

CHAPTER 7

The production and properties of printing pastes

Leslie W C Miles

7.1 THE REQUIREMENTS

All the different methods of printing normally require a liquid vehicle, in which the colorant is carried, and only in exceptional cases has it been possible to print dry colorant. In textile printing, the liquid is usually aqueous but in paper printing, as high-speed drying is necessary, more rapidly evaporated nonaqueous solvents have been used. The components of the liquid printing paste must include all necessary wetting, dispersing and fixing agents, in addition to the colorants, and may be soluble or insoluble. No separation of insoluble components must occur, and the incorporation of viscosity-increasing protective colloids helps in this respect. Finally, as the viscosity of the print paste must be suitable for the method to be employed and the substrate to be printed, appropriate amounts of thickening agents must be used.

'Viscosity' is a key word in this chapter and we have to consider why it is important, how it can be measured and how to achieve the required viscous properties. These are questions that, in the past, have been answered on the basis of experience rather than of scientific understanding, but with the availability of new materials and the need for improved productivity and reproducibility, experience alone is inadequate and understanding is required.

There are two essential reasons for the importance of the viscosity, and hence the flow, of a print paste. It affects the amounts of paste applied as well as the spread of paste, on the surface of the textile material and into its structure. For example, the paste in an engraved roller is completely transferred to the fabric pressed against the roller only if there is time for it to flow into the fabric structure. Highly viscous pastes flow slowly, so that at high speeds the time is often too short for total transfer to occur. Even at low speeds, transfer is viscosity-dependent [1]. If only a small volume of viscous paste is applied it may not spread to cover all the fibres of the three-dimensional fabric surface. The appearance of the print will be unsatisfactory if only the high spots of the



fabric surface are coloured and those parts of the yarn surfaces that are visible, but which lie at a lower level, are left uncoloured. The use of pressure helps in this respect, but the amount of pressure must be controlled for other reasons.

In practice, therefore, the upper limit of the viscosity is determined by the flatness of the fabric surface and the conditions of the printing process. The lower limit also depends on the process conditions, but is mainly determined by the need to keep the print 'smart', that is, having a sharp printed mark. All textile substrates are assemblies of fibres, and the spaces between fibres – especially where three fibres are parallel and in contact – have the dimensions and properties of capillaries. Liquids that wet the fibres are drawn by capillarity along these spaces, and the smartness of the print is lost if the viscosity is not high enough to control the spread.

It is clear, therefore, that some spread of print paste is inevitable, and indeed desirable, but that the extent must be controlled. Before considering in more detail the flow requirements of ideal pastes, it is important to recognise that the choice of materials for the production of viscous pastes will affect not only paste flow but also colour yield, because of their physical and chemical properties. Some knowledge of these properties is therefore desirable.

7.2 THICKENERS

Print pastes are traditionally made by weighing out and, if necessary, dissolving the colorants and auxiliary chemicals and then stirring them into the required weight of pre-prepared thickener. A thickener is a colourless, viscous paste made with one or more thickening agents. The use of terms such as thickener, and thin, long or short, to describe print pastes is of course descriptive rather than scientific, but is long established and a useful reminder that the materials being handled possess complex properties, not easily defined.

Four significantly different approaches may be used to produce thickeners, using:

- a low concentration of a polymer of high relative molecular mass (r.m.m.)
- a high concentration of a material of lower r.m.m. or of highly branched chain structure
- an emulsion of two immiscible liquids, similar to the emulsions used as cosmetic creams, or a foam of air in a liquid
- a dispersion of a finely divided solid, such as bentonite.

The first approach is the most important but all four have been used, sometimes in combination. Practical printers long ago discovered natural polymers with suitable properties and, by trial and error, acquired the art of using them. Because the natural products are variable materials and the requirements are complex and ill-defined,



experience and subjective judgements were essential. Now that the chemistry and physics of polymers are better understood, it is possible to select and use them more scientifically. We also have available a wider range of thickening agents, including completely synthetic polymers, and this has increased our knowledge. It must not be assumed, however, that our understanding of these complex materials and their behaviour is adequate.

In the selection of thickening agents, it is necessary to take into account requirements other than viscosity, which can usefully be classified in five categories: print paste stability, good adhesion of the dried thickener film, minimum effect on colour yield, ease of removal and acceptable cost.

7.2.1 Print paste stability

The thickener must be stable and compatible with the dyes and auxiliaries to be used. If a cationic dye is added to a thickener with anionic charges, the interaction is likely to change the viscosity and to produce insoluble complexes. Similarly, anionic thickeners cannot be used when metal salts such as aluminium sulphate (present in many azoic diazo components) are to be added.

The pH of the print paste must be considered, as some polymers, such as sodium alginate, are only usable within a limited pH range and form gels when acids or strong alkalis are added. Hydrolysis of the polymer chain links may also be significantly accelerated by acid or alkaline conditions.

Most natural polymers are also biodegradable. The micro-organisms responsible are present in the air, and thickeners provide nutrients and ideal conditions for their growth and reproduction. They produce enzymes that break down the polymer, with a consequent and often rapid fall in viscosity. To avoid this hazard thorough cleansing of thickener containers and the addition of preservatives, such as formaldehyde (methanal) or phenols (*o*-phenylphenol, for example), are recommended.

Natural starch pastes tend to gel and form insoluble aggregates over a period of time, because of the molecular association of linear polymer units. Such changes may occur slowly and not be immediately apparent, but print paste is usually required to be stable for at least one week.

7.2.2 Properties of the dried thickener film

Drying usually follows printing, and the fabric may be creased and flexed over rollers and tension rails before fixation of the print occurs. The thickening agent is deposited on the fabric surface as a dry film that sticks fibres together and contains colorant. Good adhesion to the fibre is required in order to avoid loss of colorant during



mechanical handling. Otherwise particles of coloured film may break off, leaving white spots in coloured areas and possibly giving coloured spots in unprinted areas. Freedom from these faults will depend on the flexibility of the film, in addition to its adhesion, and polymer films vary in both respects.

Linear polymers are adsorbed more strongly than highly branched polymers are, and therefore show good adhesion. However, the linear polymers that are useful thickening agents have large numbers of hydroxyl or carboxyl groups along the chain. Natural polymers of this type form brittle films because of substantial intermolecular hydrogen bonding. Thick films of such polymers on delicate fabrics can easily be broken when the fabric is creased, causing fibre fracture. Flexibility may be maintained by avoiding overdrying or by the inclusion of a plasticising agent.

The deposition of polymer films on a fabric inevitably causes some stiffening, and washing is normally required after fixation of the dye to remove thickening agent and any loose dye. If no wash-off is to be given, the thickener (and any binder) must be relatively soft and flexible. In the traditional printing of pigments, remarkably satisfactory results were obtained using albumen, which forms flexible films, as a thickener and binder. The use of emulsion thickeners has the undoubted advantage of leaving no stiffening film, and it is possible to choose synthetic-polymer binders for film softness (see section 5.2.2).

Emulsion thickeners are less popular than they were, however, because the evaporation of petroleum distillate into the atmosphere is more expensive and less acceptable than it was at one time. Paper printers use nonaqueous solvents with pigment binders, but their requirements are very different from those of the textile printer. Fortunately, many synthetic thickeners do not form such hard films as do the natural polymers.

7.2.3 Effect on colour yield

Printers have found that the fixation of dye is usually best achieved by steaming. Steam condenses on to the film of thickening agent, which swells and contains a miniature dyebath on the fibre surface. Some dye dissolves, and the next step is the diffusion of dye through the swollen film to the fibre surface [2]. Any affinity between the molecules of dye and thickening agent will reduce the speed of this diffusion process as well as the extent of dye transfer to the fibre. If both molecules have ionic charges of the same sign, the speed and efficiency of the process will be higher because of the mutual-repulsion effect. An example is provided by the use of sodium alginate for reactive dyes.

A thickener of low solids content gives higher fixation levels than one that has high solids content and otherwise similar properties. The former gives a thin film and



therefore a shorter mean diffusion path and less dye retention. Clearly, the degree of swelling of the film in steam will also affect the diffusion rate.

In addition to any effect on dye fixation, the thickener will significantly affect the penetration of print paste into the yarn and fabric structure, and this may have a dominant effect on colour yield. The highest colour yield (depth of colour for a given mass of colorant per unit area) is only obtained when penetration into and between the yarns is at a minimum. Penetration is viscosity-dependent for any thickener, but some thickeners appear to restrain penetration more than expected on the basis of viscosity. This is so for starch-based thickeners, and has been attributed to their gel-like structure [3]. In the case of printed pigments, the colour yield may also be significantly affected by the transparency of the thickener–binder film and by any tendency of the thickener to promote or prevent aggregation of the pigment.

The print fixation stage is discussed in Chapter 8.

7.2.4 Ease of preparation and removal

The time taken to prepare a thickener, and the precautions required to ensure that the paste has satisfactory and consistent properties, are variables that have greater significance today than in the past. The extent to which a thickening agent is removed in a high-speed washing process, especially after a high-temperature steaming operation, is also a vital consideration in the selection of thickening agents.

Natural starches are cheap, but to burst the grains and obtain a proper dispersion requires time or special equipment. It is also difficult to redisperse starches and remove them from the printed fabric. The physical and chemical modification of starch, and of other natural polymers, has therefore become common practice in order to provide products that are readily dispersed and have more consistent properties (as a result of blending to a standard level).

The removal of thickening agents can also be facilitated by introducing a second component in the thickener. Small additions of sodium alginate, for example, improve the removal of starch. The introduction of dispersing agents, or of hydrogen-bond breakers such as urea, can also be useful.

The actual preparation of pastes is dealt with in section 7.8.

7.2.5 Cost

Traditionally, when labour costs were low, it was common to look only at the cost of the thickening agent itself and the cheapest materials were widely used. It must already



be obvious, however, that it is essential to consider many other aspects to decide which material will give the required quality at the lowest overall cost. The concentration to be used, cost of preparation, stability, print penetration, colour yield and ease of removal can in total be more important than the basic price of the polymer. The biological oxygen demand of the effluent, due to thickener removed in the washing-off operation, can also be a vital parameter.

7.3 RAW MATERIALS: POLYSACCHARIDES

The availability of carefully standardised, modified natural products or synthetic thickening agents can reduce the printer's problems significantly, but in some situations the locally available materials will be preferred. A review of the properties of the many products and their derivatives is therefore included here. Some knowledge of the traditional thickening agents is also helpful in that they illustrate general problems and properties more clearly than the more recently developed materials do.

Nature has provided large quantities of many polymers that are soluble or dispersible in water to give viscous pastes. Each plant species synthesises one or more polysaccharides from the constituent sugars, and some plants (potatoes, for example) produce them in purity and in quantities that make extraction very simple.

The sources of useful polysaccharides may be classified as:

- plant seeds which contain starch or similar products as a food reserve and may be cultivated for industrial use (such as guar)
- seaweed, the only source of alginate
- plant gum exudates, of which the best known are gum arabic and gum tragacanth
- the cultivation of selected micro-organisms, carried out under controlled conditions, converting waste carbohydrate into useful polymers (such as xanthan)
- cellulose pulps, from which cellulose ethers are produced.

The relative importance of these different sources changes with time, as costs of collection, competition with the food and other industries and the technical need for particular properties change.

The polysaccharides may be homopolymers, composed entirely of one sugar unit, or heteropolysaccharides with two or more hexose or pentose units assembled in a relatively ordered sequence. The polar side-groups may all be hydroxyls, as in starch, cellulose and guar gum, or they may include carboxyl groups as well, as in alginate and gum arabic. Less frequently, other water-soluble groups are found.

An equally important structural feature is the degree of chain branching, which affects the solubility, film and viscosity properties. Long, linear polymers give high viscosity at low solids contents, but the viscosity falls with increasing shear. Highly



branched polymers, such as amylopectin, are more soluble and are required in higher concentrations for a given viscosity, but show less change under shear.

The interactions of polysaccharides and water are complex, but important. Water vapour is adsorbed from the atmosphere, typically to the extent of 10% of solid mass, by the accessible hydroxyl groups. In liquid water, swelling occurs as accessible segments of the polymer become fully hydrated and move away from adjacent chains. The kinetic energy of these segments then causes the rupture of some intermolecular hydrogen bonds and more chain segments can be solvated. Where polymer chains are well ordered and bonded, however, especially in crystalline regions, the structure will be maintained and such insoluble units may be linked together, forming a gel.

If enough of the intermolecular forces can be broken, the polysaccharide goes into colloidal solution. A principal feature of colloidal solutions is their instability. For example, starch pastes obtained by heating tend to form gels on cooling, as new intermolecular bonds are formed. The intermolecular bonds are of two types: hydrogen bonds and hydrophobic bonds. A proper understanding of the latter depends upon the recognition of the structure of water and the effect of solutes on that structure.

Frank and Wen proposed a 'flickering cluster' model of water structure with short-lived, ice-like molecular clusters of varying sizes in equilibrium with single water molecules [4]. At ordinary temperatures between 70 and 90% of the water molecules are assumed to be in clusters at any given moment. Organic solutes of significant size and hydrophobic character, including many alcohols, are believed to cause a tightening of the water structure around the molecules, because repulsion of the nearest water molecules encourages their orientation and hydrogen bonding. It is envisaged that each solute molecule occupies a cavity in the solvent.

There will then be a tendency to 'water-structure-enforced association' [5], because the repulsive interactions and the cavity surface areas can be minimised, and the entropy maximised, when two or more solute molecules together occupy one slightly larger cavity. In the case of polymer molecules, it will be chain segments, rather than whole molecules, that are thus associated by hydrophobic bonding. Many of the polysaccharides show sufficient hydrophobic character to engage in such intermolecular bonding, in spite of their many hydroxyl groups. Cellulose molecules are a clear example, their flat, ribbon-like shape with all the hydroxyl groups at the ribbon edges providing large central hydrophobic surfaces that associate readily. In the same way, flat dye molecules can be adsorbed on to the hydrophobic surfaces.

When the equilibrium between hydrophobic and hydrophilic character is delicately balanced, the addition of electrolytes can have significant effects. Thus magnesium sulphate reduces the solubility of amylose, because both ions compete with it for water of solvation. On the other hand lithium iodide, and other salts high in the lyotropic series, have a solubilising effect as these ions are strongly adsorbed on to the polymer.



7.3.1 Starch and its derivatives

Native starch is, after cellulose, the most abundant of the plant products and has therefore provided a readily available and low-cost source of industrial materials [6]. Starches have long been used in textile print pastes, but are less important than they were because of the increased availability of technically superior materials, some of which are starch-based.

It is sometimes argued that the importance of starch for human consumption and the continuing expansion of the world's population make it unlikely, even wrong, that its industrial use should continue. Such a simple conclusion may not be justified, however, because of the complexity of the relationships. Increased demand causes an increase in price, if supply cannot be readily increased, but also stimulates production and the search for alternative materials.

Starch is a homopolymer of glucose (D-glucopyranosyl) units, with most of the units joined by α -D(1 \rightarrow 4) linkages. Most starches contain 20–30% of the linear chain polymer, known as amylose (7.1 in Figure 7.1), together with an irregularly branched material, amylopectin (7.2 in Figure 7.1). Amylopectins have an α -D(1 \rightarrow 6) linked branch for each 15–30 glucose units. So-called waxy starches contain little or no amylose. Separation can be achieved by fractional solution or precipitation.

Whereas, in cellulose, the β -D-glucoside linkages give a nearly flat, ribbon-like molecule, in linear starch segments the α -D(1 \rightarrow 4) linkages and ${}^4C_1(D)$ chain conformations introduce a natural twist. Under certain conditions, a tightly coiled

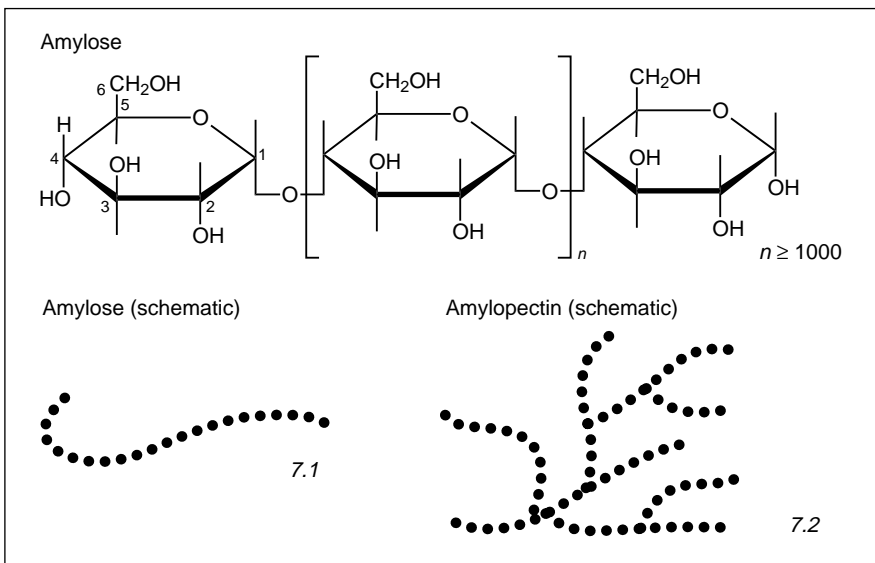


Figure 7.1 Amylose and amylopectin

helix is stabilised by hydrogen bonds between the C-2 and C-3 hydroxyl groups on adjacent chains.

In the natural state, starch is always found in a strongly aggregated state, organised in granules around crystallisation nuclei. The granules of each type of starch (rice, potato, wheat and so on) have a characteristic structure which is readily identifiable under the microscope. It is necessary to break down the granules, by boiling or by grinding and dispersion in hot water, to obtain smooth, viscous pastes. If such a paste is dried rapidly, cold-water-dispersible starches are obtained, but slow drying allows substantial reaggregation and crystallisation to occur and the product is no longer dispersible in cold water. The use of hydrogen-bond breakers, such as urea and strong alkalis, will assist dispersion in water.

Starch pastes containing amylose, as mentioned above, are not stable and may form gels and precipitates of amylose aggregates. This phenomenon has been described as retrogradation and is clearly undesirable in print pastes. The precipitates are not easily redissolved. Stability can be improved by additions of formaldehyde, probably by formation of hemiacetals.

Amylopectin, by contrast, forms clear, stable solutions, not subject to retrogradation. Chain branching evidently prevents the molecular orientation and regularity of intermolecular bonding necessary to cause gelling and precipitation. When in solution, the amylopectin molecules can be pictured as approximately spherical, with a relatively dense core and flexible, deformable, outer regions of solvated chain branches.

Different native starches have different proportions of amylose and amylopectin, and probably also different degrees of chain branching and r.m.m. distributions, so differences may be observed in paste stabilities, flow and film properties. Measured r.m.m. values range from 2 to 6×10^5 for amylose and 4.5×10^4 to 4×10^8 for amylopectin.

Although starch has certain disadvantages for use as a thickening agent, it does have the advantage of giving high colour yields. This is the result of its aggregation and very limited penetration into textile yarns and therefore the retention of dye on the fabric surface. However, it is usually desirable to reach a compromise between high colour yield, with substantial susceptibility to crush and poor levelness, on the one hand, and low colour yield with good penetration, little crushing and good levelness, on the other. A traditional method of achieving such a compromise was to use a mixture of starch and gum tragacanth.

7.3.2 British gums

An alternative approach to improving the properties of starch has been to bring about structural changes by simple roasting processes.



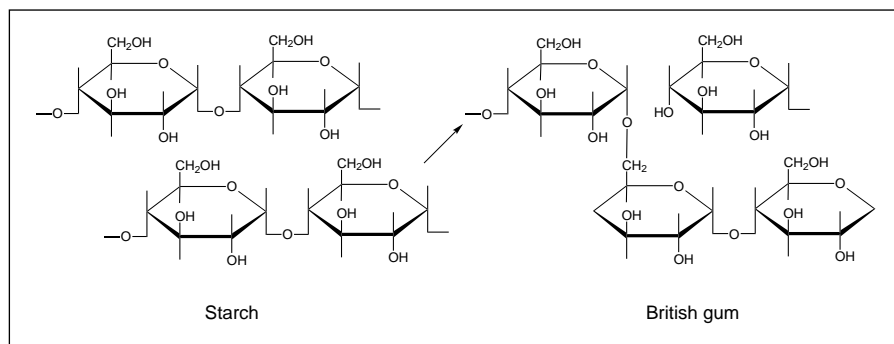
The original British gums were produced by heating batches of dry starch at 135–190 °C, with stirring to achieve uniform roasting, for 10–24 h. The process can be accelerated by addition of trace quantities of acid, and can then be carried out continuously on a conveyor belt. The use of more than trace quantities of acid leads to more hydrolysis and the formation of the so-called dextrans, which are of low r.m.m. and can be used as adhesives.

The significant chemical changes have been shown to be random hydrolysis of 1→4 bonds and the formation of 1→6 linkages (Scheme 7.1). The consequences are increased water solubility, reduction in r.m.m., more highly branched molecules, and some increase in the content of reducing end-groups. A range of products, pale to dark-brown in colour, requiring increasing concentrations for a given paste viscosity, can be blended to give the required properties.

British gum pastes have good stability to alkali and have been used for printing vat dyes. For reducible azo dyes, additions of oxidising agent must be made to avoid destruction of dye. In resist printing, when a high-solids-content thickener is desirable to act as a physical barrier, British gums have often been selected.

7.3.3 Starch and cellulose ethers

The roasting of starch changes its properties significantly, and increased dye penetration results when such modified starches are used in printing. Increased solubility can alternatively be obtained by controlled etherification, with only slight reduction in r.m.m., viscosity and colour yield. A low degree of substitution (DS 0.1–0.3) is sufficient to prevent molecular association, particularly when the substituent is bulky. Ethers are readily produced by reaction with monochloroacetic acid, epoxyethane (ethylene oxide) or dimethyl sulphate in the presence of sodium hydroxide. The first of



Scheme 7.1

these reagents gives the much-used carboxymethyl ether, which is, of course, anionic in character. A concentration of 6% gives a paste of suitable viscosity.

Zonnenberg has described the properties of such starch ethers as ideal in respect of colour yield and solubility [7]. They have been recommended for use in mixtures with galactomannans or alginate, to increase colour yield.

Cellulose ethers of appropriate r.m.m. can also be used, and have been selected for high-speed printing on engraved-roller machines because the paste viscosity is greatly reduced at the moment of printing, and transfer from the engraving to the fabric is more complete than for many thickeners.

7.3.4 Locust bean gum

The carob tree *Ceratonia siliqua* is a leguminous plant that grows on rocky soil and requires little rainfall, but does not produce much fruit in its first 15 years. The Mediterranean area provides the bulk of the world supply, which has been known by the names of carubin, gatto, Tragon, Tragasol and St John's Bread, as well as locust bean gum.

The beans consist largely of pulp (90%) and only 7% by weight of kernels (seed), and the kernel is composed of husk (30%), germ (25%), and endosperm (45%), which is the desired gum. The seeds must be dehusked and split and the germ removed, before the endosperm is ground.

The commercial gum contains about 88% of D-galactomannoglycan with small amounts of other carbohydrates and of protein. It is a linear polymer of 1→4-linked D-mannose units with about every fourth unit carrying an α -D-galactose unit on its carbon atom number 6 (7.3, page 252).

The typical r.m.m. is 300 000, and there is enough crystallinity to require the use of temperatures of 45 °C or higher for complete dispersion in water. Etherification has therefore been used to produce readily dispersed materials.

Because the locust bean gum is a nonionic polysaccharide, pH has little effect on the viscosity over the pH range 3–11. Pastes of useful viscosity are obtained at concentrations of about 2%. Additions of sodium salts have little effect on paste viscosity, but complexes (Figure 7.2) are formed with borates, producing gelling that has been exploited in the two-stage fixation of vat prints.. The borate ions complex with *cis*-hydroxyl groups of two mannose chains to form crosslinks, which are broken in the presence of low-r.m.m. glycols such as glycerol.

7.3.5 Guar gum

Guar gum is chemically similar to locust bean gum (it is also a galactomannan) and like locust bean gum is a very useful thickening agent. The guar plant *Cyanaposis*



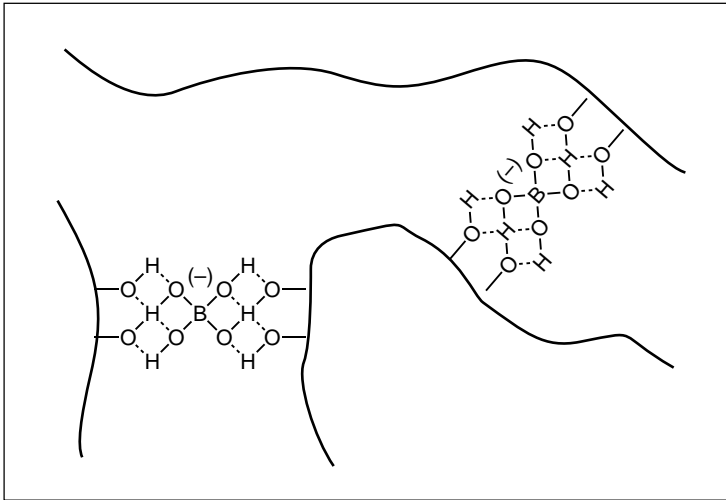


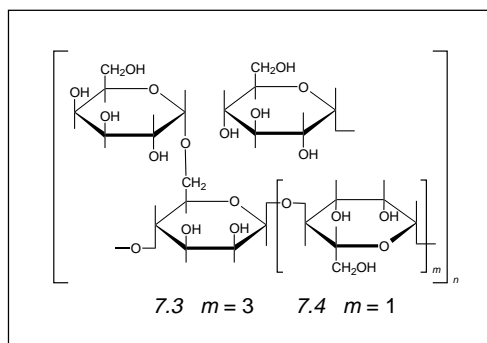
Figure 7.2 Borate dihydroxy complex (diagrammatic)

tetragonolobus is an annual leguminous plant which has been grown for centuries in India and Pakistan for food, and as a cash crop in Texas since 1946. It needs very little surface water and can be used as a rotation crop to improve soil fertility by fixing atmospheric nitrogen, and is therefore of interest in semi-arid regions where less hardy crops perish.

Each bush bears many pods, each containing between six and nine seeds. From each seed, it is necessary to remove the husk and the germ to obtain the endosperm (40% by mass). This is guaran (7.4, page 252), in which the galactose side units are approximately twice as frequent along the mannan chain as in locust bean gum. The r.m.m. has been reported as 220 000.

In contrast to locust bean gum, guar gum can be dispersed in cold water, which is probably because the greater number of side units reduces the amount of molecular association. Although its cold-water dispersibility is a major advantage, dispersion must be carried out with care in order to avoid the formation of lumps. The hydration of the powder should not be faster than the rate of surface wetting. The hydration, and the swelling, are slower in low-temperature water, so that the problem of too rapid swelling and lump formation is greater in summer than in winter. Efficient stirring accelerates the surface wetting, but excessive speed and time of stirring will cause fission of the chains and loss of viscosity. The time required for complete dispersion, and maximum viscosity, is also temperature-dependent; if 30 min is sufficient at 25 °C, it may be necessary to allow 60 min at 15 °C.





Modified products are marketed, for which the swelling is delayed by up to 5 min, allowing wetting and dispersion to be completed before swelling starts. Even safer are the 'add-acid' gums, which can be produced by introducing small amounts of borate, and which swell only when the pH is reduced.

7.3.6 Alginates

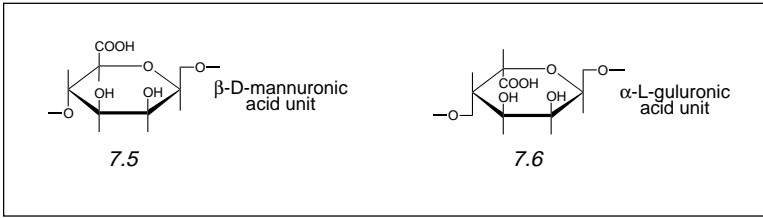
The principal carbohydrate component of brown Phaeophyceae seaweeds is alginic acid. Different carbohydrates, agar and carrageen, are found in the red seaweeds. Some species of bacteria also produce alginates. Extraction of the alginic acid from the brown seaweeds is by digestion with solutions of sodium carbonate. Purification can be accomplished by precipitation as the calcium salt, reconversion to the free alginic acid and neutralisation to give the desired salt.

Commercially produced high-viscosity alginates have r.m.m. values of over 150 000, but lower-r.m.m. materials are also sold. The monomer units are D-mannuronic acid (7.5) and L-guluronic acid (7.6), in a 1→4-linked linear polymer with blocks of β-mannuronide, α-guluronide and alternating copolymer segments. The last-named segments are apparently the most readily hydrolysed. The relative amounts of the three structural blocks vary with species and age of the seaweed, but the typical ratio of mannuronic to guluronic units is 1.5:1.

Sodium alginates have become very important for print paste thickening because of their ready solubility, even after high-temperature fixation treatments. They are especially important for pastes of reactive dyes because the extent of interaction is very small. This is due to the absence of primary hydroxyl groups and to the repulsion of dye anions by the ionised carboxyl groups of the polymer under alkaline conditions.

The viscosity of sodium alginate paste will depend on the r.m.m., concentration, method of preparation (high temperatures should be avoided to maintain the r.m.m.),





shear stress and the presence of other ions. Some high-viscosity products contain a significant concentration of calcium ions, which allow the user to modify the paste properties. The crosslinking effect of the calcium ions increases the viscosity and the pseudoplasticity of the paste, but additions of controlled amounts of polyphosphate (or other sequestering agents) reduce these effects (Figure 7.3).

The stability is good between pH 4 and pH 10, but gels are formed above pH 11.5 and below pH 3.5. Buffered alginates are sold for use in strongly alkaline conditions. Alginate pastes are compatible with a wide range of materials, including starch, cellulose ethers, tragacanth and galactomannan gums.

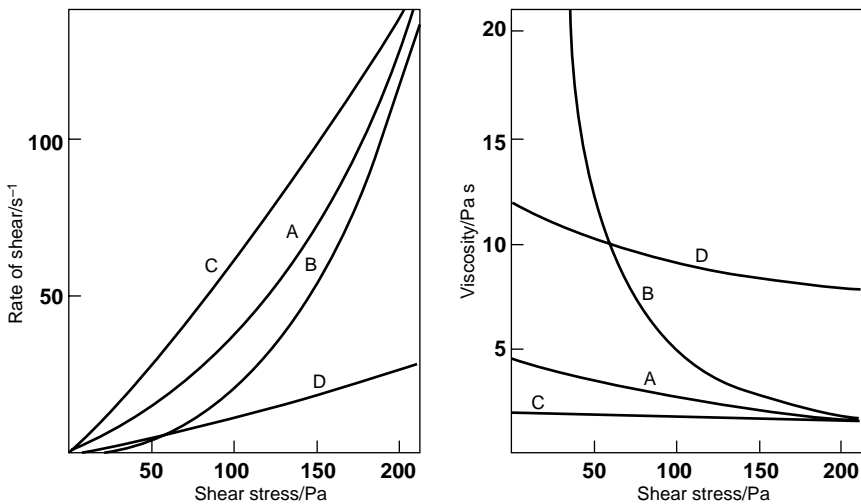


Figure 7.3 Effect of r.m.m., concentration and calcium ions on the viscosities of sodium alginate pastes; A: high r.m.m., concentration 2%, Ca sequestered
 B: high r.m.m., concentration 2%, 12% of alginate as Ca salt
 C: low r.m.m., concentration 6%, Ca sequestered
 D: low r.m.m., concentration 8.3%, Ca sequestered

Commercial materials of high r.m.m. give pastes of suitable viscosity for printing at around 2% concentration, whereas those of low r.m.m. may be used at perhaps 6%.

7.3.7 Gum arabic

Wounds in the bark of acacia trees exude a gum that has interesting properties. In spite of its very high r.m.m. (over 250 000), the polysaccharide in the gum is extremely soluble in water (50%) and shows Newtonian behaviour. Its structure is that of a 1:3 galactan (coiled) chain with numerous side-chains, including glucuronic acid units, of two-, three- and four-unit lengths. Molecular association of such a structure is impossible, so that hydration and solubility are readily achieved and no orientation of the molecule occurs under shear.

Gum arabic has been used as an adhesive more than as a thickening agent, for which purpose concentrations as high as 40% may be required. Mixing with starch is not recommended as the polymer may separate.

Karaya gum (20%) has been used as a cheaper alternative. Crystal gum is a pre-swollen and purified material made from vegetable gums such as Karaya, to be readily soluble and more reproducible in properties than the original gum.

7.3.8 Gum tragacanth

Tragacanth is also an exudate, in this case from *Astragalus gummifer*, and is obtained in the form of hard, translucent plates that swell in water but require boiling, for perhaps 6 h, to produce a homogeneous dispersion. The solids content required is much lower than for gum arabic, and may be as low as 6%. It is also a polyglycuronan, but it is less sensitive to additions of electrolyte than gum arabic and must have a less highly branched structure. An additional reason for its high, pseudoplastic viscosity is the presence of dispersed fibrils of cellulose, which are readily removed by centrifuging.

7.3.9 Biosynthetic gums

Just as the amylase used for desizing is now primarily obtained by the culture of selected bacteria, and the product is superior in many ways to that obtained from malt, so is the biosynthetic production of thickening agents of some importance.

Some species of bacteria produce alginates as extracellular mucilages, but production in this manner has not provided an economic route.

Xanthan gum, however, has been on the market since 1964. This is a cold-water-soluble polysaccharide, with a r.m.m. in excess of 1×10^6 , containing glucose, mannose



and glucuronic acid units in a branched-chain structure. It gives high viscosity at low solids content, is little affected by rise in temperature or addition of electrolyte, and is stable over the pH range 1–11. The micro-organisms that produce xanthan gum can be cultivated on waste carbohydrate material.

7.4 VISCIOUS EMULSIONS

Oil and water do not mix, if enough energy is used to break up one component of the mixture into small droplets, which are dispersed in the other component. Such simple emulsions are unstable, but their stability and ease of preparation can be considerably increased by the incorporation of a surface-active emulsifier. The nature of the emulsifier and the ratio of the volumes of the two immiscible liquids determine which liquid will be dispersed (the disperse phase) in the other (the outer, continuous phase).

Where the dispersed phase forms 70% or more of the whole, the emulsion will have significant viscosity, because work must be done to deform the droplets as they are moved relative to a stationary layer. It can be shown that if the droplets are spherical and of equal size, an emulsion containing 74% (by volume) of droplets requires a close-packing structure. Examination of emulsions under a microscope shows, however, that there are often small droplets in the spaces between the larger droplets, and that deformation from the spherical occurs. This explains how emulsions with 90% of inner phase may be formed.

The droplets range in diameter from 100 to 7000 nm, and the smaller they are the higher is the emulsion viscosity. A useful indicator of particle size is the emulsion colour, which changes from creamy-white to bluish-white as the size is reduced. Viscosity depends on volume ratio, on particle size and also on the emulsifier. Dawson, in an excellent review, has shown that anionic emulsifiers can produce higher viscosities than nonionic emulsifiers, and that this can be understood to be due to the greater mutual repulsion induced [8].

The emulsifier forms a film between the two liquids, reducing interfacial tension. Each molecule of emulsifier contains a region that is hydrophilic and another that is hydrophobic (lipophilic), and it is the balance between the dominance of these regions that determines the relative solubilities of the substance in oil and in water. This hydrophile–lipophile balance (HLB) has been evaluated for many surface-active agents and expressed in a standard manner, over the range of 1 to 40 [9]. Experience has shown that compounds with HLB values of 3–6 stabilise water-in-oil (w/o) emulsions, and those with values of 8–18 are effective for oil-in-water (o/w) emulsions.

Stabilisation can be achieved not only with conventional surfactants, but also with certain finely divided powders, many proteins and natural gums, and some synthetic polymers.



7.4.1 Emulsions for pigment printing

In 1937 it was shown that w/o emulsions could be used to thicken pigment printing pastes. Previously natural polymers had been used, but the prints were dull and stiffened in handle. Albumen was one of the best materials, giving a flexible film with good pigment-binding properties, but it was expensive. By using emulsions of water in white spirit (the petroleum distillate fraction boiling at 150–200 °C, referred to as 'heavy benzene' in the German literature), only the emulsifier remained when the thickener film was dried. Suitable polymer binders (see section 5.2.2) were incorporated as pigment binders and the fabric stiffening could be minimised by selecting a polymer forming a soft film and by restricting the penetration of paste so as not to stick the yarns together.

The use of emulsions with white spirit as the outer phase was unpopular with printers, however, as the cleaning of printing equipment could be troublesome. From about 1950, attention was turned to o/w emulsions and, in spite of the increase in cost due to the larger white spirit volume fraction, they have been developed into the more successful systems. Higher visual depths of colour and fastness properties were important factors.

The larger volumes of white spirit make it more essential to remove the vapour efficiently while drying, in order to avoid the build-up of explosive concentrations in air at the baking stage.

7.4.2 Emulsions for substantive dyes

The successful use of emulsions for thickening pigment printing pastes was followed by application to the printing of a wide range of dye classes. The incorporation of a film-former is necessary in order to prevent removal by abrasion of the dye deposited on fibre surfaces, before fixation occurs. Low concentrations of natural or synthetic thickeners are suitable for this purpose. The viscosity of the aqueous continuous phase is thereby increased, the emulsion stability is improved and the volume of white spirit may be reduced.

Because the prints produced require a washing-off treatment, and the film-former is thereby removed, the extent of viscosity increase due to the presence of film-former may be varied in order to obtain optimum printing properties. When the 'short' flow behaviour of an emulsion paste does not give a satisfactory print the printer may use a so-called 'half-emulsion', in which approximately equal quantities of stock emulsion and an alginate or guar paste are mixed. The 'half-emulsion' also offers the advantages of higher colour yield and faster drying, as compared to those obtained with a 100% natural thickener.



7.5 VISCOUS FOAMS

An alternative to an emulsion of immiscible liquids is a foam of air bubbles in an aqueous outer phase [10]. It is essential to use a surface-active agent and subsequent mechanical action to obtain the appropriate bubble size (about 50 μm diameter), and to control the volume of air in the foam relative to liquid (the blow ratio). The use of foams for the application of finishes [11] and in the dyeing of pile carpets [12] is well established, but their use in printing is more difficult, because less than 100% cover is required. During screen printing the paste is sheared under the squeegee; some is pushed through the screen but some is sheared again and again before it reaches the fabric. The stability of the foam is therefore a critical parameter. The stability, and the viscosity, of the foam can be increased by the addition of a small amount of a thickening agent or of a long-chain alkanol.

The advantages of foam printing are attractive: fabric absorbency is less critical; levelness, depth and handle of the prints are improved; drying costs and effluent BOD levels are reduced. Printers have, however, found that there are disadvantages with shade matching and longer downtimes, as well as the need for specialised equipment [13]. Some success has been achieved in India with a system that requires only a paddle stirrer [14]. It may be that application by block printing gives minimum difficulties. Greater use of this highly attractive route will depend on the solution of the reproducibility problems.

7.6 SYNTHETIC-POLYMER THICKENERS

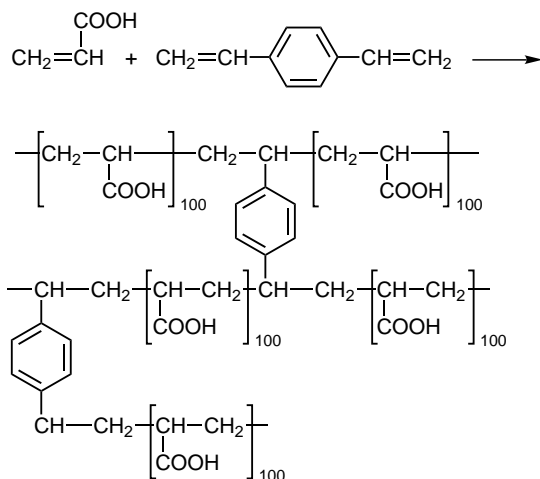
Uncertainties concerning the availability and price of natural thickening agents, and the effect of increasing petroleum prices and environmental protection measures on the use of emulsions, encouraged the development of synthetic agents.

One material that has been used to a limited extent is poly(vinyl alcohol), especially on nylon fabrics. The preparation of the paste in bulk requires time and care, however, and concentrations up to 20% may be required.

Copolymers of acrylates have been used more widely. Relatively low-cost copolymers of methacrylic acid and ethyl acrylate, for example, give low-viscosity dispersions in water in which the molecules are randomly coiled. On addition of alkali, the carboxylic acid groups are ionised and the resultant mutual repulsion of negatively charged centres causes extension of the polymer chains and substantial increases in viscosity. The viscosity obtained, however, is critically dependent on the amount of alkali added. Verbrugge has shown that the fall in viscosity is a consequence of the polymer going into solution, as a result of the solvation and intermolecular repulsion of the carboxylate ions [15].



High viscosity is obtained with copolymers of optimum ratio between acid and ester units, but the viscosity is too sensitive to pH for industrial use. The molecules can be prevented from going into solution, however, by introducing a small number of crosslinks, for example, by incorporating a bifunctional monomer. Berlenbach has described the production of a thickening agent by copolymerising 1 mol acrylic acid and 0.01 mol divinylbenzene (Scheme 7.2) [16].



Scheme 7.2

Polymers with similar properties have been produced from maleic anhydride and an olefin, crosslinked with a diamine [17].

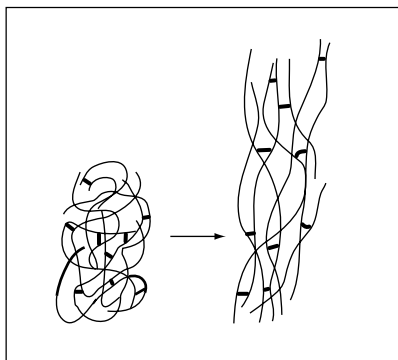


Figure 7.4 Chain straightening and swelling of a crosslinked poly(acrylic acid) on neutralisation

Such products are believed to consist of bundles of polymer chains, held together by the crosslinks. The dry materials are powders that swell in water, and are not readily dispersed unless the particles are pre-wetted in a nonswelling liquid, but swell even more powerfully when neutralised (Figure 7.4). One successful commercial product [18] is a liquid dispersion of acrylic polymer particles in a hydrocarbon solvent. It has a high solids content (50–60%) but its mobility is high, and when it is stirred into water a viscous paste is produced. The fully swollen molecular bundles may be sausage-shaped



and of substantial size, with large numbers of water molecules immobilised within and around them. Consequently high viscosities are characteristic for solutions of low solids content, and 1% pastes may be used for printing. Such polyelectrolyte thickeners are used to replace (completely or partially) emulsions in pigment printing, with only limited increases in fabric stiffness. Because they behave like emulsions, the two types of thickener have been called 'dispersion thickeners'. The swollen particles, of similar size to emulsion droplets, can be considered as a dispersed phase of water molecules, held by the polyelectrolyte, within a small continuous phase of mobile water. The ionic charge on the particles can be large enough to immobilise almost all the water molecules, and the paste then has the consistency of a gel. Slight shear, such as that exerted by stirring by hand, can introduce sufficient energy to overcome the bonding energy of the water sheath, and the paste flows.

The polyacid is usually neutralised with ammonia so that, during the drying and baking of the pigment print, the free acid is largely re-formed. A print with higher wash fastness is obtained than if neutralisation with a nonvolatile alkali, such as sodium hydroxide, had been employed. The presence of free acid during baking also has the consequence that the catalyst that is normally required for binder crosslinking can be omitted.

The use of polyelectrolyte thickeners in print pastes containing dyes rather than pigments is less attractive because of their sensitivity to electrolyte content. Even the electrolyte in a conventionally standardised disperse dye can cause a substantial drop in viscosity. By replacing the anionic dispersing agent in disperse dye formulations by nonionic products, however, the dye manufacturers have been able to reduce this problem to acceptable proportions [19].

When suitable dyes are used, and the techniques for producing print pastes of reproducible viscosity are mastered, the synthetic thickeners are found to give significantly higher fixation and colour yields, with disperse dyes on polyester fabrics, than natural polymer thickeners. The principal reason is likely to be that the thinner the film of thickening agent, the greater is the transfer of dye from the film to the fibre. This will be especially true for the low-humidity, high-temperature conditions used for fixation on polyester fibre (see Chapter 8).

The improved dye fixation may, however, be accompanied by poor resistance to abrasion before fixation occurs. A compromise may therefore be dictated, with addition of a smaller polyelectrolyte or a film-forming dispersion (perhaps a polyacrylate) to improve the abrasion resistance.

If high dye fixation can be obtained, it may be possible to omit the final washing-off process. This will not normally be the case, and the removal of thickener, in addition to unfixed dye, will be necessary. By using sodium hydroxide, rather than ammonia, to



neutralise the thickener, a faster and more complete removal is obtained. Soft water is also highly desirable.

In the case of dyes other than of the disperse class, the electrolyte effect is more serious, but satisfactory results can be obtained by selection of the best polymer [18] and increasing the concentration of thickener. The fixation of reactive dyes has been found to be increased when alginate thickeners have been replaced by synthetic products. It is unwise to use ammonia to neutralise the polyacid when printing reactive dyes as loss of the ammonia in drying can reduce the fixation.

The effect of electrolyte content on viscosity is greatest with the thickeners of large molecular size and correspondingly low solids content. The charge on the molecular surfaces is partially neutralised by counterions and fewer water molecules can therefore be held.

7.7 PRINT PASTE RHEOLOGY

7.7.1 Viscosity

An early student of rheology (the science of flow) was Sir Isaac Newton, who showed that for each simple liquid there is a constant coefficient of frictional resistance to flow, which we call its viscosity. An understanding of this resistance to flow is most simply obtained by considering the movement of liquid between two flat plates, when the top plate is moved. The liquid is sheared, as shown diagrammatically in Figure 7.5.

The shearing force (F) which gives the top plate (of area A) a velocity v relative to the lower plate, is dissipated as heat in overcoming the internal friction between the imaginary thin layers of liquid. The layer adjacent to, and in good contact with, the top plate also moves at velocity v , but intermediate layers move more slowly, and the lowest layer remains stationary.

The viscosity, η , of the liquid is defined as the ratio of the applied shearing stress S ($= F/A$) to the rate of shear produced, D ($= dv/dx$), also known as the velocity gradient (Eqn 7.1):

$$\eta = \frac{S}{D} \quad 7.1$$

The viscosity of a liquid that requires a shearing stress of 1 N m^{-2} to produce a rate of shear of 1 s^{-1} is 1 Pa s (10 poise).

The viscosity of liquids is often determined by measuring the velocity of flow through a capillary tube, the calculation being based on a simple extension of the Newtonian analysis given above. The velocity will be high in the middle and low near the walls, a phenomenon readily appreciated by anyone who has rowed against the



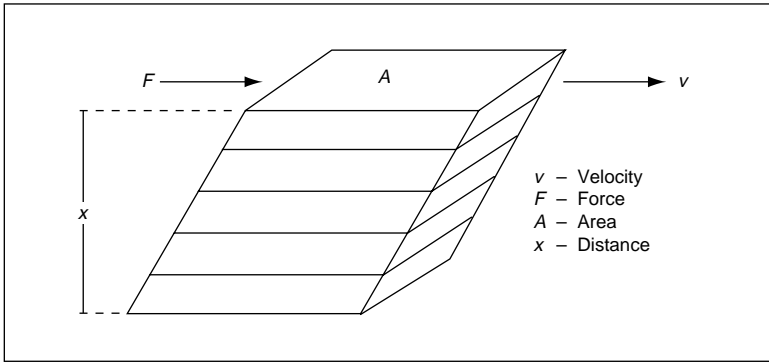


Figure 7.5 Diagrammatic representation of a shearing force producing movement of (imaginary) layers of liquid, relative to their adjacent layers

current in a river. Further, the velocity gradient will not be constant, but high near the walls and zero in the middle. For simple Newtonian liquids such as water, glycerol, sugar solutions and many oils, the viscosity is independent of the rate of shear. Typical print pastes are described as non-Newtonian, because their viscosity changes as the rate of shear is changed. Measurement of their viscosity, therefore, is not so straightforward. Information is required, nevertheless, because the viscosity of a print paste during the shearing that occurs in the printing process will determine the quality of the print.

7.7.2 Viscometers

If viscosity measurements are required only to assess the reproducibility of batches of a given thickener or print paste, then any simple, convenient type of viscometer may be satisfactory. When problems, new products or procedures are investigated, however, an instrument that can provide a more complete picture of flow properties is highly desirable.

Instruments of several types may be used [20], but in many respects the cone-and-plate type is especially suitable. The principal features of such a viscometer are shown in Figure 7.6.

A small sample of paste is placed on the centre of a flat, temperature-controlled plate (A), which is then raised to bring it almost into contact with a cone (B). The angle between A and B (α) is small (typically 0.3°) and the size of cone is chosen to be suitable for the conditions of measurement; it may be of 1–5 cm radius (r).

A motor and gearbox provide a range of precisely known velocities, and the drive shaft incorporates a torque transducer giving an electrical output that is proportional to

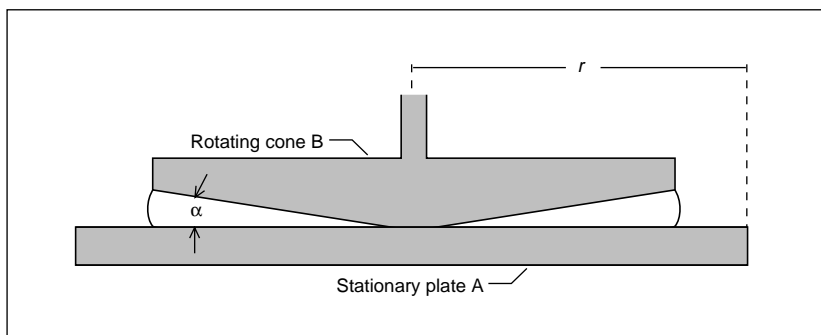


Figure 7.6 Diagrammatic illustration of the cone-and-plate viscometer

the force required to maintain the chosen velocity against the viscous drag. From the velocity and the known dimensions of the cone, the constant velocity gradient is obtained, and the shear stress is calculated from the torque and the surface area of the cone. The small space between plate and cone must, of course, remain filled and not be emptied by centrifugal force. So-called flow curves, of rate of shear against stress, can therefore be plotted, and provide a most useful picture of the behaviour of polymer solutions, dispersions or melts. The ratio of shear stress to rate of shear for a particular shear is known as the apparent viscosity.

A more complex instrument, of similar pattern, which is often called a rheogoniometer, also measures the force generated normal to the cone by viscoelastic liquids. Fortunately, these forces are not significant for most print pastes.

7.7.3 Non-Newtonian flow

From the flow curves thus obtained, it is found that the behaviour of viscous liquids can be classified into five categories, shown diagrammatically in Figure 7.7. A few materials, such as gum arabic pastes, poly(vinyl alcohol) solutions, and silicone oils, are essentially Newtonian (curve A in Figure 7.7), with viscosity independent of shear. Most print pastes show shear-thinning properties (B), with a significant reduction in apparent viscosity as the shearing stress is increased. The change is reversible, the viscosity increasing immediately shearing is reduced. A significant number of pastes do not flow at all until the shear stress exceeds a minimum value, known as the yield value (curve C in Figure 7.7). Beyond this value, they may show either linear or nonlinear flow properties. The former have been called Bingham systems, after E C Bingham, who defined the term 'plastic viscosity' as the ratio (shear stress – yield value):rate of shear. The concept of plastic viscosity has been extended to shear-thinning print



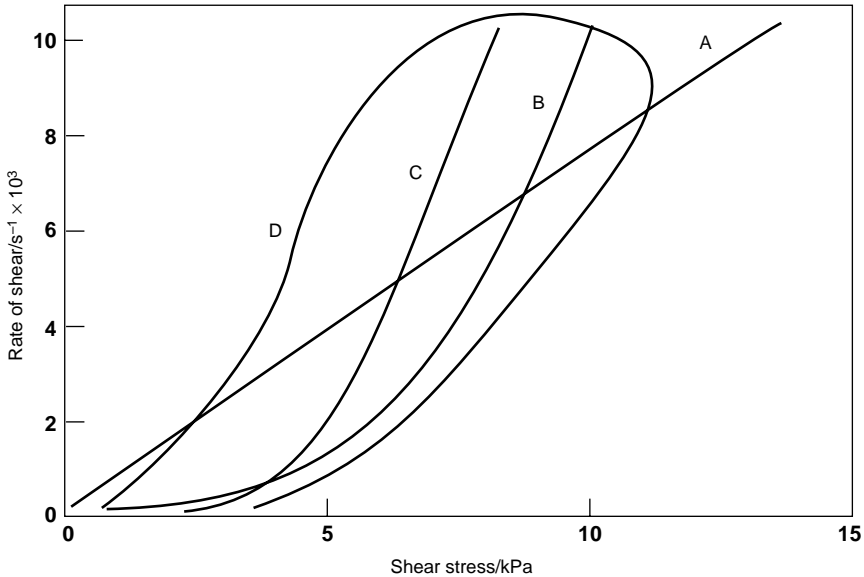


Figure 7.7 Typical flow curves demonstrating behaviour of viscous liquids

pastes, with flow curves that approach linearity at high shear, by extrapolating the linear section of the curve back to the stress axis to define a yield value.

A fourth type of behaviour, found in pastes with high pigment concentrations, has been called dilatant, but is better described as ‘shear thickening’ to avoid the assumption that volume expansion necessarily occurs. This is the phenomenon seen on wet sand, when pressure causes particles to touch and the friction between particles prevents their movement into expanded spaces. Free liquid is drawn into these spaces, making the system look dry.

Finally, there is the phenomenon known as thixotropy, shown by gelatine solutions and bentonite suspensions, for example (curve D). In this case the measured values of viscosity depend on the duration of shear as well as on the rate of shear, and increased resistance to shear is observed after a long rest time than after shorter rest times (Figure 7.8). The probable explanation is that intermolecular bonds are broken by shear and slowly re-formed after shearing ceases.

The distinction between shear thinning and thixotropic behaviour is therefore clearly defined, although superficially they are similar and the term ‘thixotropic’ has sometimes been used to cover both categories. Shear thinning is believed to occur:

- when the liquid flow draws long polymer chains, initially randomly oriented, into closer alignment (as in fibre extrusion) and therefore they move more easily, relative to one another



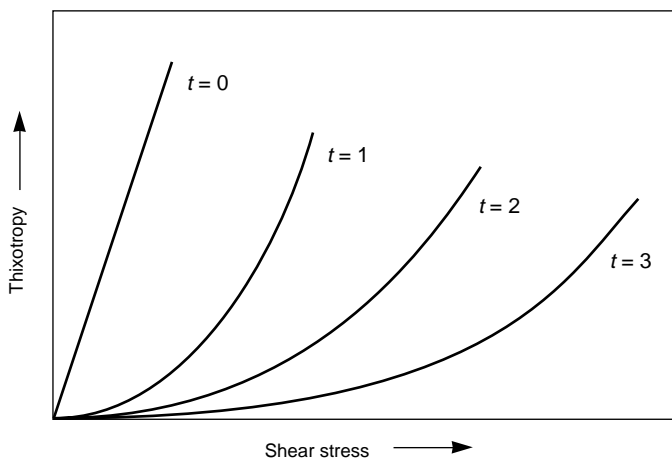


Figure 7.8 Flow curves for a thixotropic bentonite suspension immediately after agitation and after different setting times

- when large droplets, particles or solvated molecules, approximately spherical in shape, are deformed by shearing stresses to cigar-like shapes
- if the solvent sheaths held by polymer molecules are torn away by shearing forces and the dimensions of the packaged molecules therefore reduced.

If the molecules in a thixotropic paste are able to form intermolecular bonds very rapidly, however, the behaviour may resemble shear thinning because viscosity measurements cannot be made instantaneously. Muller has reported changes in apparent viscosity of synthetic thickenings, at a low, constant rate of shear, occurring over a period of 0.5 s [21]. Using sophisticated instrumentation, it is now possible to measure differences in the rate of recovery of viscosity, after the shear occurring in the printing operation, which could result in significant differences in print quality. It is necessary to study the changes occurring over times as short as 0.01 s.

The amount of data available on the rheology of printing pastes is limited and its interpretation is difficult. The collection of data, and correlation with printing results, could be very worthwhile. The importance of the difference between pastes with good 'flow' and those with a yield value is recognised by the practical printer. Pastes that do not flow under gravity from a paddle or stirrer, remaining on the paddle or falling off in lumps, are described as 'short'. This type of paste shows a yield value on flow curves and may give sharp fine lines, but may not be suitable for blotch printing.

Specific examples of the flow properties of thickeners are shown in Figure 7.9, which shows the substantial shear thinning of a poly(acrylic acid) (Carbopol) paste.



The significance of the r.m.m. of the polymer is seen in Figure 7.3, which shows the shear-thinning effect of orientation on a long-chain alginate. The shorter-chain alginate shows almost Newtonian behaviour, unless the concentration is high. The effect of molecular interaction is seen in the much higher viscosity, at low shear, of the paste containing unsequestered calcium ions. Clearly, high shearing stresses can overcome the bonding forces and separate, then orient, the polymer chains.

The concentration of thickening agent often has a significant effect on the character of the paste flow, more energy being required to separate and untangle the polymer chains in the more concentrated solutions. Figure 7.10 shows the effect of increasing concentration in the case of locust bean gum pastes.

Additions of dyes and auxiliaries may, of course, change the rheology of a paste. Jullander has reported increases in apparent viscosity of cellulose ether pastes on addition of three direct dyes [22]. The extent of molecular interaction was related to the amount of van der Waals bond formation expected. Kassenbeck and Neukirchner were unable to detect viscosity differences between alginate pastes containing CI Reactive Blue 99 and CI Reactive Orange 12, but differences in jet-flow properties of the pastes appeared to be related to the spread that occurred in rotary-screen printing [23].

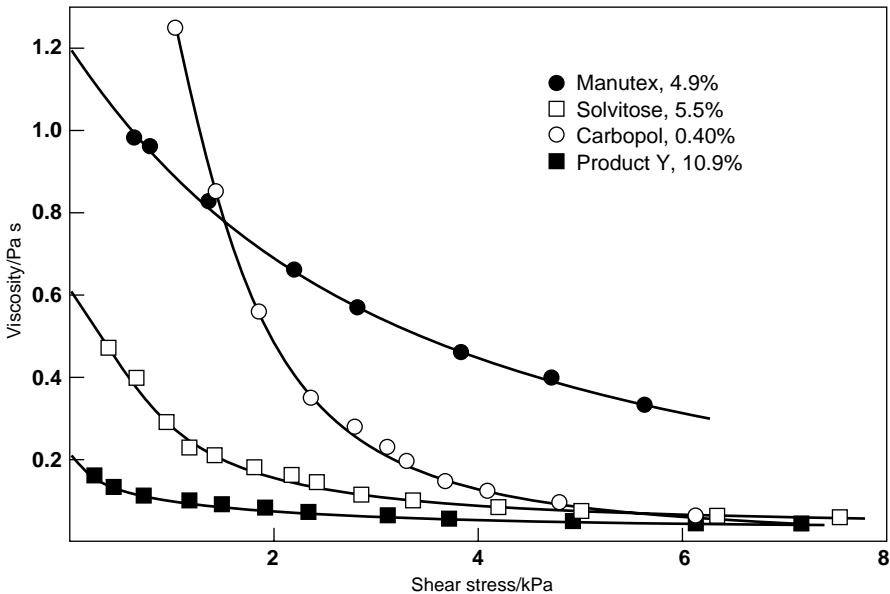


Figure 7.9 Thixotropic behaviour in pastes, increased resistance to shear being exhibited after longer rest times

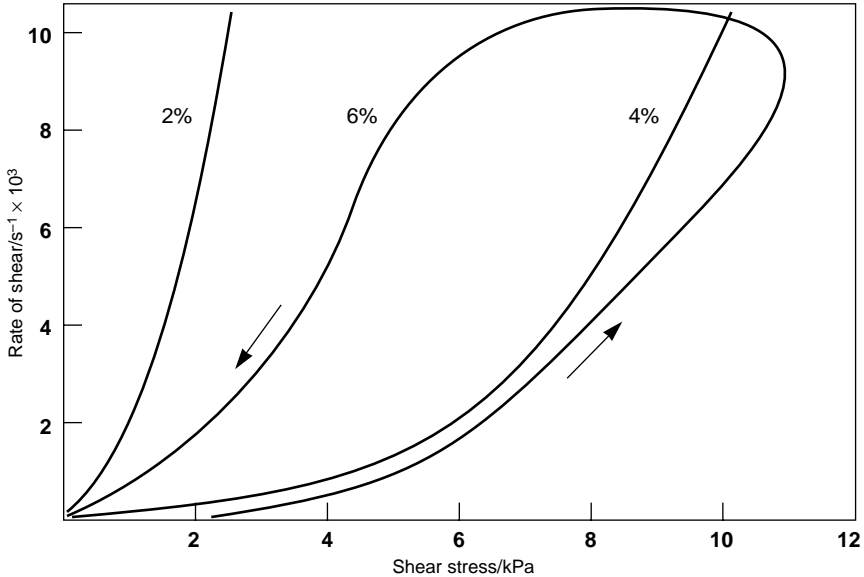


Figure 7.10 Effect of concentration on the flow of locust bean gum pastes

7.7.4 Paste flow in engraved-roller printing

For all printing processes, it is necessary to know what factors control:

- the volume of paste applied
- the penetration
- the spread,

as these are the parameters that together determine the sharpness of mark and the levelness of the print.

The print paste viscosity is obviously the major factor but, as the viscosity changes under changing shearing stresses, we need to know what stresses are applied during the printing process. No single measurement of viscosity, or concentration of thickening agent, will serve to characterise a paste or predict its behaviour in all respects.

Higginbotham was the first to analyse the relationship between printing behaviour and the effects of shear [24]. He argued that it should be possible to use the extent of spread as a measure of print paste viscosity at the moment of printing. Specifically, if three pastes made from different thickeners gave the same spread, then they must have had the same viscosity. The assumptions were:

- that pressure on the printing roller forced the fabric into the paste-filled engraving and the paste was therefore sheared as it moved through the capillaries of the fabric structure
- that the volume of paste applied did not change when a paste of different viscosity was used
- that spread occurred only in the short time of pressure application
- that if this time were constant, then the distance travelled along the capillaries (the spread) was a measure of viscosity.

Smooth curves were obtained when measured spread values of printed lines were plotted against concentration of thickening agent, for tragacanth, Nafka crystal and arabic gums (Figure 7.11). The concentration of each gum that would give a selected value of spread was therefore found. A cone-and-plate viscometer was used to obtain the apparent viscosity of the three pastes over a range of shear stress. Figure 7.12 shows the curves for pastes giving a spread of 0.02 cm when printed as stripes on a cotton poplin fabric. The curves intersect at a point corresponding to a shear stress of 400 N m^{-2} ($4000 \text{ dyne cm}^{-2}$).

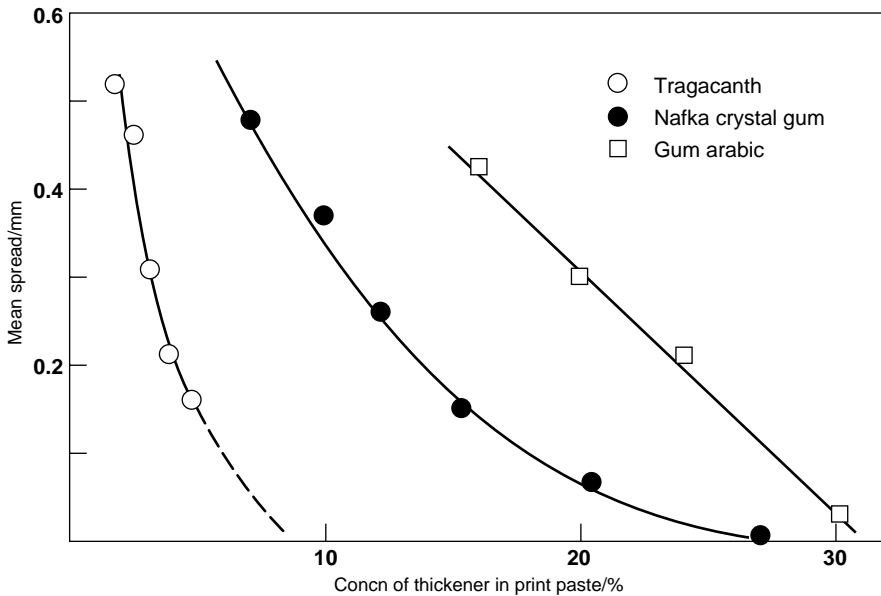


Figure 7.11 Spread of printed stripe at different concentrations of three thickeners

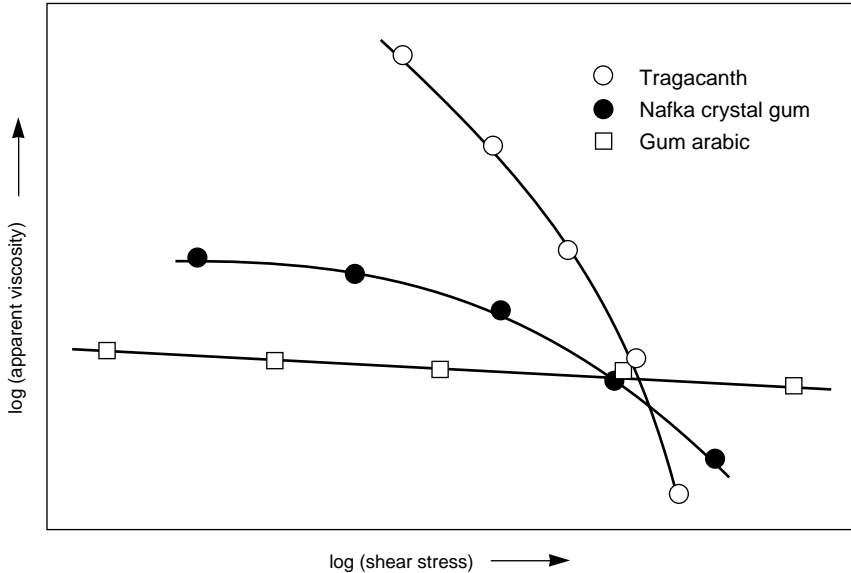


Figure 7.12 Viscosity as a function of shear stress for pastes giving equal spread

Similar values were obtained when the exercise was repeated for spread values of 0.04 and 0.005 cm, and the mean value of shear stress was found to be 450 N m^{-2} . Measurement of viscosity at this shear stress was therefore recommended, to predict the level of spread to be expected.

Subsequently, however, when the experiment was repeated using different thickeners, no correlation between spread and viscosity was observed [3]. Cheslett [1] also failed to obtain the expected intersection of rheograms when printing on polyester. The explanation in both cases was that the volume of paste transferred from engraving to fabric was significantly reduced when viscosity was increased. The results that Higginbotham obtained were probably valid for his conditions, but his assumption that the volume of paste applied was a constant is not generally valid.

It has long been known that the sharpness of the printed mark is improved by printing at high speed. This is clearly because less paste is transferred in the shorter contact time. By using the Washburn equation for liquid movement in a capillary, it can be shown that the transfer, penetration and spread of print paste could be due primarily to capillary forces. The value of the forces is certainly large enough to produce a substantial fall in the viscosity of shear-thinning pastes. The pressure that must be applied to the printing roller may also shear the paste as the fabric is forced into the paste, but may only be required to bring the paste into contact with the fabric capillary surfaces.

Sometimes, especially when a blotch has been printed, paste is visible on the fabric surface and is not uniformly distributed. Some of this paste is removed on the following roller (part of the crushing effect) and an improvement in levelness observed. Paste on the fabric surface adheres to the engraved roller as well as to the fabric and, as the roller continues its rotation, is stretched. Stretching produces ‘fibrillation’ of the paste (Figure 7.13); then the threads of paste break and collapse into small mounds of paste on the fabric surface. Higginbotham observed that his single-colour prints were only smooth if the viscosity at low shear (10 N m^{-2}) was below 3 Pa s , so that flow and levelling occurred.

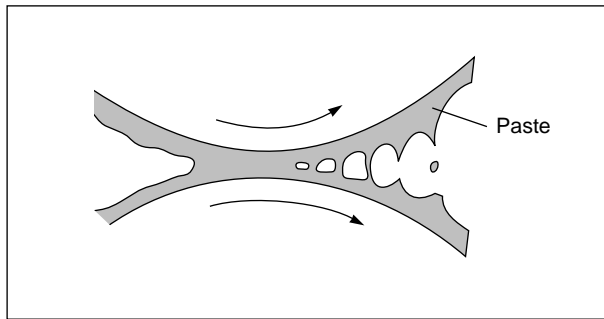


Figure 7.13 Fibrillation of paste between separating surfaces

Schmidt [25] and Kassenbeck [26] have examined the thread-forming properties of print pastes, and it has been suggested that the tack values, measured by paper printers, are probably related to this phenomenon. It is not yet clear, however, what is the best measure of this property or how it can be correlated with printing behaviour.

Summing up, it is clear that the viscosity of a print paste is usually changed by shearing forces, both under the doctor blade and as it enters the fabric. When the paste viscosity has been reduced and good contact with the fabric established, capillarity forces are probably dominant. The time available will often be too short to empty the engraving, however, and the paste between the fabric surface and the roller surface is split between the separating surfaces. This splitting occurs with the production of threads of paste that break and leave a non-uniform deposit on the fabric surface, resulting in a ‘mealy’ appearance of the print. This phenomenon is a greater problem for the paper printer, who uses a measurement of tackiness to control his ink formulation.

7.7.5 Paste flow in screen printing

Dowds has pointed out that the printer is usually left to manipulate the viscosity, squeegee setting and printing speed to obtain a satisfactory print, because there is no complete analysis of the screen-printing process [27]. He made a useful contribution himself, by reporting the volumes of paste applied under specified conditions, showing that this volume may be increased by a factor of five by reducing the squeegee angle. Japanese workers took Dowds' approach further and found that the volume applied can be related, at constant printing speed, to squeegee angle and size of the pressure zone by Eqn 7.2 [28]:

$$V = KB^{0.4} \cos A^{1.6} + C \quad 7.2$$

where B is the base length of the squeegee, A is the squeegee angle and K and C are constants.

In early work at UMIST, the volume applied was related to the dimensions of the screen mesh fabric, and the flow rates of pastes, flowing through the mesh under constant pressures, were measured [29]. Boyacigiller was the first to report measurements of the pressure profiles under squeegee blades, using apparatus in which the mesh fabrics were moved under fixed squeegees, as in a rotary screen [30]. Glastra [31] and Cropper [32] were later to confirm that the pressure profiles were consistent with the theory developed by Fuller to describe the pressures in hydraulic bearings [33].

Several workers have attempted to relate the volume of paste applied to the printing variables. The most recent [34] uses a multifactor regression analysis to solve a polynomial equation shown to relate the volume applied by a rotary screen to four variables: speed, load on squeegee, level of paste and viscosity at 1312 s^{-1} , when the mesh, squeegee type and substrate were held constant. Application of this approach can lead to the specification of squeegee load required to reproduce a given volume applied. Guion has shown that pastes giving prints of similar sharpness have the same viscosity at a shear rate of 20 s^{-1} [35].

The essential basis for an understanding of the process is therefore available. Whatever the squeegee type, whether moving or stationary, hard or flexible blade or rotating rod, paste is collected under the squeegee and pressure is developed because the paste cannot escape, except through the open holes of the screen mesh. The higher the speed and viscosity and the smaller the squeegee angle, the higher is the pressure that is developed. The time of pressure application is, of course, shorter at higher speed and also shorter for hard vertical squeegees than for flexible or large-diameter squeegees, forming a small angle with the screen.

The pressure developed under the squeegee may be just sufficient to fill the screen



pores and force the paste into contact with the substrate. Capillarity forces will then draw some of the paste from the screen pores into the fabric. The volume applied under such conditions may be less than the volume filling the mesh of screen pores. If the mesh is large, the viscosity low and a large, high-pressure zone squeegee is used, however, much more than one volume of the screen pores is applied (if the substrate is able to absorb such a volume).

The evidence is that the first stage of each printing cycle is the filling of the screen pores. Some pressure is required for this to happen and, on some automatic flat-bed machines, a flood stroke of the squeegee can be used, while the screen is suspended, to do this. A longer time is then available in the actual printing stroke for paste to be forced through the mesh. The time of pressure application in the flood stroke operation must be short (perhaps 0.01 s) because premature passage of paste through the screen does not occur. If it did, it would cause smudging. The continuous application of small pressures does produce flow, even through fine-mesh screens [24].

The second stage of the cycle occurs when the substrate is brought into close contact with the underside of the paste-filled screen. A small rise in pressure, overcoming the forces of surface tension, brings paste into contact with the substrate and, if the viscosity of the paste is low enough (having been sheared), it moves rapidly into the capillaries of the substrate.

The capillarity forces can be calculated for any particular situation. A fine-mesh nylon screen (186 mesh) with pores of 40 μm radius (r_1) would lose liquid to a cotton fabric substrate with interfibre capillaries of 15 μm mean radius (r_2) as a result of the net capillary pressure P given by Eqn 7.3:

$$P = 2\gamma \left(\frac{1}{r_2} - \frac{1}{r_1} \right) = 10(0.6 - 0.25) \times 10^3 = 3.5 \times 10^3 \text{ N m}^{-2} \quad 7.3$$

where γ is the surface tension of the liquid. The effective force would be greater during the short time during which the pressure under the squeegee was higher than the capillary pressure of the liquid in the screen pores.

The Washburn equation can be used to find the distance that the paste would move into the fabric capillaries, within the time available. If the squeegee pressure zone was 5 mm across and the printing speed 60 m min^{-1} , the time available would be 5×10^{-3} s. Paste of viscosity 0.1 Pa s would move 0.12 mm into capillaries of 15 μm radius, and this would be sufficient to empty the screen pores if there were at least 10 interfibre capillaries for each screen pore.

When paper of low absorbency is screen-printed, it is commonly observed that the paper is darker in areas between, rather than under, the screen holes. This must also be a result of capillarity forces, drawing paste into the smaller spaces.



After transfer to the substrate, spread into the substrate will continue until absorption of water raises the viscosity to a level at which spread is very slow. In the case of some low-solids-content pastes, water may be drawn into capillaries more strongly than it is held by the thickening polymer, with excessive spread of dye.

The final stage of the process starts when separation of screen and substrate causes extension and splitting of the paste. Schmidt was the first to measure the length of thread that can be drawn from print pastes under standard conditions [25]. More recently, Kassenbeck and Neukirchner have examined the dimensions of jets of moving paste to compare the tack of different print pastes [26]. No clear understanding of the phenomena, or correlation with printing behaviour, has yet emerged.

7.8 PRINT PASTE PRODUCTION

The preparation of print pastes requires great care, and the attention to reproducibility of quantities and conditions. Printers usually prepare thickener pastes in advance of actual requirements, in order to allow cooling, escape of trapped air and completion of swelling. The colorants and chemicals are then added to these pastes later. Now that easily dispersed thickening agents are more readily available, some printers have adopted the very different approach of making up a final print paste in a single operation, directly from raw materials. This would not usually be economical in labour for the larger printing units, and the risk of having printing machines waiting for pastes would be increased.

As already indicated (section 7.2.4), the selection of thickening agent may be determined by its ease of dispersion and the equipment available. Natural gums require pre-swelling and, like starches, boiling in a double-walled heating pan with constant stirring. Powerful, slow-moving stirrers are used, which ensure thorough mixing without dragging air into the viscous paste. Where large quantities of starch pastes are required, they can also be produced in continuous-action vortex-type blending and heating units.

The thickener thus produced is likely to contain a few lumps of imperfectly dispersed thickening agent and insoluble impurities that must be removed before printing. It is good practice to strain the thickener before addition of dye. This can be done by pumping it through a set of wire mesh sieves, of increasing fineness, during transfer from boiling pan to storage tank.

A typical procedure for the preparation of thickener from gum tragacanth, in flake form, illustrates the extreme requirements of time and attention. The solid flake (70 parts) is stirred with 1000 parts of cold water and allowed to swell for 1–3 days, with occasional stirring. The mixture is then raised to the boil, in a jacketed and stirred pan, and held at the boil until solution is obtained (at least 5 h). After cooling, the paste is bulked to 1000 parts and strained.

The readily dispersed thickening agents, for example, starch and locust bean gum



ethers and the alginates, can be simply sprinkled into cold water, with dispersion assisted by high-speed stirring. The stirrer must be of a size and design that moves the whole mass quickly enough to disperse aggregates before significant swelling occurs. Addition of the dry thickening agent should be at a rapid but controlled rate, so that lumps will break down almost immediately. An hour or more is required for swelling to occur and maximum viscosity to be attained.

When the thickening agent swells very rapidly, it can be difficult to avoid the formation of lumps unless special techniques are used to obtain dispersion. This is the case for synthetic thickening agents, which are therefore often purchased as liquid concentrates. The essential step in the preparation of such a concentrate is the initial dispersion of solid powder in a nonswelling liquid. For example, a poly(acrylic acid) (15 parts) can be stirred into white spirit (30 parts) containing a dissolved water-in-oil emulsifier (5 parts of sorbitan mono-oleate). Water, containing the alkali to neutralise the poly(acrylic acid), is then added steadily, with stirring. Finally, the total amount is made up to 100 parts with a hydrophilic surfactant (4 parts, nonionic type, HLB about 15), which ensures rapid wetting when the 15% concentrate is diluted to approximately 1% in the print paste. This encapsulation of thickening agent within a hydrophobic coating produces a low-viscosity concentrate that is easy to handle and already contains the alkali required to produce the full viscosity; only dilution is required to increase the viscosity.

A stock oil-in-water emulsion thickener is readily made, using a high-speed stirrer to disperse 800 parts by mass of white spirit into 190 parts of water containing 10 parts of emulsifier.

From weighed quantities of a stock thickener, print pastes are made by stirring in the required auxiliaries and colorants, as solution, dispersion or solid, according to the amount of water required and the solubility of the materials added. Reactive dyes can be sprinkled into the thickener, with high-speed stirring, provided that their physical form and solubility are suitable and time can be allowed for dissolution to take place.

7.9 COLOUR SHOP ORGANISATION

In order to obtain maximum efficiency in the colour shop, it is usual to pre-prepare standard colour pastes. Provided that the pastes have adequate stability they can be prepared in large quantities and stored in containers equipped with large-bore taps. Print pastes may then be made up quickly and conveniently by weighing the required amounts of pastes into tared tubs on a balance that moves on a rail track between the stock containers. This final stage can be automated for maximum speed and reproducibility. It is good practice at this stage to strain the paste through a fine-mesh sieve into a clean tub within an evacuated chamber.



The particular systems used are selected according to local requirements and tradition. For pastes of vat dyes, for example, it has been common practice to make concentrated standard pastes and a standard 'reduction' paste, with which to reduce the dye concentration. A range of concentrations can be obtained by mixing in ratios of 1:2, 1:3 and so on, known as 'reductions'. Traditionally, pastes were measured out and mixed by volume but, provided reliable balances are available, it is now more convenient to measure by mass.

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