light, 0.4 to 0.8 μm, the difference in scattering of plane and perpendicular polarized light is dependent on the ratio of the particle size to the light wavelength. Using polarized light sources at several wavelengths and detectors at several angles it is possible to produce accurate particle size data for these very small particles. Particle size analysis was carried out at Roe Lee Paper Chemicals Co. Ltd. using a Coulter LS130 with PIDS assembly. The instrument is regularly calibrated using a polystyrene latex standard, Latron 300LS, with a mean particle diameter of 0.307 ± 0.13 μm and a garnet G15 standard with a mean particle diameter of 15.18 ± 1.75 μm. The machine is correctly aligned and functioning properly when the mean particle diameters are determined within the limits of the associated errors.

4.5 Adsorption Techniques For Surface Area Measurement

4.5.1 Adsorption

Jaycock and Parfitt (1981) contains a complete discussion of adsorption of gases and liquids on solids. Adsorption defines the attraction of fluid molecules, the absorbate, to a solid surface, the adsorbent. Adsorption can be divided into two categories, chemisorption and physisorption. Physisorption occurs when the surface of the adsorbent attracts the adsorbate molecules by a physical mechanism, i.e. van der Waals' forces, hydrogen bonding. Chemical bonding results in chemisorption. Initial attraction to the surface is caused by a physical mechanism but if the energy barrier is sufficiently low, chemical bonds are formed and a more thermodynamically stable state is achieved.

Chemisorption involves the sharing of electrons between the absorbing molecule and the surface to form a chemical bond. For this reason the absorbed
layer is never more than one molecule deep, although physisorption on the
chemisorbed layer can occur. Physisorption can produce an adsorbed layer many
molecules deep, typically 10 to 20, multilayer adsorption. A chemisorbed layer has
a higher heat of adsorption than physical adsorption and desorption requires a
larger energy input.

In a closed, isothermal system the adsorption of a gas onto a solid results in
a drop in gas pressure and an increase in the weight of the solid. The amount of
gas adsorbed can be calculated from the decrease in gas pressure.

Adsorption of a solute from solution or one component of a binary liquid
mixture is accompanied by a corresponding reduction in solution concentration or
of the mole fraction of the component in the mixture. The amount of solute can be
calculated by the concentration change.

Adsorption measurements at constant temperatures are used to generate
adsorption isotherms. There are five general types of isotherms, shown in
Fig. 4.5.1. Most adsorption isotherms are identified as one of these classes
although some are a combination of two types.

Type I is typical of chemisorption without physisorption. Type II
represents multilayer physisorption onto a non-porous solid.

4.5.2 Adsorption of Gases

(a) The BET Method

This discussion is restricted to gas adsorption onto a non-porous solid
corresponding to the Type II isotherm. The best known mathematical model for
this gaseous adsorption was proposed by Brunauer, Emmett and Teller (1938),
and results in the BET equation. It can be used to calculate the specific surface
area of a solid.
Fig. 4.5.1 Common Types of Adsorption Isotherm
Langmuir (1918), regarded the adsorbent surface as a series of adsorption sites capable of adsorbing only one molecule, and that an equilibrium between adsorption and desorption is established for this monolayer. This model describes Type I isotherms.

The BET approach extends the Langmuir model to include the effects of multilayer adsorption. At equilibrium layers of molecules are adsorbed onto the surface, each layer has its own dynamic equilibrium where the rate of molecules evaporating from the \( i \)th layer is equal to the rate of condensation of molecules onto the \((i-1)\)th layer.

The two main assumptions of the theory are;

1. The heat of desorption from the first layer is \( Q_1 \) and from subsequent layers is \( Q_v \), the latent heat of vaporization of adsorbate as a liquid.
2. All desorption is localised and there are no interactions between adsorbed molecules.

The final equation used in surface area measurement is,

\[
\frac{P}{V(P_0-P)} = \frac{1}{V_m C} + \frac{(C-1) P}{V_m C} - \frac{4.2}{P_0}
\]

where \( P \) is the pressure of the gas, \( P_0 \), the saturated vapour pressure of the gas \( (P/P_0 \) is called the relative pressure), \( V \), the equivalent volume of gas adsorbed at standard temperature and pressure (STP), \( V_m \), the equivalent volume of gas adsorbed at monolayer coverage, also at STP and \( C \), a constant. A plot of \( P/V(P_0-P) \) versus relative pressure, \( P/P_0 \) is linear within a limited range of \( P/P_0 \), typically \( 0.05<P/P_0<0.35 \). From the gradient, \( (C-1)/V_m C \), and intercept, \( 1/V_m C \), the BET constant, \( C \), and \( V_m \) can be calculated. Since one mole of ideal gas occupies 22.4dm\(^3\) at STP, the number of moles of gas adsorbed at monolayer coverage per
gram of adsorbent, \(a_m\), can be calculated.

This value, \(a_m\) or monolayer capacity, is used to calculated the specific surface area, \(S\), of the solid.

\[ S = a_m L A \]  

(4.3)

where \(L\) is Avagadro's constant and \(A\), the coverage area of an adsorbed molecule.

(b) \(t\)-plots

This method is fully discussed by de Boer (1966) and is used to determine if a sample undergoing nitrogen adsorption is microporous. Using the value of \(V_m\) determined by the BET method the statistical thickness, \(t\), of the multilayers adsorbed can be calculated,

\[ t = 0.354 \left( \frac{V}{V_m} \right) \]  

(4.4)

where 0.354nm is the thickness of one layer of adsorbed nitrogen molecules.

A plot of relative pressure, \(P/P_0\), against statistical thickness produces a \(t\)-curve. Schüll (1948) showed non-porous solids were represented by a single \(t\)-curve. Comparing an experimental \(t\)-curve to a standard indicates if a sample is porous. Data for a standard \(t\)-curve is found in Lippens (1964).

A plot of \(V_{\text{sample}}\) versus \(t\) is an indication of porosity, a straight line through the origin occurs if no porosity is present, positive deviation from the straight line is due to an increased uptake of nitrogen than would occur with multilayer adsorption. Two such curves are shown in Fig. 4.5.2. The gradient of a linear plot can be used calculate the specific surface area of a sample, \(S_t\), in \(m^2/g\), using the equation,

\[ S_t = 1.547(V/t) \]  

(4.5)

where \(V/t\) is the gradient of the \(t\)-plot. Usually the pressure range for these measurements is larger than the linear range for the BET method, \(P/P_0\) up to 1.0. In this work \(t\)-plots were produced from data limited to the BET relative pressure.
Fig. 4.5.2  t-Plots Showing Deviation from Straight Line
range and the results used as a guide to porosity. However, Albacar PO was examined at high relative pressures and the t-curve for this filler was compared to the standard curve, as described above.

4.5.3 Adsorption Isotherm Determination

There are three techniques for determining adsorption isotherms; volumetric, gravimetric and dynamic methods. The commonest, volumetric determination, was used to determine surface areas throughout this research.

(a) Outgassing

Outgassing refers to the exposure of the adsorbent to a vacuum at elevated temperatures to remove any previously adsorbed layers, usually adsorbed water. Elevated temperatures reduce the time required for outgassing but are carefully chosen to avoid sintering of the sample or any change in the nature of the surface. An empirical equation giving a rough guide to outgassing times and temperatures is,

\[ t = 14.4 \times 10^4 T^{-1.77} \]  

where \( t \) is the time of heating in hours and \( T \), the outgassing temperature in degrees Celsius and a vacuum better than \( 5 \times 10^{-6} \) mm Hg (Young 1962). All samples were outgassed at 105°C in a moderate vacuum for at least two hours, for convenience. A repeat, outgassed at 30°C, was run to check for sintering effects.

(b) Volumetric Adsorption

Several gases are employed for determining adsorption isotherms, nitrogen, argon and krypton are the commonest. Nitrogen is the most frequently employed because it is readily available and inexpensive. Modern apparatus to measure
nitrogen adsorption can measure specific surface areas as low as 1 m²g⁻¹. The Micromeritics ASAP 200 system was used, with nitrogen gas, to determine the surface areas of the fillers. The machine was calibrated using a solid of standard surface area, 198 ± 7 m²g⁻¹.

A known volume of nitrogen gas is allowed into the system and reading taken from the pressure transducer. The sample bulb is immersed in liquid nitrogen and gas condenses on the adsorbent surface. When equilibrium has been reached between the gas and the condensed layer another pressure reading is recorded. The process is repeated for increasing volumes of gas and the results are used to produce a linear plot, according to the BET theory, to determine the specific surface area of the sample. Five measurements were made to produce a linear BET plot, at relative pressures increasing from 0.11 to 0.31. All final adsorption volumes calculated are expressed at STP. Since all gases are non-ideal the deviations from ideal behaviour are a possible source of error. This error is generally insignificant except if high pressures are used.

4.5.4 Adsorption of Liquids

This refers to the adsorption of a liquid, made up of two components, onto a solid surface. Equilibria exist between the adsorbed molecules and those in the bulk solution. Unless there is preferential adsorption of one component, the isotherm, produced by measuring the concentration change of one component, is a composite of the two individual adsorption isotherms and shows apparent adsorption. For dilute solutions, any change in the solvent concentration is negligible compared to solute concentration changes, the resulting isotherm is for solute adsorption alone. These systems are used for surface area measurement. The isotherms are all the same shape as the Type I gas adsorption isotherm, Fig.
4.5.1, although the solution adsorption mechanism does not necessarily follow the Langmuir model. However, an expression analogous to the Langmuir equation, replacing gas pressure with equilibrium concentration, $C_e$, describes the isotherm.

$$\theta = \frac{bC_e}{1+bC_e} \quad -(4.7)$$

Where $\theta$ is the fraction of the surface occupied and $b$ is a constant. Since,

$$\theta = \frac{a}{a_m} \quad -(4.8)$$

where $a$ is the number of moles of solute adsorbed and $a_m$, the number adsorbed at monolayer coverage. If measured per gram of solid, $a$ is the adsorption and $a_m$, the monolayer capacity. Rearrangement of (4.7) and (4.8) gives,

$$C_e = \frac{C_e}{a} \frac{1}{a_m} + \frac{1}{a_m b} \quad -(4.9)$$

A plot of $C_e/a$ versus $C_e$ is linear and the gradient is used to determine $a_m$. Specific surface area is calculated using equation (4.3), section 4.5.2(a).

Many systems have been used to examine adsorption from solution and to measure specific surface areas. Kipling (1965) lists systems of non-electrolytes and Giles (1969) extensively discusses the use of dyes and paranitrophenol in aqueous solution to determine surface areas. Adsorption from solution was introduced to the research to provide a quick, inexpensive and robust method of specific surface area measurement for use in the field. The initial results contained such interesting information about the nature of the filler surfaces that there was a
change in the direction of the research. The systems used for adsorption from solution during this research are discussed below.

(a) Dyes as Adsorbates

Surface area measurements made by the adsorption of dyes from aqueous solution are regarded as less accurate than those made using gas adsorption. Results from dye adsorption and gas adsorption can differ due to the size of the molecules. Smaller gas molecules are able to adsorb on the inside of small pores that dye molecules cannot enter. The chemical nature of the solid surface and the dye will affect the adsorption. Most dyes are ionic in aqueous solution and selective adsorption onto particular sites of polar surfaces can be a source of error. The nature of the bonding and the number of adsorption sites available affects the orientation of molecule on the surface. A flat molecule vertical to the surface occupies a smaller surface area than the same molecule lying flat, but more dye molecules can be accommodated and the concentration change of the dye in solution will be artificially high. This effect was investigated by West (1952, 1953, 1954) using cyanine dyes adsorbed on silver halide "grains". Dye molecules stacked at an intermediate angle between flat lying and vertical, $\theta$, will have a coverage area dependent on $\theta$. This is shown schematically in Fig. 4.5.4(a)(i). It is necessary to know the orientation of dye molecules on the surface to correctly calculate the specific surface area of the solid.

Giles (1966) suggested an alternative theory to account for the increase in dye concentration change. It was proposed that dye molecules exist as micelles in aqueous solution and for each dye molecule adsorbed to the surface there will be several molecules removed from the solution. This would lead to high results for specific surface area unless the number of molecules removed from solution per
Fig 4.5.4 (a)(i) Coverage area of adsorbed molecule
dye molecule adsorbed was known.

The three dyes used during this work were methylene blue (MB), orange II (OII) and paranitrophenol (pnp). The molecular structure of the dyes are shown in Fig. 4.5.4(a)(ii). All three have strong absorption bands in the uv/visible spectrum. The uv/visible absorbance, $A$, was used to determine the concentration and hence the number of moles of solute adsorbed on the surface. According to the Lambert-Beer law,

$$A = \varepsilon lc$$  

where $\varepsilon$ is the molar extinction coefficient, $l$, the pathlength of the sample cell and $c$, the sample concentration. Absorption measurements were made at 664nm for MB, 484nm for OII and 303nm for pnp, the spectra of these compounds are shown in Figs. 5.1.5(a) to (c). The coverage areas of MB and OII were taken as $1.2\text{nm}^2$ and $0.25\text{nm}^2$ for pnp (Giles 1969), assuming that the molecules were adsorbed horizontally onto the surface. The correction for micellar adsorption of MB and OII were taken to be two and three respectively (Giles 1969). The values for surface area without corrections for micellar adsorption were used to determine the orientation of the dye molecules to the surface.

(b) Adsorption from Non-Aqueous Solution

Experiments were carried to utilize the small coverage areas of pnp and stearic acid, $(0.205\text{nm}^2$, Adams 1941), in a non-aqueous solvent, in an attempt to produce specific surface areas approaching the results from gas adsorption. It was assumed that adsorption from a non-aqueous solution would be non-site specific and that the small size of these molecules would enable them to enter pores too small for the dye molecules. Giles (1969) suggests using pnp with hexane and xylene, Woodings (1966) successfully determined the surface of iron oxide powder by adsorption of stearic acid (octadecanoic acid) in heptane. Systems of
Fig 4.5.4 (a)(ii)
Structures of dyes used in solution adsorption
pnp and stearic acid in heptane were tried. Stearic acid concentration was measured by titration with sodium hydroxide in the presence of warm, neutral ethanol (Kipling, 1962).

4.5.5 Experimental

Adsorption was carried out at 25°C, with constant agitation, for 24 hours to ensure equilibrium was achieved. Spectra were recorded on a Shimadzu uv/visible spectrophotometer.

4.6 Fourier Transform Infrared Spectroscopy

This technique has considerable advantages over conventional infrared spectroscopy. Fourier transform infrared spectroscopy (FTIR) has higher energy throughput, uses an He-Ne laser as a reference to produce near absolute accuracy in frequency and can scan all required wavelengths at the same time. A large number of scans are recorded and averaged in the time taken for a conventional scan to be processed. The averaging procedure increases the signal to noise ratio of the FTIR machine as compared to a conventional spectrophotometer.

FTIR spectroscopy relies on the Michelson interferometer to produce an infrared beam made up of a complicated combination of modulating frequencies. The beam passes through the sample compartment and is focused onto the detector. The detector signal produced is called an interferogram and is used to compose the final spectrum using the mathematical process Fourier transformation.
4.6.1 Fourier Transform Mathematics

An infrared spectrum is usually presented as a function of frequency, or wavenumber, and amplitude. The interferogram of the FTIR spectrophotometer is a function of time and amplitude. The frequency-amplitude function, $F(v)$ and the time-amplitude function, $f(t)$ contain the same information and are a Fourier transform pair. Fourier transformations convert the interferogram to a conventional spectrum.

4.6.2 Diffuse Reflectance Infrared Fourier Transform

Diffuse reflectance infrared Fourier transform (DRIFT) is a technique used to examine solid samples that are difficult to analyse by other methods. It is also used to study the surfaces of solid samples. There is little sample preparation involved and sample morphology is unaffected. A photograph of the DRIFT cell and a schematic diagram of the light path of the beam are shown in Figs. 4.6.2(a) and (b).

The technique requires a near normal angle of incidence of the beam on the sample, for maximum energy throughput. The uneven surface of the sample reflects the radiation in random directions. The diffusely scattered radiation is collected by the ellipsoidal mirror and transmitted to the detector. A limited amount of specular reflection is detected.

Samples are analysed directly or as an uniform dispersion in KBr or KCl. The dispersing medium is measured as the background. The KBr or KCl scatters the radiation, so that it only penetrates the surface of the sample before being reflected at a random angle. During direct analysis the incident radiation
Fig. 4.6.2(a) Photograph of DRIFT Attachment

Fig. 4.6.2(b) Diagram Showing the Light of DRIFT Attachment
penetrates beyond the surface layer. Ishida (1987) reviews DRIFT and other techniques used with FTIR.

4.6.3 Sample Preparation

All spectra were recorded on a Nicolet 20 DXC FTIR fitted with a Spectra Tech diffuse reflectance attachment. The dry fillers were mixed with finely ground KBr at 3 to 5% dilution. KBr was taken as background. 50 scans were averaged for background and sample to produce the spectra and the resolution was set to 4.0 cm⁻¹.

4.7 X-ray Photon Spectroscopy (XPS)

XPS is also known as electron spectroscopy for chemical analysis (ESCA). This technique is used to determine the atomic composition of surfaces by measuring the binding energies of core electrons. A high energy x-ray beam is targeted at the sample and inner electrons are ejected. The x-ray photon may penetrate beyond the outer layer but only electrons at the surface can escape to be detected. Most electrons detected are emitted from the outer 2nm of the sample. The kinetic energy, $E_k$, of the ejected electron is related to the binding energy, $E_b$, by the following equation,

$$E_b = h\nu + E_k + \phi$$  \hspace{1cm} (4.11)

where $h\nu$ is the energy of the incident x-rays and $\phi$ is the work function of the spectrophotometer. The intensities of the spectra peaks are dependent on the cross sections of the individual elements and the number of atoms of the element present. This allows quantitative measurements to be made, usually involving computers.
4.8 **pH Measurement**

Throughout this work pH measurements were taken using a Corning pH meter model 220 with a universal electrode. Before use the meter was calibrated at pH 4 and 7 using buffer tablets made up according to the manufacturers instructions. Slurries of the fillers were prepared for pH measurement by mixing 0.05g of filler with 10g of water. The water had been left with nitrogen bubbling through it for at least half an hour to remove any dissolved carbon dioxide gas. Measurements were taken while nitrogen gas was bubbled through the sample to prevent any reaction with atmospheric carbon dioxide and the slurries were stored in a nitrogen atmosphere.

4.9 **Standard Tests**

The Cobb test (Cobb 1934), TAPPI standard T441, is used to express the degree of sizing of a sheet. Ashing, TAPPI standard T413, measures the amount of non-organic material present. Copies of both these standards are included in Appendix I. Similar tests were routinely used throughout this work.

4.9.1 **Cobb Test**

The test was carried out using a Messmer Cobb tester built to TAPPI standards. A weighed paper sample is clamped between a metal ring and a rubber mat, tap water is poured into the ring and a timer begun. The length of the test is constant, in this case 60 seconds. After approximately 45 seconds the water is decanted away, the sheet removed and the wetted side placed under a blotter without
contact. After exactly 60 seconds the sample is blotted to remove excess water and the reweighed. The increase in weight is expressed per unit contact area, grams per metre square. Handsheets produced on the glass handsheet machine were tested with a ring providing a contact area of 10cm² and 10ml of water. Larger samples used a 100cm² ring and 100ml of water.

Paper produced in a industrial mill, where any size and filler added are retained to the maximum possible by recycling backwater commonly have a Cobb values of 20gm⁻² or less. The sheets produced in this work without backwater recycling are accepted to be adequately sized if the Cobb value is below 40gm⁻². The Cobb values obtained for each handsheet produced were adjusted for the weight of the sample involved. The value was divided by the weight of the sheet and multiplied to give a value for a three gram sheet. This process removes some of the errors created by unavoidable differences in sheet weight at identical size or filler loadings but makes the assumption that Cobb value is a linear function of size addition.

4.9.2 Ash Test

This test used a small furnace heated to 490°C. A sample of known weight was placed in a pre-weighed silica crucible, uncovered, and inserted in the furnace. After 5 minutes, when all the cellulose and other carbon material had been burnt away, the sample was removed, cooled and reweighed until a constant weight was achieved. The ash weight is expressed as a percentage of the sample weight. An unfilled paper sample was ashed so the % filler present in a sheet could be determined, by subtracting the unfilled sheet ash weight from the filled.
Chapter 5

Results and Discussion
5.1 Examination of Papermaking Fillers

This chapter has been sub-divided into two sections, firstly, the examination of fillers, and then, their effect on paper sizing, their retention in paper and the effect of retention agent addition on these properties.

5.1.1 Scanning Electron Microscopy

Figs. 5.1.1(a) to (i) are micrographs taken as described in section 4.2. Figs. (a) to (d) are photographs of the PCCs produced by Pfizer Speciality Minerals, Albacar HO, PO, LO and Albasfil respectively, all magnified 10,000 times. Fig. (e) is Young's PCC slurry and (f) the dried sample, also 10,000 times magnified. Fig. (g) is ground chalk at one fifth of the previous magnification, 2,000 times. Figs. (h) and (i) are Albacar HO and PO magnified 20,000 times. Table 5.1.1 summarises the similarities and differences between the fillers, as seen from the micrographs.

The regular, lozenge shape apparent in most of the fillers is associated with the calcite form of calcium carbonate. The other particle shapes could be the other two crystal structures of calcium carbonate, aragonite and vaterite, or possibly crystals produced by deformed or controlled growth. It seems likely that this is true for the PCCs but that the variety of particles in ground chalk are produced by the grinding process. The increase in surface area that would result from the smaller particle sizes of the PCCs accounts for the increased opacity of these fillers compared to ground chalk. The micrographs of Young's PCC shows unaggregated particles exist in the slurry that become aggregated on drying.
Figs. 5.1.1 SEM Photographs

(a) Albacar HO Magnified 10,000 Times

(b) Albacar PO Magnified 10,000 Times
Fig. 5.1.1 SEM Photographs

(c) Albacar LO Magnified 10,000 Times

(d) Albafil Magnified 10,000 Times
Fig. 5.1.1  SEM Photographs

(e) Young's PCC (Slurry) Magnified 10,000 Times

(f) Young's PCC (Dried) Magnified 10,000 Times
Fig. 5.1.1 SEM Photographs

(g) Ground Chalk Magnified 2,000 Times
Fig. 5.1.1 SEM Photographs

(h) Albacar HO Magnified 20,000 Times

(i) Albacar PO Magnified 20,000 Times
Table 5.1.1

Comparison of SEM Photographs of Fillers

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>Approximate Particle Size/μm</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albacar HO</td>
<td>1 x 0.25 x 0.25</td>
<td>Particles of regular, lozenge shape. Aggregates = 7 x 2.5μm</td>
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<tr>
<td>Albacar PO</td>
<td>All dimensions less than 0.5</td>
<td>Possible to discern small, lozenge shaped particles in the 1st aggregate. The 2nd aggregate size is similar to Albacar HO aggregates</td>
</tr>
<tr>
<td>Albacar LO</td>
<td>1 x 0.25 x 0.25</td>
<td>Some lozenge shaped particles. Aggregates formed with smaller, irregular particles. Aggregates of similar size to Albacar HO's.</td>
</tr>
<tr>
<td>Albafil</td>
<td>0.5 is largest dimension</td>
<td>Particles rounded, little evidence of lozenge shape, aggregate size same as Albacar HO's</td>
</tr>
<tr>
<td>Young's PCC</td>
<td>0.5 is average dimension</td>
<td>Many lozenge shapes apparent. Aggregates of similar size to Albacar HO's</td>
</tr>
<tr>
<td>Ground Chalk</td>
<td>0.5 to 10 range</td>
<td>Irregular size and shape particles. Aggregates of different size particles, larger than the Albacar HO aggregate.</td>
</tr>
</tbody>
</table>
5.1.2 X-ray Powder Diffraction

This suggested that all the fillers existed as calcite, with no evidence for aragonite, (maximum intensity peak at d spacing of 3.40Å), or vaterite, (3.58Å). Calcite is the most stable form of calcium carbonate, and the other two crystal structures, although relatively stable as powders, rapidly become calcite in water slurries. The powder produced from Young's slurry was examined, hence aragonite and vaterite were not expected to be present. Table 5.1.2 lists the d spacings and the relative intensities obtained by x-ray powder diffraction of the fillers. Differences in relative intensities between the experimental data and the x-ray powder diffraction file data can be attributed to the orientation of the filler crystals in the sample. Fig. 5.1.2 is a copy of the powder diffraction file entry for calcite.

5.1.3 Particle Size Measurement

This work was carried out by Dr. Darren K. Swales at Roe Lee Paper Chemicals Co. Ltd research laboratory. Since most paper chemistry occurs at surfaces, the particle size distributions are shown in terms of percentage surface area, %S.A.. This is the total surface area of particles with diameter Nμm as a percentage of the total surface area of all particles, %S.A. = (∑S.A.(Nμm)/∑S.A.). The measured particle sizes were used to determine the surface areas, assuming the particles were spherical.
### Table 5.1.2: X-Ray Powder Diffraction Data for Calcite

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<th>1.5106</th>
<th>Fig. 5.1.2 X-Ray Powder Diffraction Data for Calcite</th>
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**Fig. 5.1.2** X-Ray Powder Diffraction Data for Calcite
### Table 5.1.2

**X-ray Powder Diffraction Data For Fillers**

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>d Spacing/Å</th>
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<td>100</td>
<td>Calcite (3.035, 100)</td>
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<td></td>
<td>2.27</td>
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<td>Calcite (2.095, 18)</td>
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<td>1.86</td>
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<td>Calcite (1.875, 17)</td>
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<td>1.86</td>
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</tr>
</tbody>
</table>

Figs. 5.1.3(a) to (h) show the particle size distributions for the fillers and Table 5.1.3 lists the mean particle sizes of these distributions, measured by laser diffraction and polarization intensity diffraction scattering, (PIDS), as described in section 4.2.3. The duplicate results for Albacar LO show the high reproducibility of this technique. The associated errors were calculated using the tolerances of the
Fig. 5.1.3 Particle Size Distributions

(a) Albacar HO

(b) Albacar PO
Fig. 5.1.3 Particle Size Distributions

(c) and (d) Albacar LO

(d) Albafil
Fig. 5.1.3 Particle Size Distributions

(e) Young's PCC

(f) Young's PCC with Ultrasound
Fig. 5.1.3 Particle Size Distributions

(h) Ground Chalk
polystyrene latex standard and the garnet standard.

Table 5.1.3
Mean Particle Size of Fillers

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>Mean Particle Diameter/μm</th>
<th>SEM Particle Size /μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albacar HO</td>
<td>2.0 ± 0.8</td>
<td>1 x 0.25 x 0.25</td>
</tr>
<tr>
<td>Albacar PO</td>
<td>2.1 ± 0.9</td>
<td>All dimensions less than 0.5</td>
</tr>
<tr>
<td>Albacar LO</td>
<td>0.6 ± 0.3, 0.8 ± 0.3</td>
<td>1 x 0.25 x 0.25</td>
</tr>
<tr>
<td>Albafil</td>
<td>0.9 ± 0.4</td>
<td>0.5 is largest dimension</td>
</tr>
<tr>
<td>Young's PCC</td>
<td>2 ± 1</td>
<td>0.5 is average dimension</td>
</tr>
<tr>
<td>after u.sound</td>
<td>0.8 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>Ground Chalk</td>
<td>0.8 ± 0.3</td>
<td>0.5 to 10 range</td>
</tr>
</tbody>
</table>

u.sound = ultrasound

Comparing the laser diffraction particle sizer results with the estimates made from SEM micrographs suggests that some fillers flow through the sample cell as aggregates and some as individual particles, the aggregates dispersed by hydrodynamic forces. The results for Young's PCC before and after ultrasonic treatment give evidence for this. It appears that Albacar HO, LO and Albafil exist as single particles in the system. The result for Albacar PO suggests it exists in the system as the primary aggregate seen in the SEM photographs. The particle diameters in Table 5.1.3 support the observations made by SEM apart from the
result for ground chalk. SEM suggested a wide range of particle sizes, the mean diameter of which would be higher than the mean for the PCCs. This anomalous result could be due to the visual selectivity of SEM, the eye is naturally drawn to larger objects. Alternatively, the large particles in ground chalk could be sedimenting in the weak slurry used for particle sizing producing a low result. The surface area measurements made by adsorption of nitrogen gas generally support the conclusions drawn from these results.

5.1.4 Surface Area Measurements By Gas Adsorption

(a) BET Method

This work was carried out in the university's particle sizing laboratory by Martin Kerry. Due to constraints on apparatus availability, a complete adsorption isotherm, covering the relative pressure range $0.001 < P/P_0 < 0.90$ was only determined for Albacar PO. Adsorption of nitrogen gas on the remaining fillers was carried out in the linear range associated with the BET method, $0.05 < P/P_0 < 0.35$ section 4.5.2(a). Fig. 5.1.4(a) is the adsorption isotherm produced for Albacar PO outgassed at 105°C; this is clearly a type II isotherm as discussed in the BET theory. The two results for Albacar PO show there is no sintering or destructive effects at 105°C and indicate the reproducibility of the technique. A standard solid, with a specific surface area of $192 \pm 7 \text{m}^2\text{g}^{-1}$, was used to calibrate the apparatus and produced a result of $182 \text{m}^2\text{g}^{-1}$. The results were normalized to account for this bias,

$$N = \frac{1}{182} \times V$$

where $N$ is the normalized result. Assuming that the tolerance of the standard would be transmitted as errors in the measurement of gas volumes, the errors associated with the specific surface areas could be determined. Table
Fig. 5.1.4(a)
Nitrogen Gas on Albacar PO Adsorption Isotherm

Volume Adsorbed/cm$^3$ g$^{-1}$ @ STP

Relative Pressure, $P/P_0$
5.1.4(a) lists the experimental parameters, the C constants and the specific surface areas determined for the fillers. Figs 5.1.4(b) to (h) are the BET plots for the fillers.

Table 5.1.4(a)
Specific Surface Areas Determined By Gas Adsorption

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>Outgassing Temp/°C</th>
<th>Relative Pressure Range</th>
<th>Number of Points</th>
<th>C Constant</th>
<th>Specific Surface Area/m²g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albacar HO</td>
<td>105</td>
<td>0.11-0.27</td>
<td>4</td>
<td>113 ± 6</td>
<td>10.1 ± 0.4</td>
</tr>
<tr>
<td>Albacar PO</td>
<td>105</td>
<td>0.11-0.26</td>
<td>4</td>
<td>152 ± 5</td>
<td>20.5 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.11-0.26</td>
<td>4</td>
<td>128 ± 5</td>
<td>19.9 ± 0.7</td>
</tr>
<tr>
<td>Albacar LO</td>
<td>105</td>
<td>0.11-0.22</td>
<td>3</td>
<td>167 ± 3</td>
<td>6.7 ± 0.2</td>
</tr>
<tr>
<td>Albafil</td>
<td>105</td>
<td>0.11-0.22</td>
<td>3</td>
<td>147 ± 5</td>
<td>9.3 ± 0.3</td>
</tr>
<tr>
<td>Young's PCC</td>
<td>105</td>
<td>0.11-0.26</td>
<td>4</td>
<td>104 ± 7</td>
<td>14.9 ± 0.5</td>
</tr>
<tr>
<td>Ground Chalk</td>
<td>105</td>
<td>0.17-0.27</td>
<td>3</td>
<td>113.2 ± 0.9</td>
<td>0.98 ± 0.03</td>
</tr>
</tbody>
</table>

Albacar PO has the highest specific surface area as suggested by its small particle size. The specific surface area of ground chalk, 0.98 ± 0.03m²g⁻¹, implies it is made up of large particles. This supports the SEM observation and the theory that sedimentation is occurring in the particle sizer, producing the low result for particle size of 0.8 ± 0.3μm.
Fig. 5.1.4(b)

BET Plot For Albacar HO Using Normalized Results

\[ y = 0.0038 + 0.4292x \quad r^2 = 1.0000 \]

\[ \frac{P}{V}(P_0-P)/\text{gcm}^{-3} \at \text{STP} \]
Fig. 5.1.4(c)

BET Plot For Albacar PO Using Normalized Results

\[ y = 0.0014 + 0.2114x \quad r^2 = 1.0000 \]

\[ \frac{P}{V(P_0-P)} \text{gcm}^{-3} @ \text{STP} \]
Fig. 5.1.4(d)
BET Plot For Albacar PO, Outgassed at Room Temperature, Using Normalized Results

\[ y = 0.0017 + 0.2171x \quad r^2 = 1.0000 \]

\[ \frac{P}{V(P_0 - P)} \text{gcm}^{-3} \text{ @ STP} \]
Fig. 5.1.4(e)

BET Plot For Albacar LO Using Normalized Results

\[ y = 0.0039 + 0.6464x \quad r^2 = 1.0000 \]

\[ \frac{P}{V} \left( \frac{Po-P}{gcm^{-3}} \right) @ STP \]

Relative Pressure, \( \frac{P}{Po} \)
Fig. 5.1.4(f)
BET Plot For Albafil Using Normalized Results

\[ y = 0.0032 + 0.4659x \quad r^2 = 1.0000 \]

\( \frac{P}{V(Po-P)} \) g cm\(^{-3} \) @ STP

Relative Pressure, \( \frac{P}{Po} \)
Fig. 5.1.4(g)

BET Plot For Young's PCC Using Normalized Results

\[ y = 0.0028 + 0.2891 x \quad r^2 = 1.0000 \]

\[ \frac{P}{V(Po-P)}/\text{gcm}^{-3} \text{ @ STP} \]

Relative Pressure, \( \frac{P}{Po} \)
Fig. 5.1.4(h)

BET Plot For Ground Chalk Using Normalized Results

\[ y = 0.0393 + 4.4079x \quad r^2 = 0.9996 \]

\[
\frac{P/V(Po-P)}{gcm^{-3}} @ STP
\]
(b) t-Plots

Table 5.1.4(b)
Specific Surface Areas Determined By t-Plots

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>Outgassing Temp/ C</th>
<th>Relative Pressure Range</th>
<th>Number of Points</th>
<th>Specific Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>t-Plot/m²g⁻¹</td>
</tr>
<tr>
<td>Albacar HO</td>
<td>105</td>
<td>0.11-0.32</td>
<td>5</td>
<td>10.1 + 0.4</td>
</tr>
<tr>
<td>Albacar PO</td>
<td>105, 30</td>
<td>0.11-0.31, 0.11-0.31</td>
<td>5, 5</td>
<td>19.8 + 0.7</td>
</tr>
<tr>
<td>Albacar LO</td>
<td>105</td>
<td>0.11-0.32</td>
<td>5</td>
<td>6.3 + 0.2</td>
</tr>
<tr>
<td>Albasil</td>
<td>105</td>
<td>0.11-0.32</td>
<td>5</td>
<td>8.7 + 0.3</td>
</tr>
<tr>
<td>Young's PCC</td>
<td>105</td>
<td>0.11-0.31</td>
<td>5</td>
<td>15.2 + 0.5</td>
</tr>
<tr>
<td>Ground</td>
<td>105</td>
<td>0.11-0.32</td>
<td>5</td>
<td>0.91 + 0.03</td>
</tr>
<tr>
<td>Chalk</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5.1.4(i) compares the t-curve for Albacar PO to the standard t-curve (Lippens 1964). Both curves are identical suggesting that Albacar PO is nonporous. Fig. 5.1.4(j) is the t-plot for Albacar PO showing the associated errors and 5.1.4(k) includes the t-plots for all the fillers. All these plots are linear passing through, or close to, the origin, suggesting that the fillers are not microporous. Table 5.1.4(b) lists the specific surface areas determined by this method and compares them to the area determined by the BET method. The results are almost identical further indicating that no microporosity is present. Errors determined during the calculation of the BET results for surface areas are used to calculate the
Fig. 5.1.4(i)

Standard t-Curve Compared to Albacar PO t-Curve

Statistical Thickness, t/nm

- Standard t-Curve
- Albacar PO t-Curve

Relative Pressure, P/Po
Fig. 5.1.4(j)

t-Plot For Albacar PO

\[ y = 0.168 + 12.791x \quad R^2 = 0.999 \]

Volume Adsorbed, \( V/\text{cm}^3\text{g}^{-1} \)

\[ \begin{array}{c|cccc}
\hline
V/\text{cm}^3\text{g}^{-1} & 0 & 5.00 & 10.00 & 15.00 \\
\hline
Statistics Thickness, t/\text{nm} & 0 & 0.50 & 1.00 & 1.50 \\
\hline
\end{array} \]
Fig. 5.1.4(k)

t-Plots For All Fillers

Volume Adsorbed, V/cm³ g⁻¹

- Albacar PO
- Albacar HO
- Albacar LO
- Albafil
- Young's PCC
- Ground Chalk

Statistical Thickness, t/nm
errors associated with the results from the t-plots

5.1.5 Adsorption From Aqueous Solution

The absorbance peaks in the uv/visible spectra of methylene blue (MB), orange II (OII) and paranitrophenol (pnp) are shown in Figs. 5.1.5(a) to (c), respectively. The peaks chosen for use were 664nm for MB, 484nm for OII and 303nm for pnp. Since all aqueous solutions were produced by weight, the extinction coefficient for each peak, in kgmol\(^{-1}\)cm\(^{-1}\), has been determined. The absorbance of standards were measured routinely and these results were used to produce the Lambert-Beer plots in Figs. 5.1.5(d) and (e). The scatter plots in these figures are the experimental data used to determine the extinction coefficients, the second lines are the Lambert-Beer plots produced using the literature values of the extinction coefficients, 7.8 \times 10^4 lmol\(^{-1}\)cm\(^{-1}\) for methylene blue (Bergmann 1963) and 2.4 \times 10^4 lmol\(^{-1}\)cm\(^{-1}\) for orange II (Shonsenji 1978). The extinction coefficients used to determine specific surface areas are listed in Table 5.1.5. It is possible that the low extinction coefficient determined for MB is due to contamination with azure blue which would not affect its medicinal uses. Using statistical techniques, (Miller 1984), it is possible to calculate the error in the gradient of a line and therefore to calculate the errors associated with the extinction coefficients. This method assumes that all errors occur in the y direction, i.e. in uv/visible absorbance. It is probably true that the major errors occur in absorbance, not in concentration, since all standard solutions were made up by weight.
Fig. 5.1.5 UV/Visible Absorption Spectra

(a) Methylene Blue

(b) Orange II
Fig. 5.1.5 UV/Visible Absorption Spectra

(c) Paranitrophenol
Fig. 5.1.5(d)
Lambert-Beer Plot for Methylene Blue Peak at 664nm

\[ y = -0.0450 + 0.0658x \quad r^2 = 0.9761 \]

Absorbance (664nm)

\[ \begin{align*}
  &0.0 \quad 10.0 \quad 20.0 \quad 30.0 \quad 40.0 \\
  &0 \quad 1 \quad 2 \quad 3 \\
\end{align*} \]
Fig. 5.1.5(e)

Lambert-Beer Plot for Orange II Peak at 484nm

\[ y = -0.0165 + 0.0214x \quad r^2 = 0.9487 \]

Absorbance (484nm)
Table 5.1.5

Dye Extinction Coefficients

<table>
<thead>
<tr>
<th>Dye</th>
<th>Absorbance Peak/nm</th>
<th>Extinction Coefficient/kgmol⁻¹cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>664.5</td>
<td>$6.6 \times 10^4 \pm 2%$</td>
</tr>
<tr>
<td>OII</td>
<td>484</td>
<td>$2.14 \times 10^4 \pm 3.5%$</td>
</tr>
</tbody>
</table>

5.1.6 Adsorption Of Methylene Blue

Fig. 5.1.6(a) shows the adsorption of MB on ground chalk increasing with time, with equilibrium being reached after 15 hours. 10g of ground chalk were mixed with 10g of a standard solution and adsorption carried out as described in section 4.8.2.

Fig. 5.1.6(b) is the adsorption isotherm for this system. At low solution concentrations only a fraction of the surface available is covered with adsorbed molecules, an increase in concentration results in an increase in adsorption. At monolayer capacity no further adsorption can occur and there is a plateau in the isotherm. This is a typical "Langmuir" isotherm. This isotherm has a second increase in adsorption at high solution concentrations due to either multilayer adsorption or reorientation of the methylene blue molecules, as discussed in section 4.5.4(a). Fig. 5.1.6(c) is the linear plot used to determine the specific surface area of the solid. The specific surface area of ground chalk was calculated as $0.45 \pm 0.07\text{m}^2\text{g}^{-1}$, assuming the coverage area of a MB molecule was 1.2nm² (Giles 1969). This is less than the BET result, $0.98 \pm 0.03\text{m}^2\text{g}^{-1}$, which suggests
Fig. 5.1.6(a)

Methylene Blue on Ground Chalk
Time Adsorption Isotherm

Adsorption, a/umol g⁻¹

Time/hrs
Fig. 5.1.6(b)

Adsorption Isotherm for Methylene Blue on Ground Chalk

Adsorption/umol g\(^{-1}\)

\[
\begin{array}{c}
0.80 \\
0.60 \\
0.40 \\
0.20 \\
0.00 \\
\end{array}
\]

\[
\begin{array}{c}
0.0 \quad 0.5 \quad 1.0 \quad 1.5 \quad 2.0 \quad 2.5 \quad 3.0 \quad 3.5 \\
\end{array}
\]

Ce/mmolk\(^{-1}\)
Langmuir's Plot for Methylene Blue Adsorption on Ground Chalk

\[ y = -90.11 + 1590.57x \quad r^2 = 0.98 \]
that either the adsorption sites for methylene blue are too far apart to allow complete monolayer coverage or that pores exist which are large enough for the nitrogen gas molecules to enter but too small for the methylene blue molecules. If the correction for micellar adsorption is made, the surface area is measured as \(0.23 \pm 0.04\) m\(^2\)g\(^{-1}\). This is very low compared to the value produced by nitrogen gas adsorption and does not give any evidence to support the theory of micellar adsorption.

Attempts were made to adsorb MB on the surfaces of PCCs but there was so little adsorption that no isotherms could be produced. MB is a cationic dye and, this result suggested that the ground chalk may have a majority of neutral or anionic adsorption sites, but that the surface sites of PCCs are cationic (Saunders 1992). For this reason OII, an anionic dye with the same coverage area as MB, (Giles 1969), was used in solution adsorption onto PCCs.

5.1.7 Adsorption of Orange II

The equilibration isotherm for OII on Albacar LO is shown in Fig. 5.1.7(a), equilibration occurs after 15 hours. Fig. 5.1.7(b) is the adsorption isotherm for this system and Figs. 5.1.7(c) to (g) are the Langmuir plots for the fillers. Table 5.1.7(a) summarises the experimental parameters, the calculated specific surface areas for the PCCs, with and without the correction for micellar adsorption, and compares them to the results produced by gas adsorption measurements. For Young's PCC, all solution adsorption experiments were carried out on the powder produced by drying the slurry. Mixtures of OII and ground chalk generated so little adsorption that no isotherm could be produced.
Fig. 5.1.7(a)

Orange II on Albacar LO Time Adsorption Isotherm

Adsorption, a/umolg⁻¹

Time/hrs
Fig. 5.1.7(b)
Orange II on Albacar LO
Adsorption Isotherm

Adsorption, a/umolg⁻¹

Ce/mmolk⁻¹
Fig. 5.1.7(c)

Langmuir's Plot For Orange II Adsorption On Albacar HO

\[ y = 86.62 + 372.97x \quad r^2 = 0.94 \]
Fig. 5.1.7(d)
Langmuir's Plot For Orange II Adsorption On Albacar PO

\[ y = 6.85 + 13.66x \quad r^2 = 0.98 \]
Fig. 5.1.7(e)

Langmuir's Plot For Orange II Adsorption On Albacar LO

\[ y = 20.89 + 81.22x \]

\[ r^2 = 0.92 \]
Fig. 5.1.7(f)

Langmuir's Plot For Orange II Adsorption On Albafil

\[ y = 18.99 + 11.03x \quad r^2 = 0.98 \]
Fig. 5.1.7(g)

Langmuir's Plot For Orange II Adsorption On Young's PCC

\[ y = 13.67 + 36.27x \quad r^2 = 0.91 \]
Table 5.1.7(a)

Specific Surface Areas of PCCs

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>Weight of Filler/g</th>
<th>Weight of Soln./g</th>
<th>Figure No.</th>
<th>Specific Surface Areas/m²g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albacar HO</td>
<td>5</td>
<td>10</td>
<td>5.1.7(c)</td>
<td>1.9 ± 0.3 Corr. 0.6 BET 10.1 ± 0.4</td>
</tr>
<tr>
<td>Albacar PO</td>
<td>0.5</td>
<td>20</td>
<td>5.1.7(d)</td>
<td>53 ± 2 Corr. 18 BET 20.5 ± 0.7</td>
</tr>
<tr>
<td>Albacar LO</td>
<td>1</td>
<td>10</td>
<td>5.1.7(e)</td>
<td>8.9 ± 0.6 Corr. 3.0 BET 6.7 ± 0.2</td>
</tr>
<tr>
<td>Albafil</td>
<td>0.5</td>
<td>20</td>
<td>5.1.7(f)</td>
<td>66 ± 3 Corr. 33 BET 9.3 ± 0.3</td>
</tr>
<tr>
<td>Young's PCC</td>
<td>1</td>
<td>10</td>
<td>5.1.7(g)</td>
<td>19.9 ± 0.6 Corr. 6.6 BET 14.9 ± 0.5</td>
</tr>
</tbody>
</table>

Corr. = Micellar Correction (i.e. divide by 3)

The result for Albacar HO, 1.9 ± 0.3m²g⁻¹, is low compared to the specific surface area determined by nitrogen adsorption, 10.1 ± 0.4m²g⁻¹. As with the adsorption of methylene blue on ground chalk, this could be due to the presence of larger distances between adsorption sites than the molecule dimensions, or the existence of many pores too small for the large dye molecule to enter. The result for the remaining PCCs are higher than the values determined by nitrogen gas adsorption, this is probably due to the a change in the orientation of the dye molecules on the surface, assumed to be lying flat, towards the vertical, Fig. 5.1.7(h). This would lower the coverage area of each molecule and allow more molecules to adsorb on the surface. The coverage area of each molecule can be calculated by dividing the surface area determined using gas adsorption by the number of molecules adsorbed at monolayer coverage. These results, and the
Fig 5.1.7 (h) Orientation of Orange II
coverage area for ground chalk, are listed in Table 5.1.7(b).

Table 5.1.7(b)

Angles of Orientation

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>Monolayer Capacity, $a_m$/molg$^{-1}$</th>
<th>Molecules Adsorbed</th>
<th>Molecule Coverage Area/nm$^2$</th>
<th>Angle to Surface, $\theta/\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground Chalk</td>
<td>6.3 ± 0.9 x $10^{-7}$</td>
<td>3.8 ± 0.6</td>
<td>2.58 ± 0.09 x $10^{17}$</td>
<td>Adsorbed d Flat</td>
</tr>
<tr>
<td>Albacar HO</td>
<td>2.7 ± 0.2 x $10^{-6}$</td>
<td>1.6 ± 0.2</td>
<td>6.3 ± 0.8 x $10^{18}$</td>
<td>Adsorbed d Flat</td>
</tr>
<tr>
<td>Albacar PO</td>
<td>7.3 ± 0.3 x $10^{-5}$</td>
<td>4.4 ± 0.2</td>
<td>0.47 ± 0.03 x $10^{19}$</td>
<td>67 ± 2</td>
</tr>
<tr>
<td>Albacar LO</td>
<td>1.2 ± 0.1 x $10^{-5}$</td>
<td>7.4 ± 0.5</td>
<td>0.91 ± 0.07 x $10^{18}$</td>
<td>40 ± 8</td>
</tr>
<tr>
<td>Albafil</td>
<td>9.07 ± 0.09 x $10^{-5}$</td>
<td>5.5 ± 0.2</td>
<td>0.169 ± 0.008 x $10^{19}$</td>
<td>Assumed to be 90</td>
</tr>
<tr>
<td>Young's PCC</td>
<td>2.76 ± 0.08 x $10^{-5}$</td>
<td>1.66 ± 0.05</td>
<td>0.90 ± 0.04 x $10^{19}$</td>
<td>40 ± 6</td>
</tr>
</tbody>
</table>

Since the coverage area of Albafil was so small, 0.169 ± 0.008nm, it was assumed that this was vertically orientated to the surface. West (1952, 1953, 1954) used the van der Waals' thickness of a benzene ring, 0.37nm to estimate the edge length of one of the dimensions one of the vertical coverage area, i.e. $0.169\text{nm}^2 = 0.37\text{nm} \times 0.46\text{nm}$. The knowledge of these dimensions facilitates the calculation of the third dimension of the molecule, i.e. $1.20\text{nm}^2 = 0.46 \times 2.6$, and
hence the angles of orientation of the OII molecules to the surfaces of Albacar PO, Albacar LO and Young's PCC. These angles are also listed in Table 5.1.7(b). These results suggest that Albafil has a large number of positive adsorption sites for the anionic dye, Albacar PO has less, but more than Albacar LO and Young's PCC which have a similar number. Albacar HO has the lowest number of all.

It was postulated that as the PCCs are produced from calcium hydroxide, some of this precursor may remain on the surface or as the core of the filler particles. The calcium hydroxide could dissolve in aqueous solution, release calcium ions into solution that then adsorb onto the particle surface making it cationic. The presence of this compound would not be seen by x-ray powder diffraction which is a bulk technique. To provide evidence for the presence of calcium hydroxide groups on the filler surface, the samples were analysed using Fourier transform infrared spectroscopy (FTIR). The use of aqueous solutions of pnp was introduced in an attempt to determine specific surface areas by non-site specific adsorption from solution that would not be affected by a difference in surface charge.

5.1.8 Adsorption of Paranitrophenol and Stearic Acid

Aqueous solutions of pnp have a peak in the uv/visible spectrum at 303nm, as shown in Fig. 5.1.5(c). On addition to calcium carbonates the solution becomes bright yellow and a gas is given off. This indicates the classic acid/carbonate reaction is occurring. The aromatic ring of pnp produces an acidic hydrogen atom by conjugation with the hydroxide group and the calcium carbonate reacts to form the calcium salt of pnp, as shown below. This salt is soluble in water and produces the uv/visible spectrum shown in Fig. 5.1.8(a).

\[
\text{HO-C}_6\text{H}_4\text{-NO}_2 + \text{H}_2\text{O} \rightarrow \text{O-C}_6\text{H}_4\text{-NO}_2^+ + \text{H}_3\text{O}^+
\]
Fig. 5.1.8(a) UV/Visible Absorption Spectrum of the Calcium Salt of Paranitrophenol
\[2\text{HO-C}_6\text{H}_4\text{-NO}_2 + \text{CaCO}_3 = \text{Ca}^4(\text{O-C}_6\text{H}_4\text{-NO}_2)_2 + \text{H}_2\text{O} + \text{CO}_2\]

In order to prevent this reaction, solutions of pnp in dry heptane were made for adsorption work. In the hydrophobic solvent the acidic hydrogen remains attached to the hydroxide group. However even in this situation the same acid/carbonate reaction occurred with all the fillers. There was less reaction with ground chalk than the PCCs which is indicative of its lower surface area.

As suggested in section 4.8.4(b), stearic acid (octadecanoic acid) adsorption from heptane was tried as an alternative to pnp adsorption. The system was used to build up an equilibration isotherm with ground chalk, adsorption proceeding for more than 70 hours. This isotherm is included as Fig. 5.1.8(b) and a similar isotherm produced for Albacar HO, over a shorter time period is Fig. 5.1.8(c). In both cases the adsorption was shown to be much less than expected. Table 5.1.8 compares the results of these adsorption experiments to the specific surface areas measured by nitrogen adsorption. These results suggest that both the ground chalk and the PCCs have low site densities for adsorption of stearic acid.

Table 5.1.8
Comparison of Specific Surface Areas
(Stearic acid result based on 15 hour adsorption point)

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>Specific Surface Area/m²g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stearic Acid</td>
</tr>
<tr>
<td>Ground Chalk</td>
<td>0.043</td>
</tr>
<tr>
<td>Albacar HO</td>
<td>3.06 x 10⁻³</td>
</tr>
</tbody>
</table>
Fig. 5.1.8(b)

Stearic Acid on Ground Chalk Time Adsorption Isotherm

Adsorption, a/umolg$^{-1}$

Time/hr
Fig. 5.1.8(c)

Stearic Acid on Albacar HO Time Adsorption Isotherm

Adsorption, a/umolg\(^{-1}\)

<table>
<thead>
<tr>
<th>Time/hr</th>
<th>Adsorption, a/umolg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
</tr>
<tr>
<td>10</td>
<td>0.30</td>
</tr>
<tr>
<td>15</td>
<td>0.40</td>
</tr>
<tr>
<td>20</td>
<td>0.50</td>
</tr>
</tbody>
</table>
5.1.9 **Fourier Transform Infrared Spectroscopy**

Diffuse reflectance infrared Fourier transform (DRIFT), as described in section 4.3.2, produces infrared spectra of the first tens of nanometres of the surface and was used to look for surface differences between the fillers that could cause the difference in surface charge. Figs. 5.1.9(a) to (f) are the resulting infrared spectra of the fillers, Table 5.1.9 summarises the peaks seen and attributes them.

**Table 5.1.9**

Interpretation of DRIFT Spectra

<table>
<thead>
<tr>
<th>Wavenumber/cm(^{-1})</th>
<th>Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3650</td>
<td>Bonded Hydroxide Group</td>
</tr>
<tr>
<td>3600 to 2400</td>
<td>Water Hydroxide Group</td>
</tr>
<tr>
<td>3000 and 2850</td>
<td>Adsorbed Organic Material</td>
</tr>
<tr>
<td>2500</td>
<td>Atmospheric Carbon Dioxide</td>
</tr>
<tr>
<td>1800</td>
<td>Carbonate</td>
</tr>
<tr>
<td>1400</td>
<td>Carbonate</td>
</tr>
<tr>
<td>1150 and 1072</td>
<td>Carbonate</td>
</tr>
<tr>
<td>850</td>
<td>Carbonate</td>
</tr>
<tr>
<td>704</td>
<td>Carbonate</td>
</tr>
</tbody>
</table>

All the samples show a strongly absorbing, peak at 1400cm\(^{-1}\) due to the carbonate ion. In all the spectra there is a low, broad band above 2400cm\(^{-1}\) produced by hydrogen bonded hydroxide groups, probably from water adsorbed to the sample surface. The small peak at 3650cm\(^{-1}\) is generated by vibrations in a bonded hydroxide group, most likely to be Ca(OH)\(_2\). This peak is only present in
Fig. 5.1.0(a) DRIFT Spectrum of Alnecar NO
Fig. 5.1.9(b) DRIFT Spectrum of Albacar PO

Nicolet DX Sample File 02 Aug 83 15:29:56
Fig. 5.1.9(c) DRIFT Spectrum of Albacar LO
Fig. 5.1.9(d) DRIFT Spectrum of Albafil
Fig. 5.1.9(c) Drift Spectrum of Young's PCC
Fig. 5.1.9(f) Drift Spectrum of Ground Chalk

Wavelength (cm⁻¹) 4000, 3600, 3200, 2900, 2400, 2000, 1800, 1600, 1400, 1200, 1000, 800, 600, 400
the Pfizer chemicals, Albacar HO, Albacar LO and Albafl. This evidence supports the theory that the cationic surface is created by calcium hydroxide in the above fillers but suggests that an alternative mechanism is responsible for any cationic sites on Albacar PO. It is possible that any calcium hydroxide on the surface of Albacar PO is in the first ten nanometres and not detected by DRIFT. XPS is the most common technique for analysing the outer layer of a surface. It is not surprising to see no evidence for calcium hydroxide in the DRIFT spectrum of Young's PCC as it would have dissolved in the water of the slurry and much of it been converted to calcium carbonate by atmospheric carbon dioxide.

5.1.10 X-ray Photon Spectroscopy

This analysis was carried out by Dr. Robert Bradley at the University’s surface characterization laboratory. Table 5.1.10(a) lists the surface composition of each filler as % atoms in the outer layer, the error associated with each result is ± 10%. An ideal calcium carbonate surface would be Ca = 20%, C = 20% and O = 60%.

The percentage of calcium atoms present in Young's PCC is much higher than the other fillers, this could be due to the presence of a layer of calcium ions adsorbed from the water in the slurry and produced by the dissolution of calcium hydroxide. The amount of carbon present in each surface is similar, within experimental error except that of ground chalk which is much higher. The presence of magnesium and nitrogen in the surface of Albacar PO could be due to the presence of magnesium nitrate, Mg(NO₃)₂, or another compound containing magnesium and nitrogen, added during the manufacturing process to control the crystal growth and produce the very small particles seen in the SEM photographs, Figs. 5.1.1(c) and (i).
Table 5.1.10(a)

Surface Analysis of Fillers By XPS

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>% Ca</th>
<th>% C</th>
<th>% O</th>
<th>% Mg</th>
<th>% Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albacar HO</td>
<td>17.4</td>
<td>20.2</td>
<td>61.3</td>
<td>-</td>
<td>1.3(F)</td>
</tr>
<tr>
<td>Albacar PO</td>
<td>20.1</td>
<td>16.2</td>
<td>56.3</td>
<td>3.4</td>
<td>4.0(N)</td>
</tr>
<tr>
<td>Albacar LO</td>
<td>19.3</td>
<td>20.6</td>
<td>54.8</td>
<td>4.7</td>
<td>0.5(F)</td>
</tr>
<tr>
<td>Albasil</td>
<td>18.4</td>
<td>23.8</td>
<td>52.6</td>
<td>5.2</td>
<td>-</td>
</tr>
<tr>
<td>Young's PCC</td>
<td>27.4</td>
<td>20.0</td>
<td>52.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ground Chalk</td>
<td>18.1</td>
<td>32.3</td>
<td>49.7</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

If each atom is assigned its common oxidation state, Ca = $2^+$, C = $4^+$ and O = $2^-$, the surface charge of each filler can be calculated. The errors related to the experimental results will be multiplied by this calculation. Table 5.1.10(b) shows the results of this process assuming no organic material is present on the surface of ground chalk.

The surface charge of Albacar HO, Albacar PO and Albacar LO are electrically neutral within the associated errors, Albasil and Young's PCC have cationic surfaces, as does the ground chalk. This work suggests that the surface of ground chalk is almost twice as cationic as the PCC surfaces. The result contradicts the evidence provided by dye adsorption, ground chalk adsorbs a cationic dye suggesting its surface is anionic. A possible explanation is that the highly positive surface of ground chalk rapidly adsorbs a layer of water molecules on contact with an aqueous solution that reduces the surface charge and adsorbs the anionic dye. Since the XPS results indicate cationic surfaces for all the calcium carbonate fillers, it is possible that the crystal form produced (calcite) preferentially forms crystal planes at its surfaces containing more cations than anions.
Table 5.1.10(b)
Surface Charge of Fillers

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>+</th>
<th>-</th>
<th>Surface Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albacar HO</td>
<td>115.6</td>
<td>123.9</td>
<td>-8.3</td>
</tr>
<tr>
<td>Albacar PO</td>
<td>111.8</td>
<td>124.6</td>
<td>-12.8</td>
</tr>
<tr>
<td>Albacar LO</td>
<td>130.4</td>
<td>110.1</td>
<td>+20.3</td>
</tr>
<tr>
<td>Albafil</td>
<td>142.4</td>
<td>105.2</td>
<td>+37.2</td>
</tr>
<tr>
<td>Young's PCC</td>
<td>134.8</td>
<td>105.2</td>
<td>+29.2</td>
</tr>
<tr>
<td>Ground Chalk</td>
<td>165.4</td>
<td>99.4</td>
<td>+66.0</td>
</tr>
</tbody>
</table>

5.1.11 pH Measurements

pH measurements were taken as described in section 4.7. The purpose of these measurements was to determine if any calcium hydroxide was present as a core in the fillers particles. Calcium oxide, which turns to calcium hydroxide in the presence of water, was freshly prepared by drying a sample of calcium hydroxide in a furnace at 1000°C overnight. A slurry of this and specified laboratory grade calcium carbonate were also used in pH measurement for comparative purposes. Young's PCC, which was provided as a three month old slurry, was not tested for pH as it was assumed any calcium hydroxide that had been present would have been converted to calcium carbonate by atmospheric carbon dioxide. Figs. 5.1.11(a) to (g) show the pH variation of the calcium carbonate, calcium oxide and fillers over a week, and Table 5.1.11 summarizes these graphs.
Fig. 5.1.11(a)

pH of S.L.R. Calcium Carbonate Slurry

-0.301 0.699 1.699 2.699 3.699
Log(Time)/Log(min)
Fig. 5.1.11(b)
PpH of Calcium Oxide Slurry

pH

14
12
10
8
6
4
2
0

-0.237
0.763
1.763
2.763
3.763

Log(Time)/Log(min)

1 min
10 min
1 hr
1 day
1 week
Fig. 5.1.11(d)

pH of Albacar PO Slurry

\[ \text{Log(Time)} / \text{Log(min)} \]

- 0.301 0.699 1.699 2.699 3.699
Fig. 5.1.11(e)

pH of Albacar LO Slurry

Log(Time)/Log(min)
Fig. 5.1.11(c)

pH of Albacar HO Slurry

pH

Log(Time)/Log(min)
Fig. 5.1.11(f)

pH of Albafil Slurry

![Diagram showing pH values over time]

- pH values are marked at intervals: 1 minute, 10 minutes, 1 hour, 1 day, and 1 week.
- The pH decreases over time, stabilizing around a lower value after 1 week.
Fig. 5.1.11(g)

pH of Ground Chalk Slurry
Table 5.1.11
pH of Filler Slurries Under Nitrogen Atmosphere

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>pH after 1 minute</th>
<th>pH after 1 day</th>
<th>pH after 1 week</th>
<th>Max. pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Carbonate</td>
<td>9.8</td>
<td>9.4</td>
<td>9.4</td>
<td>9.8</td>
</tr>
<tr>
<td>SLR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium Oxide</td>
<td>12.4</td>
<td>13.3</td>
<td>13.2</td>
<td>13.3</td>
</tr>
<tr>
<td>Albacar HO</td>
<td>9.4</td>
<td>9.6</td>
<td>9.5</td>
<td>9.6</td>
</tr>
<tr>
<td>Albacar PO</td>
<td>10.2</td>
<td>9.3</td>
<td>8.8</td>
<td>10.2</td>
</tr>
<tr>
<td>Albacar LO</td>
<td>10.0</td>
<td>9.6</td>
<td>9.7</td>
<td>10.0</td>
</tr>
<tr>
<td>Albafil</td>
<td>10.2</td>
<td>9.0</td>
<td>9.0</td>
<td>10.2</td>
</tr>
<tr>
<td>Ground Chalk</td>
<td>9.1</td>
<td>8.7</td>
<td>8.8</td>
<td>9.1</td>
</tr>
</tbody>
</table>

The pH of a saturated solution of calcium carbonate in carbon dioxide free water is 10.23 \(\text{(Lea 1970)}\), whereas the calcium oxide slurry, effectively a saturated solution on calcium hydroxide, had a maximum pH of 13.3. After a period of one week any calcium carbonate present would be expected to dissolve and produce an increase in pH above 10.2.

These results provide no further evidence for a particle core of calcium hydroxide. Albacar PO, Albacar LO and Albafil rapidly achieve pHs of 10 or above, but over a week these slowly decrease. This effect is probably due to the absorption of atmospheric carbon dioxide. If the filler slurries contain small amounts of calcium hydroxide then any increase in pH could be masked by these decreases.
5.1.12 X-ray Powder Diffraction

In an attempt to determine if any calcium hydroxide was present in the sample bulk, the x-ray powder diffraction work was repeated with the low intensity peaks, less than 15%, amplified to look for any traces of portlandite, the only crystal structure of calcium hydroxide, which has a maximum intensity peak at 2.62Å.

All the low intensity peaks were attributed to the calcite form of calcium carbonate and there was no evidence to suggest the presence of a calcium hydroxide core to the particles.

5.2 Effects of Fillers in Paper

This section examines the properties of papers produced on the Adirondack handsheet machine at Roe Lee Paper Chemicals Co. Ltd. research laboratory, as described in section 2.4.3.

5.2.1 Experimental Parameters

The paper was made with a 50:50 mixture of bleached hard and softwood kraft/pulps beaten using a laboratory scale, industrial beater at East Lancashire paper mill, (beating on an industrial scale is described in section 2.3.1). The pulp was squeezed to remove excess water during transportation and redispersed in tap water at the research laboratory. The size, provided at 30% solids, was diluted by 10 before use, as was the papermaker's alum which was supplied at 47% solids.

The upper chamber of the papermachine was filled with water and an aliquot of pulp dispersed to produce the thinstock. The filler was loaded from a
constantly agitated slurry and dispersed. The required volumes of diluted size and alum were premixed in a beaker for five seconds and then dispersed in the thinstock, they were added in the ratio 1:2 size:alum. Retention agent, added at 0.03% dsf (dry solids on fibre), i.e. 300g per tonne, was dispersed at this stage if required. The thinstock was drained on the wire and the sheet formed. If necessary, the drained water was retained in the lower tank for recycling.

All the fillers were used to produce handsheets and a 30:70 mixture of Albacar LO and Albacar PO was also used, this is referred to as the LO:PO mix. This mixture was recommended by Pfizer Speciality Minerals Inc. as giving the sheet a lower porosity than other PCCs. Young's PCC was added from the original slurry provided.

5.2.2 Recycling of Fillers

Figures 5.2.2(a) to (g) show the retention of filler in the sheet, as a percentage of the amount loaded, as the backwater is recycled ten times. Zero recycles refers to the first pass retention of the filler and is how the sheets were made for testing in the following sections.

The retention of the PCC fillers, except the mixture of Albacar LO and Albacar PO is comparable to that of the ground chalk. First pass retention is as low as 20% but after 10 recycles of the backwater it is increased to approximately 80%. The retention of LO:PO mix was similar to the other fillers at first pass retention but remained low on recycling. In a commercial environment, retention of more than 50% is required for cost efficiency and effective running of a papermachine.
Fig. 5.2.2(a)

Effect of Recycling Backwater on Albacar HO Retention

% Filler Retained

Recycle Number

- Without Retention Agent
- With Retention Agent
Fig. 5.2.2(b)

Effect of Recycling Backwater on Albacar PO Retention

% Filler Retained

Recycle Number

- ■ Without Retention Agent
- ■ With Retention Agent
Fig. 5.2.2(c)

Effect Of Recycling Backwater on Albacar LO Retention

% Filler Retained

Recycle Number

- Without Retention Agent
- With Retention Agent
Fig. 5.2.2(d)

Effect of Recycling Backwater on Albafil Retention

% Filler Retained

0 1 2 3 4 5 6 7 8 9 10
Recycle Number

- Without Retention Agent
- With Retention Agent
Fig. 5.2.2(e)

Effect of Recycling Backwater on Young's PCC Retention

% Filler Retained

![Graph showing the effect of recycling backwater on Young's PCC retention. The graph compares the percentage of filler retained without and with a retention agent, with recycle number on the x-axis and percentage of filler retained on the y-axis. The graph includes data points for both conditions, showing variations in retention over recycle numbers.]
Fig. 5.2.2(f)

Effect of Recycling Backwater on LO:PO Mix Retention

% Filler Retained

0 1 2 3 4 5 6 7 8 9 10
Recycle Number

- With Retention Agent
- Without Retention Agent
Fig. 5.2.2(g)

Effect of Recycling Backwater on Ground Chalk Retention

% Filler Retained

Recycle Number

- Without Retention Agent
- With Retention Agent
5.2.3 Filler Retention

Figs. 5.2.3(a) to (g) show the percentage filler retained in paper as the amount loaded is increased, all sheets formed first pass. The rosin size is loaded at 1% dsf, a common size loading in the paper industry to produce paper with an acceptable Cobb value. All fillers, including the LO:PO mix, are retained between 20 and 30 percent when no retention agent is present. The retention is improved, dramatically in the case of Albacar PO, when Percol 63, a cationic polyacrylamide retention agent, is added. The retention agent is assumed to work by the bridging mechanism (section 3.4.1). This increase in retention is shown in the SEM photographs of paper containing Albacar HO, without and with retention agent, Figs. 5.2.3(h) and (i). This suggests that any variations that exist in surface charge of the fillers are not affecting this aspect of the papermaking process.

5.2.4 Effect of Increasing Filler Levels

Fig 5.2.4(a) shows the effect of increasing ground chalk levels in the sheet, measured by ashing (section 4.9.2), when size is loaded at 1% dsf. The ground chalk produces acceptable Cobb values at high filler levels, up to 9% dsf filler present was measured.

Figs. 5.2.4(b) to (f) are similar graphs for the PCCs. The PCCs produce acceptable Cobb values up to about 4% dsf filler present, without retention agent, this value is extended with retention agent, providing evidence that the amount of rosin size retained in the sheet is increased on addition of Percol 63. Fig. 5.2.4(g) is the graph of Cobb value versus increasing LO:PO mix levels at 1% dsf size loading and appears to produce an analogous result to the ground chalk filler.
Fig. 5.2.3(a)

Variation of Albacar HO Retention, Size Loaded at 1% dsf

% Filler Retained

- Without Retention Agent
- With Retention Agent

% Filler Loaded dsf
Fig. 5.2.3(b)

Variation in Albacar PO Retention, Size Loaded at 1% dsf

% Filler Retained

Without Retention Agent
With Retention Agent
Fig. 5.2.3(c)

Variation of Albacar LO Retention, Size Loaded at 1% dsf

% Filler Retained

% Filler Loaded dsf
Fig. 5.2.3(d)

Variation in Albafil Retention, Size Loaded at 1% dsf

% Filler Retention

- Without Retention Agent
- With Retention Agent

% Filler Loaded dsf
Fig. 5.2.3(e)

Variation in Young's PCC Retention, Size Loaded at 1% dsf

% Filler Retained

- Without Retention Agent
- With Retention Agent

% Filler Loaded dsf

100 80 60 40 20 0

0.0 10.0 20.0 30.0
Fig. 5.2.3(f)

Variation in LO:PO Mix Retention, Size Loaded at 1% dsf

% Filler Retention

- Without Retention Agent
- With Retention Agent

% Filler Loaded dsf
Fig. 5.2.3(g)

Variation in Ground Chalk Retention, Size Loaded at 1% dsf

% Filler Retained

□ Without Retention Agent
■ With Retention Agent

% Filler Loaded dsf
Fig. 5.2.3(h) SEM Photograph of Paper Containing Albacar HO

Fig. 5.2.3(i) SEM Photograph of Paper Containing Albacar HO and Retention Agent
Fig. 5.2.4(a)

Variation in Cobb Value With Ground Chalk Levels, Size Loaded at 1% dsf

Weight Adjusted Cobb Value/gm$^{-2}$

- Without Retention Agent
- With Retention Agent
Fig. 5.2.4(b)
Variation of Cobb Value With Albacar HO Levels, Size Loaded at 1\% dsf

Weight Adjusted Cobb Value/gm^{-2}

\[\begin{array}{c}
\text{Without Retention Agent} \\
\text{With Retention Agent}
\end{array}\]

\[\begin{array}{c}
\text{\% Filler Present dsf}
\end{array}\]
Fig. 5.2.4(c)

Variation in Cobb Value With Albacar PO Levels, Size Loaded at 1% dsf

Weight Adjusted Cobb Value/gm$^{-2}$

- □ Without Retention Agent
- ■ With Retention Agent

% Filler Present dsf
Fig. 5.2.4(d)

Variation of Cobb Value With Albacar LO Levels, Size Loaded at 1% dsf

Weight Adjusted Cobb Value/gm$^{-2}$

- □ Without Retention Agent
- ■ With Retention Agent

% Filler Present dsf
Fig. 5.2.4(e)

Variation in Cobb Value With Albafil Levels, Size Loaded at 1% dsf

Weight Adjusted Cobb Value/gm$^{-2}$

- Without Retention Agent
- With Retention Agent
Fig. 5.2.4(f)

Variation in Cobb Value With Young’s PCC Levels, Size Loaded at 1% dsf

Weight Adjusted Cobb Value/gm⁻²

% Filler Present dsf

- Without Retention Agent
- With Retention Agent
Fig. 5.2.4(g)

Variation in Cobb Value With LO:PO Mix Levels, Size Loaded at 1% dsf

Weight Adjusted Cobb Value/gm$^{-2}$

- Without Retention Agent
- With Retention Agent

% Filler Present dsf

0.0 2.0 4.0 6.0 8.0 10.0 12.0
The theory that this mixture produces lower porosity sheets could account for this similarity. If the filler is packing closely in the sheet, the surface area exposed and the size necessary to produce an acceptable Cobb value will be less than for other PCC fillers. However, bearing in mind the lower amounts of filler retained on recycling, there is evidence that these results would not be repeated on an industrial scale, obviously further investigation is needed in this area.

5.2.5 High Filler Loadings

It is common for ground chalk to be loaded at 20% dsf in industrial paper mills. Fig. 5.2.5(a) shows the Cobb values of sheets produced at this loading with increasing sizing levels. As expected from the results of the previous section, an acceptable Cobb value is achieved at 1% dsf size loading. Addition of retention agent makes little difference to this result.

When PCCs are loaded at this level 1.5 to 2% dsf size loadings are necessary to produce an acceptable Cobb value, Figs. 5.2.5(b) to (f). The result for the LO:PO mix, Fig. 5.2.5(g), is again similar to those for ground chalk, an acceptable Cobb value produced on addition of 1% size dsf. This result could be due to the same effects discussed in the previous section.

5.2.6 Constant Cobb Values

A series of handsheets were produced using a selection of size and filler loadings to determine the levels of each that would produce a constant Cobb value. The Cobb value of these sheets was required to fall between 20 and 25gm⁻². Fig. 5.2.6(a) is the result for ground chalk, as expected this is a horizontal line, 1% dsf size loaded producing an acceptable Cobb value with all filler levels.
Fig. 5.2.5(a)

Variation in Cobb Value With Size Levels, Ground Chalk Loaded at 20% dsf

Weight Adjusted Cobb Value/gm\(^{-2}\)

- Without Retention Agent
- With Retention Agent

% Size Loaded dsf
Fig. 5.2.5(b)

Variation of Cobb Value With Size Levels, Albacar HO Loaded at 20% dsf

Weight Adjusted Cobb Value/gm$^{-2}$

- Without Retention Agent
- With Retention Agent

% Size Loaded dsf
Fig. 5.2.5(c)

Variation in Cobb Value with Size Levels, Albacar PO Loaded at 20% dsf

Weight Adjusted Cobb Value/gm\(^{-2}\)

- Without Retention Agent
- With Retention Agent

% Size Loaded dsf
Variation of Cobb Value With Size Levels, Albacar LO Loaded at 20% dsf

Weight Adjusted Cobb Value/gm$^{-2}$

- Without Retention Agent
- With Retention Agent
Fig. 5.2.5(e)

Variation in Cobb Value With Size Levels, Albafil Loaded at 20% dsf

Weight Adjusted Cobb Value/gm$^{-2}$

- Without Retention Agent
- With Retention Agent
Fig. 5.2.5(f)

Variation in Cobb Value With Size Levels, Young's PCC Loaded at 20% dsf

Weight Adjusted Cobb Value/gm$^{-2}$

- Without Retention Agent
- With Retention Agent
Fig. 5.2.5(g)

Variation in Cobb Value With Size Levels, LO:PO Mix Loaded at 20% dsf

Weight Adjusted Cobb Value/gm$^{-2}$

- Without Retention Agent
- With Retention Agent
Fig. 5.2.6(a)

Ground Chalk and Size Levels Producing a Constant Cobb Value

% Size Loaded dsf

% Filler Present dsf
The graphs for the PCCs, shown in Figs. 5.2.6(b) to (g), show a minimum in the amount of size required then a rapid increase. The rapid increase is also repeated for the LO:PO mix. The minimum could be due to the close packing of the fillers, as described in section 5.2.4. The shift in its position would be due to the differences in the packing of the fillers and when the least surface area was achieved. The rapid increase after the minimum has been attributed to the increase in the surface areas of the PCCs and suggests that these fillers are more difficult to size than ground chalk because of their increased surface area. Some of the graphs show a plateau beginning to form at higher filler levels, Figs. 5.2.6(b) and (c), and the graph for the LO:PO mix has a decrease. This is possibly due to further close packing of the fillers resulting in the sheet becoming thicker rather than an increase in surface area and an increase in the sizing level necessary to produce the required Cobb value. The result for the LO:PO mix is not similar to that of the ground chalk in this case and this aspect of the research does warrant further investigation.
Fig. 5.2.6(b)

Albacar HO and Size Levels
Producing a Constant Cobb Value

% Size Loaded dsf

% Filler Present dsf
Fig. 5.2.6(c)

Albacar PO and Size Levels
Producing a Constant Cobb Value

% Size Loaded dsf

% Filler Present dsf
Fig. 5.2.6(d)

Albacar LO and Size Levels Producing a Constant Cobb Value

% Size Loaded dsf

% Filler Present dsf
Fig. 5.2.6(e)
Albafil and Size Levels Producing a Constant Cobb Value

% Size Loaded dsf

% Filler Present dsf
Fig. 5.2.6(f)

Young's PCC and Size Levels
Producing a Constant Cobb

% Size Loaded dsf

% Filler Present dsf
Fig. 5.2.6(g)

LO/PO Mix and Size Levels
Producing a Constant Cobb Value

% Size Loaded dsf

% Filler Present dsf
Chapter 6
Conclusions
6.1 General Conclusions

The SEM photographs and the specific surface areas determined by nitrogen gas adsorption and dye adsorption from solution establish that the PCCs contain much smaller particles than ground chalk. Paper sizing, i.e. enhancing the sheet's water repellency, requires the rosin to coat the surface of the fibres and filler in the paper. The increased sheet surface area produced by using a PCC could account for the inability to rosin size paper at low size addition levels. This conclusion is substantiated by the linear portion of the relationship between size and filler loadings producing a constant, acceptable Cobb value, section 5.2.6.

SEM microscopy and laser diffraction particle sizing suggest that ground chalk has the largest particle size, greater than Albacar HO and Albacar LO which are approximately equal, and are larger than Albafl and Young's PCC, which also have similar particle sizes, and all these fillers are made up of much larger particles than Albacar PO. The specific surface areas determined by nitrogen gas adsorption are a function of particle and aggregate size. These results show that Albacar PO has the highest surface area, Young's PCC, the next highest, then Albacar HO, Albafl, Albacar LO and ground chalk. The surface areas determined for Albacar HO, Albacar LO and Albafl are similar, \(10.1 \pm 0.4 \text{ m}^2\text{g}^{-1}\), \(6.7 \pm 0.2 \text{ m}^2\text{g}^{-1}\) and \(9.3 \pm 0.3 \text{ m}^2\text{g}^{-1}\) respectively. This provides evidence that the particle and aggregate sizes are similar for these fillers. In comparison to these fillers, Young's PCC appears to consist of similarly sized particles and aggregates, although the specific surface area determined is higher. This suggests that the aggregates formed are more open, providing more adsorption sites for nitrogen gas during surface area measurement. Laser diffraction particle sizing indicates that Albacar PO forms aggregates of a similar size but the small, sub-micron particles forming these aggregates produce a high surface area.
There is little difference, except for the effects of surface area, between the fillers in paper. Although higher size loadings are required with PCCs, it is possible to produce paper with an acceptable Cobb value, section 5.2. Similar percentages of PCCs and ground chalk are retained in paper whether the backwater is discarded, i.e. first pass retention, or recycled. This is not seen for the recycling of backwater using the LO:PO mixture, suggesting the combination would not be cost effective in a commercial environment. The LO:PO mixture required similar size levels as ground chalk at high filler loadings but had a comparable "constant Cobb" relationship to the other PCCs, section 5.2.6. This is an area that would require further experimental work to clarify the behaviour of this PCC mixture.

The tests carried out on paper produced using the cationic, polyacrylamide retention agent, Percol 63, show that it is effective in increasing the retention of the PCCs fillers in a closed papermaking process, i.e. when the backwater is recycled. The retention agent increases the retention of all the fillers and rosin size when used in a first pass system.

6.2 Surface Characteristics

There are many conflicting results in this thesis comparing the surfaces of the PCC fillers to that of ground chalk. The results of dye adsorption from solution suggest that ground chalk has a different surface charge to the PCCs in a water slurry, i.e. ground chalk readily adsorbs a cationic dye but not an anionic one, and visa versa for the PCCs. The DRIFT spectra of the fillers suggest that detectable quantities of calcium hydroxide, Ca(OH)$_2$, may be present on the surface of Albacar HO, Albacar LO and Albafil. Positive adsorption sites could be created by the presence of Ca(OH)$_2$, dissolving in the water of the slurry and Ca$^{2+}$
readsorbing onto the particle surface. X-ray powder diffraction, pH measurements and x-ray photon spectroscopy (XPS) produced no evidence to suggest the presence of calcium hydroxide in the bulk of the particles or on the surface.

The results of XPS and subsequent charge calculations, (section 5.1.10), gave evidence that ground chalk as a dry powder has a very positive surface charge, higher than for the PCCs. This could mean that in the water slurry the surface charge of ground chalk particles is affected. It was postulated in the discussion, that on contact with the aqueous dye solution, the highly positive ground chalk surface adsorbed a layer of water molecules that reduced the surface charge and produced adsorption sites for the cationic dye, methylene blue. The same mechanism could reduce the number of adsorption sites available for the anionic dye, orange II. This explanation could account for the low number of adsorption sites available for methylene blue. The XPS results indicated that the PCC surfaces were naturally positive, and hence any Ca(OH)_2 present causing the readsorption of Ca^{2+} onto the surface would increase the number of adsorption sites available to the anionic dye. This could be used to explain the high number of adsorption sites for orange II on the surface of Albafil and the fact that Albacar HO, which XPS suggested had an electrically neutral surface, adsorbed anionic, orange II. There was no evidence for Ca(OH)_2 associated with Albacar PO, also theorized to have an electrically neutral surface, but the dye adsorption experiments indicated that a large number of adsorption sites were available for orange II. The presence of magnesium nitrate, Mg(NO_3)_2, suggested by the XPS results for Albacar PO, could create the positive adsorption sites, by a similar mechanism to calcium hydroxide.

For both ground chalk and the PCCs there are very few adsorption sites available to stearic (octadecanoic) acid in heptane solution. This is an interesting result, of no immediate bearing on the previous surface characterization work, that
could not be investigated further due to time constraints.

The surface charges of ground chalk and PCCs in aqueous solution appear to be different but this has had no observable effect on their behaviour in paper.

6.3 **Adsorption Experiments**

Comparing the results of specific surface area determination by nitrogen gas adsorption using the BET equation and t-plots shows that these methods produce similar results over the linear portion of the adsorption isotherm.

The work involving the adsorption of dye from solution showed that this system is difficult to apply to surface area determination of non-comparable solids. However the research has been a useful tool in examining the surfaces of the fillers. It has also supported the theory that increased adsorption of dyes is due to changes in the orientation of adsorbed dye molecules (West 1952, 1953, 1954) and not the existence of dye micelles.
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Appendix 1
Specialty Minerals

PFIZER MINERALS FOR HIGH PERFORMANCE PAPERS

ALBACAR HO®

This unique mineral filler from PFIZER is designed to provide an economical increase in paper opacity and brightness. ALBACAR HO®, a scalenohedral precipitated calcium carbonate, is recommended for use in uncoated fine papers and coating base stock. Particle morphology, average particle size and particle size distribution are precisely controlled to maximize light scattering, while also increasing paper bulk.

### Typical Properties

**PHYSICAL**

<table>
<thead>
<tr>
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<th>Value</th>
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<td>Mean Particle Size, μm</td>
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</tr>
<tr>
<td>Dry Brightness (Y, Rd.)</td>
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</tr>
<tr>
<td>(Hunter 0.28)</td>
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</tr>
<tr>
<td>% Solids</td>
<td>*</td>
</tr>
<tr>
<td>+ 225 Residue, %</td>
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<tr>
<td>Einlechner Abrasion, mg</td>
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<td>(AT 1000 @ 174K rev.)</td>
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* Average Dry, 20% & 40% Solids Survey

**CHEMICAL**

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<th>Value</th>
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<tr>
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### Particle Size Distribution

- Mass - μm Finer Than
- Equivalent Spherical Diameter (μm)

---

This paper contains Pfizer PCC
Albacar PQ, a scalenohedral precipitated calcium carbonate, is recommended for use in filling applications in which closing sheet porosity is required. Albacar PO, particle morphology, average particle size and particle size distribution are uniquely controlled during synthesis to maximize its capability to tighten sheet porosity. Albacar PO is an economical source of paper opacity and brightness, while contributing to a more closed sheet (increased Gurley porosity).

**Typical Properties**

**PHYSICAL**

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<td>Einlechner Ablation, mg.</td>
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**CHEMICAL**

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<td>Acid Insolubles, %</td>
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**PARTICLE SIZE DISTRIBUTION**

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<th>Mass % Finer Than</th>
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<td>100</td>
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<td>0.27</td>
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*All information in this document is based upon our own experience and is furnished to the best of our knowledge. Other information is provided or obtained from various sources. Pfizer Minerals represents that such information has been obtained from sources believed to be reliable, but it is not responsible for errors in any third party information.*
Specialty Minerals

PFIZER MINERALS FOR HIGH PERFORMANCE PAPERS

ALBACAR LO®

Albacar LO® is a scalenohedral precipitated calcium carbonate mineral filler for use where maximum paper caliper (bulk) is required. Albacar LO® particle morphology, average particle size and particle size distribution are controlled during synthesis to enhance sheet caliper (bulk). Albacar LO® provides economical paper opacity and brightness, while maximizing caliper (bulk).

Typical Properties

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<td>+ 325 Residue, %</td>
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<tr>
<td>Einlehner Abrasion, mg</td>
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CHEMICAL

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<td>MgCO₃, %</td>
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<tr>
<td>Fe₂O₃, %</td>
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<td>Acid Insolubles, %</td>
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PARTICLE SIZE DISTRIBUTION

This paper contains Pfizer PCC.
Specialty Minerals

PFIZER MINERALS FOR HIGH PERFORMANCE PAPERS

ALBAFIL®

This unique fine particle mineral filler from PFIZER, with a narrow particle size distribution, provides the papermaker with an optically efficient filler. Albafl®, a rhombohedral precipitated calcium carbonate, provides improved paper opacity and brightness.

Typical Properties

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<td>Einleher Abrasion, mg.</td>
<td>4.0</td>
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<td>(AT 1000 @ 174K rev.)</td>
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*Analysed Dry, 5% Solids Slurry

Typical Properties

CHEMICAL

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<td>Insolubles</td>
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PARTICLE SIZE DISTRIBUTION

This paper contains Pfizer PCC.
**PERCOL 63**

**CATIONIC RETENTION AID AND SAVE-ALL FLOCCULANT**

**Description**

PERCOL 63 is a high molecular weight, cationic polyelectrolyte. It is supplied in micro-bead form which renders it non-dusting and free flowing. PERCOL 63 is completely soluble in water and because of its carefully controlled particle size has a very rapid dissolving rate.

**Principal uses**

PERCOL 63 has found application over a wide variety of papermaking conditions. Being cationic in character PERCOL 63 performs independently of alum concentration and has given marked improvements in retention and drainage throughout the pH range encountered in paper production. PERCOL 63 is particularly effective in neutral or alkaline sized systems where the sizing material has only a limited cationic charge.

Addition levels are of course dependent on the particular application but are generally between 100 and 300 g per tonne for optimum retention. Improvements in dewatering have been recorded with addition rates of up to 450 g.

PERCOL 63 is also very successful in flotation and filtration save-alls. Significant improvements in efficiency and plant capacity have been experienced.

**Typical properties**

<table>
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<td>Physical form</td>
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<tr>
<td>Particle size</td>
<td>100% through 200 mesh</td>
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<tr>
<td>Bulk density</td>
<td>900 g per litre</td>
</tr>
<tr>
<td>pH, 1% solution</td>
<td>3.5±0.5</td>
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<tr>
<td>Viscosity</td>
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**Apparent Viscosity vs Concentration**

(For pumping, pipeline & agitator guidelines only)
Recommended solution concentrations:

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<th>Solution</th>
<th>Concentration</th>
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<td>Stock solution</td>
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</tr>
<tr>
<td>Feed solution</td>
<td>0.05 to 0.1% max</td>
</tr>
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</table>

Recommended storage periods:

<table>
<thead>
<tr>
<th>Product</th>
<th>Storage Period</th>
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</thead>
<tbody>
<tr>
<td>as supplied</td>
<td>up to 2 years</td>
</tr>
<tr>
<td>Stock solution</td>
<td>2 to 3 days</td>
</tr>
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</table>

Storage of product, as supplied, should be in a cool dry place.

Details on preparation and feeding are obtainable upon request. Fully automatic and semi-automatic preparation systems are available from Allied Colloids.

Shipping and handling

PERCOL 63 is supplied in 25 kg polyethylene bags or 600 kg big bags. The packages are completely water proof but if only partially used should be sealed to prevent entry of moisture.

PERCOL 63 has a low order of toxicity and no special precautions are necessary in handling.

Spillages of the dry material should be swept up to prevent slippage.

Technical service

Advice and assistance in conducting off-machine retention tests to select the correct polymer and to determine the best application, is given by representatives of Allied Colloids. Assistance can also be given during the preparation and running of plant trials.

Health and safety

Detailed information on handling and any precautions to be observed in the use of the product(s) described in this leaflet can be found in the relevant health and safety information sheet.

Quality assurance

The quality procedures of Allied Colloids are recognised by British Standards Institute as complying with the requirements of BS5750 (Part 1)—1987 and the International Standard ISO9001—1987.

Trade marks

PERCOL is a trade mark of Allied Colloids Ltd.

Warranty

The information contained in this leaflet is given in good faith but no liability is assumed, nor is freedom from any patent owned by Allied Colloids Ltd. or others implied.
Water absorptiveness of sized (non-bibulous) paper and paperboard (Cobb test)

1. Scope

1.1 This method describes a procedure for determining the quantity of water absorbed by non-bibulous paper and paperboard in a specified time under standardized conditions. It is based on studies by Cobb and Lowe (1), Cobb (2) and other investigators (3, 4).

1.2 Water absorptiveness is a function of various characteristics of paper or board such as sizing, porosity, etc. This method is generally applicable to sized paper and paperboard, but it is not recommended as a sizing test for writing paper.

1.3 For testing unsized and absorbent paper or paperboard, see T 432 "Water Absorbency of Bibulous Paper" and T 492 "Water Absorption of Paperboard (Non-Bibulous)" (water drop test); for slack sized paper and paperboard, see T 433 "Water Resistance of Sized Paper and Paperboard (Dry-indicator Method)."

2. Apparatus

2.1 Water absorption apparatus, to permit one side of the specimen to be wetted uniformly at the moment the soaking period begins, and to allow controlled rapid removal of the water from the specimen at the end of the test period. The specimen holder (J) as shown in Fig. 1 comprises a metal ring with a machined lower face, 11.28 ± 0.02 cm inside diameter (corresponding to a cross-sectional area of 100 cm²), 2.5 cm high and about 0.6 cm thick, clamped to a flat base plate about 15 x 15 cm with a metal cross bar 17 x 2.5 x 0.6 cm and two wing nuts on a pair of studs. The cross bar has a hole at one end and a slot at the other to facilitate assembly and use. On the base plate is a rubber mat, larger than the outside dimensions of the ring, on which the specimen is clamped.

NOTE 1: The metal parts should preferably be of brass or other corrosion-resistant material.

NOTE 2: Several versions of the water absorption apparatus are now available. Although the basic procedure for performing the test is not changed, the clamping mechanism is. This may affect the speed at which the sample can be removed from the apparatus.

2.2 Metal roller, solid brass having a smooth face 20 cm wide and weighing 10.0 ± 0.5 kg.

2.3 Timer, stopwatch or clothic timer reading in seconds.

2.4 Graduated cylinder, 100 mL.

2.5 Balance, with an accuracy of 0.01 g, or better.

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3. Materials

3.1 Blotting paper, sheets of blotting paper, 200-250 g/m², with a capillary rise of 50-100 mm of water (mean of MD + CD) as measured by the Klemm method (see Appendices). Normally, the blotter specified in T 205 "Foming Handsheets for Physical Tests of Pulp" will meet this requirement.

3.2 Water, distilled or deionized.

NOTE 3: The temperature of the water is important and must be maintained at 23 ± 1°C. Renew the water for each determination.

4. Sampling and test specimens

Obtain a sample from the paper in accordance with T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product." From each test unit, cut specimens to a size slightly greater than the outside dimensions of the ring of the apparatus, i.e., squares 12.5 x 12.5 cm. The specimens should be free from folds, wrinkles, or other blotches not commonly inherent in the paper. For hard-sized papers (absorbing less than 100 g of water/m²), use 10 specimens per test unit. For soft-sized papers (absorbing more than 100 g/m²), use 20 specimens.

5. Procedure

5.1 Condition the specimens in an atmosphere in accordance with T 402 "Standard Conditioning and Testing Environments for Paper, Pulp Handsheets, and Related Products."

5.2 Weigh each specimen to the nearest 0.01 g.

5.3 Test half the specimens with the wire side up, the other half with the felt side up.

5.4 Place a dry rubber mat on the metal plate and lay a weighed specimen on it. After wiping the metal ring perfectly dry, place it upon the specimen, and fasten it firmly enough in place with the crossbar to prevent any leakage between the ring and the specimen. For reporting, the test side is the one that is in contact with the water during the test.

NOTE 4: For materials where leakage between the ring and the upper surface of the test specimen may occur during the test, a soft, elastic non-absorbing insert may be used. The insert should have the same internal dimensions as the ring.

5.5 Pour 100 mL of water into the ring as rapidly as possible, giving a head of 1 ± 0.1 cm. Start the stopwatch immediately. At 15 ± 5 s before the expiration of the predetermined test period, usually 120 s (see 8.3, 8.4, and 8.5), pour the water quickly from the ring, taking great care not to drop any of the water upon the outside portion of the specimen. Promptly loosen the wire data, swing the crossbar out of the way while holding the ring in position by pressing it down with one hand. Carefully, but quickly, remove the ring and place the specimen with its wet side up on a sheet of blotting paper resting on a flat rigid surface.

5.6 Exactly at the end of the predetermined test period, place a second sheet of blotting paper on top of the specimen and remove the surplus water by moving the hand roller once back and once forward over the pad without exerting any additional pressure on the roller. Specimens which contain an excess of surplus water after blotting, as shown by glossy areas on the surface, should be rejected and the test repeated, decanting the water from the ring sooner. Fold the specimen with the wetted area inside. Immediately reweigh it to the nearest 0.01 g.

5.7 Subtract the conditioned weight of the specimen from its final weight, and multiply by 100 to obtain the gain in weight in grams to obtain the weight of water absorbed in grams per square meter.

NOTE 5: If any liquid has passed through the sheets to the rubber mat, the test is not acceptable. When this occurs, either discard the ring or allow the time to 60 s, or tape two or more specimen sheets together outside the test area. In such a case, the calculated test result remains that of the inside ring. For hard-sized papers, a longer period (e.g., 300 s) may be found advisable.

6. Report

Report the absorptiveness, calculated as the average weight of the water absorbed in grams per square meter, for the wire and the felt side of the paper separately. If desired, state also the maximum and minimum values for each side.

NOTE 6: Unless otherwise noted in the report, it is assumed that an exposure period of 120 s on a single thickness has been employed. Such conditions are suitable for most well-sized papers.

7. Precision

Based on limited data for hard sized papers and for means of five specimens on the same side, the repeatability is within 8% and the reproducibility between laboratories is within 10%, as defined by TAPPI T 1206 "Precision Statement for Test Methods."

8. Additional Information

8.1 Effective date of issue: April 20, 1990.

8.2 The standard test area is 100 cm². If the available specimens are too small, a proportionately smaller test
area may be used providing that the volume of water is reduced to provide a pressure head of 1 ± 0.1 cm. The change in area should be noted in the report.

8.3 This test is designed for non-bituminous papers and paperboards, but satisfactory results have been obtained with up to about 20 sheets of highly absorbent paper stapled together and tested for 60 instead of 120 s.

8.4 For very hard-sized or specially treated papers, the test may be extended to periods up to 18 h, to increase the sensitivity.

8.5 For layers of absorbent papers, the quantity of water absorbed is almost proportional to the time of exposure. For well-sized papers, the quantity is approximately proportional to the square root of this time.

8.6 An effect of natural aging has been noticed in many papers. For example, results on cupstock papers, aged a few weeks, are usually about 2 g/qm less than on papers tested immediately after being made.

8.7 The Cobb test may also be suitable with other (water base) solutions, such as dilute lactic acid and hot coffee for food board and cup stock and possibly ink for writing and printing papers.

8.8 Weighing the wetted specimen can be facilitated by using tared water-vapor-proof containers which will eliminate evaporation losses. Metal cans or polyethylene bags about 11 cm x 23 cm x 0.0076 cm with wire closure have been reported to be satisfactory for this purpose.

8.9 For specimens that have long penetration times or have surfaces that are difficult to wet, substitute the distilled or deionized water with water having a known concentration of wetting agents. With the results also indicate the exposure time, total head, wetting agent and concentration.

8.10 This method was revised in 1947, 1945, 1958, 1960, 1963, 1969, 1977, and 1990. The 1969 revision incorporated standardization of the test area at 100 cm² and the pressure head depth at 1.0 ± 0.1 cm, standardization of the blotting method with specification of the blotter and rollers used, and specification of the water as distilled or demineralized. The 1977 revisions were editorial. This 1990 revision makes mention of the use of alternate clamping mechanisms.

References


Appendix

Measurement of blotter absorptiveness (Klemm method)

Make the test on samples conditioned according to T 401. Cut parallel specimen strips about 15 mm wide and at least 200 mm long in both machine and cross directions. Immerse the specimen strips suspended vertically to a depth of 10 mm in distilled or deionized water maintained at a temperature of 23 ± 1°C. After an immersion time of 10 min, read the height in millimeters to which the water rises above the water level in the container.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Divisions Administrator.
Ash in paper and paperboard

1. Scope
This method for determination of ash can be applied to all types of paper and paperboard.

2. Summary
Paper or paperboard is ignited in a muffle furnace at 900 ± 25°C. The resulting ash is weighed and calculated as a percentage of the moisture-free paper or paperboard.

3. Significance
3.1 The ash in paper and paperboard may consist of (a) mineral matter in the pulp from which the paper was made, (b) residues of chemicals used in its manufacture, (c) extraneous mineral matter picked up during manufacture, and (d) loading and coating materials.

3.2 When the paper or paperboard contains loading and mineral coating materials which undergo only a negligible change in weight on ignition (for example, titanium dioxide), the ash content may be taken as an approximate measure of the amount of this material present in the paper or board, if it is known that other inorganic materials stable at 900°C are not present. In practice, however, the ash content in paper or paperboard may include inorganic residue from the pulp, inorganic residues from alum used with hard water, and so on.

3.3 With most of the other materials, such as china clay and calcium carbonate, for example, there will be a substantial loss in weight on ignition at 900 ± 25°C. The amount of loading material in this case could be estimated only when the chemical composition and changes in weight of this material on ignition are known.

4. Definition
The ash in paper and paperboard is the inorganic residue after combustion to constant weight at a temperature of 900 ± 25°C.

5. Apparatus
5.1 Crucibles, platinum, porcelain or silica, 30 to 100 mL, with covers.

5.2 Electric muffle furnace, suitable for maintaining a temperature of 900 ± 25°C.

6. Sampling
Obtain a sample of paper or paperboard in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product."

7. Test specimens
7.1 Condition the sample in the atmosphere near the balance to the moisture equilibrium.

7.2 From each test unit, weigh two test specimens to the nearest 1 mg. The weight of a test specimen shall be not less than 1 g moisture-free, and sufficient to give not less than 10 mg of ash.

7.3 At the same time, weigh test specimens for moisture determination in accordance with TAPPI T 412 "Moisture in Paper and Paperboard."

8. Procedure
8.1 Heat the empty crucible and cover in a muffle furnace at 900 ± 25°C to constant weight, generally 30-60 min. Place in a desiccator and cool for 45 min when a porcelain or silica crucible is used, or for 15 min when using platinum. Weigh to the nearest 0.1 mg.

8.2 Transfer the test specimen to the crucible and place it, with the cover removed, in a muffle furnace at a temperature not higher than about 100°C. Raise the temperature gradually to 900 ± 25°C so that the material becomes carbonized without flaming. Leave the door of the muffle furnace open during this period to allow ample access of air.
NOTE 1: If the crucible is too small to hold the entire specimen, the material may be carbonized in several successive portions.

8.3 Ash: x the material to ignite at 900 ± 25°C until the combustion of carbonaceous matter is complete, as indicated by the absence of black particles in the ash.

8.4 Cover the crucible, cool in a desiccator (see 8.1) and weigh to the nearest 0.1 mg.

8.5 Return the crucible with ash to the furnace and ignite at 900 ± 25°C for an additional 30 min. Cool in a desiccator and weigh again.

8.6 If the weight differs from the previous weight by more than 0.5 mg, repeat the procedure of ignition and weighing (8.3) until the constant weight is attained, i.e., until two consecutive weighings do not differ by more than 0.5 mg.

9. Calculation

Calculate the ash content as follows:

\[
\text{Ash, } \% = \frac{A \times 100}{B}
\]

where

- \(A\) = weight of ash, g
- \(B\) = weight of test specimen, g moisture-free

10. Report

Report the ash content in paper or paperboard as an average of two determinations to the nearest 0.01% when the ash content is below 10%, or to the nearest 0.1% if the ash content is 10% and higher.

11. Precision

11.1 Repeatability, as defined in TAPPI T 1206 “Precision Statement for Test Methods,” is found to be dependent on the ash content as follows:

<table>
<thead>
<tr>
<th>Ash content, %</th>
<th>Repeatability, absolute (as ash content, %)</th>
<th>Repeatability, relative (as percentage of ash content)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 1</td>
<td>0.03</td>
<td>6.8</td>
</tr>
<tr>
<td>1-5</td>
<td>0.07</td>
<td>2.8</td>
</tr>
<tr>
<td>5-10</td>
<td>0.17</td>
<td>2.4</td>
</tr>
<tr>
<td>10-20</td>
<td>0.32</td>
<td>2.0</td>
</tr>
<tr>
<td>Over 20</td>
<td>0.42</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The data are obtained in one laboratory by testing 25 samples in each group by several operators.

11.2 Reproducibility and comparability: not known.

12. Additional information


12.2 It is important to note that TAPPI T 211 “Ash in Wood and Pulp” requires a lower temperature for the ash determination. The conditions specified in this method, T 413, are for use with paper and paperboard only and must not be used for pulp or wood.

12.3 Related methods: BS 3631, TAPPI T 211, CPPA G.11, ISO 2144.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Test Methods Administrator.