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BINDERS FOR PAPER COATING : STARCHES, PROTEINS AND LATICES

by

Nils-Olaf Bergh

ABSTRACT

There are many chemicals, both natural and synthetic, which are used for surface application of paper and board. In this overwiev shall the use of starch and protein be discussed as representatives of products arriving from renewable resources and the use of latex as the representative of products arriving from chemical synthesis. Starch is used for coating of paper both in combination of pigments - coating colours, and for surface application in size press, film press or other application units. As the influence of the starch properties - both from the chemical and from viscosity point of view - is of great importance for the runnability of the machines and the paper quality, will starch quality be discussed to a great extend. The influence of starch quality on the rheological properties of coating colours of the different types of coating colours will thereafter be discussed. Protein and latex are mainly used as binders in coating colours. The influence of the chemical and physical properties of these binders on the pigment - binder interaction and the subsequent paper properties will be discussed as far it is possible from a general point of view.

INTRODUCTION

Nature has shown how the principles of binding can be used and how different binder systems work. For example molluscs produce binders to anchor their shells to rocks. The cells in our bodies are in principle held together in much the same way as a stamp is glued to an envelope. Bees and swallows use binders too to hold together cellulosic structures in building their nests. The only problem we have in using more of these techniques of nature is the very costly industrial processes which would be needed.
However Nature has shown us the two main criteria for efficient binding - adhesion and cohesion.

Since bonding strength increases as the bonding area increases, it is essential that the maximum area of substrate is covered and that the binder has good *adhesion* to the substrate. For good *cohesion* a technical binder should remain in a "fluid" form during application to ensure that it covers as much of the surface of the substrate as possible. The binder is then converted to the solid state by evaporation of its solvent or by chemical reaction. In the case of paper coating binders the solvent is usually water and the binding process is completed by evaporation of the water in the drying section.

Coatings can be divided into two categories - pigmented and non-pigmented. Coating without pigment simply means the placing of the coating material onto the paper, where it should adhere to the surface when dry. Where pigmented coatings are concerned the binder needs to fulfil a wider range of functions. It must :

- Bind the pigment particles together
- Bind the pigment to the paper substrate
- Give the coating mix the optimum rheology
- Control the rate of water desorption of the coating colour
- Improve certain paper properties such as stiffness and surface strength
- Control flatness of the paper sheet
- Control the penetration of ink in subsequent printing operations

There are many types of binder used in the paper industry, and they can be generally split into two groups - natural and synthetic. In this paper discussion on natural binders will be restricted to starch and protein, and the synthetic binders will be covered under the general description of "latex" dispersions.

STARCH

INTRODUCTION

Starch is the most widely used additive deriving from renewable rawmaterial used by the paper industry. Of the 2.8 mio tons of starch used in all industrial applications within the EU in 1995, more than 46 % (1.3 mio tons) was consumed by the paper industry, making it the largest single customer group of the starch manufacturer. Consumption of starch used by the paper industry has almost doubled in the last 10 years. This increase is not just due to the growth of the paper industry itself, but also as a result of the increased amount of starch used in individual grades of paper. An average of 1.8 kg of starch were used per ton of paper in 1995. This statistical average figure, specific starch demand, hides the fact that some grades of paper contain no starch, while others can contain up to 70 kg starch per tonne. The growth of starch usage in the paper industry has in recent years been due to economic as well as technological reasons.

Grade	Production 1000 tonnes	Starch kg/tonne paper
Newsprint	10000	1
Uncoated Mechanical	6000	50
Uncoated Woodfree	9000	47
Coated Mechanical	7500	11
Coated Woodfree	7000	25
Other Packaging P&B	12000	12
Sanitary and Household	4000	0.4
Special P& B	400	6

Table 1. Starch consumption for different paper grades

After fibres and pigments, starch is the third most important material for the paper industry in tonnage terms.

The application areas are devided as follows:

surface application	68 %
wet-end addition	16 %
coating	11%
spray	5%

The starch used in the paper industry is derived from different plants. Potato, maize and wheat are the more frequently used starch sources, but small quantities of starch from tapioca,barley and waxy-maize are used in the European paper industry.(see fig No. 1).

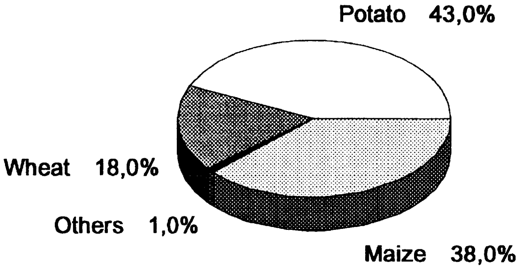


Fig. 1. Starch consumption in the paper industry - 1995
- divided by raw materials

PRINCIPLES OF STARCH TECHNOLOGY

Chemical principles

All higher plants which contain chlorophyl form carbohydrates such as starch and cellulose as deposits and skeletal substances from the reactions of carbon dioxide, water and light energy.

In this chemical process - which is without doubt one of the most important in life, but which is still not yet completely understood - long chain molecules are produced from the initially formed D-glucose by way of enzymatic polymerization. Both starch and cellulose are built up in this way, the difference between them being due to minor differences in molecular linkage.

In the case of water-insoluble cellulose, the individual glucose units are linked by so-called *beta*-glucosidic bonds, while the same units are linked by *alpha*-glucosidic bonds in water-soluble starch. Thus identical monomer units linked together to form different structures produce natural polymers with completely different chemical and physical properties (Fig. 2).

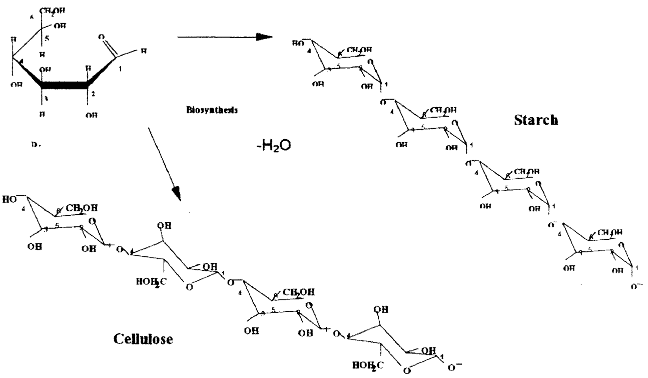


Fig. 2. Biosythesis of cellulose and starch

Starch is stored mainly in the roots and seeds of plants in the form of granules. The granules possess a characteristic morphology and granulometry for the respective plant types.

Potato starch consists of relatively large and oval granules, while maize starch granules are smaller and round or polygonal. Wheat starch possesses a binodal granule size distribution, whereby the larger grains account for only 20% of the total number but for 90% of the total weight.

If starch granules are observed under the microscope, using polarized light, it is possible to see characteristic crosses as the result of birefringence. The center of the cross indicates the growth center (Fig. 3).

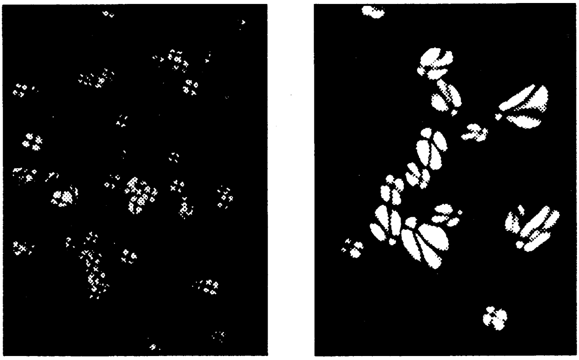


Fig. 3. Different form of starch granules as seen under polarised ligth; left maize and right potato starch granules

All starches consist of two types of molecule, namely amylose and amylopectin.

Amylose is made up of chains of 600-3000 glucose units which are linked by alpha-1:4 bonds and fixed in a helical structure by intramolecular hydrogen bridging. The amylopectin fraction is branched by additional alpha-1:6 bonds (Fig. 4).

The proportion of amylose to amylopectin varies, depending on the type of plant. Genetic selection makes it possible to breed types where these polymer fractions exist in a specific ratio. One of the most important hybrids of this kind is waxy maize starch, which contains 99% amylopectin (see Table 2).

The total quantity of starch in the various plant types also differs greatly, depending on whether it is obtained from roots (tapioca), tubers (potatoes) or seeds (wheat, maize).

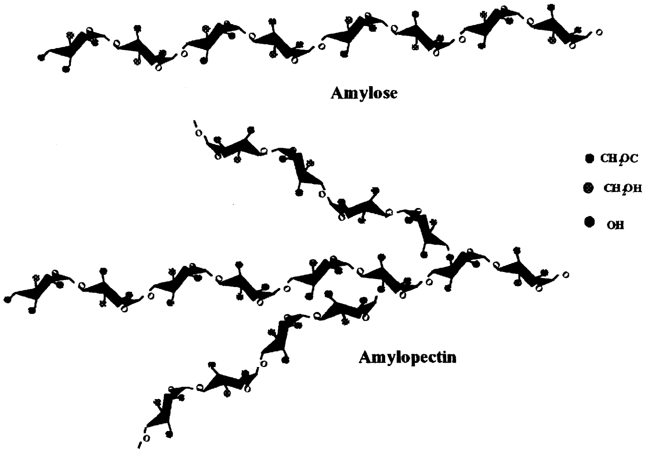


Fig. 4. Polymer fraction of starch

It is of interest to note that for the production of one tonne of starch the following growing area, in hectares, and tons of raw material are required:

potato : 0.14 HA ;	5 tons of raw material
maize : 0.24 HA ;	1.6 tons of raw material
wheat : 0.33 HA ;	2 tons of raw material

PHYSICAL PROPERTIES OF STARCH

The moisture content, or equilibrium moisture content, under normal conditions (20 °C, 65% relative humidity) is 13% for maize and wheat starch, and 19% for potato starch.

Native starch is insoluble in cold water. Owing to their higher density, the starch granules drop out of suspension as soon as agitation is removed. When the concentration of a starch slurry reaches 45% or more, it becomes dilatant, and it can no longer be stirred or pumped.

	Maize	Wheat (A)	Waxy maize	Potato	Tapioca
Moisture [%]	13	13	13	18	13
Particle size [µm]	5-25	15-40	3-26	15-100	5-25
Gelatinisation Temperature [°C]	67	61	68	63	65
Amylopectine [% starch]	75	78	99	77	80
Proteins [%HB]	<0,4	<0,3	<0,5	Traces	0,1
Lipids [% HB]	0,2	0,2	0,2	-	-
Phosphates	<0,1	<0,2	<0,1	0,3	<0,1

Table 2. Starch parameters of interest to the paper industry

If the starch suspension is heated, the granules begin to swell at a temperature which is characteristic for each starch type.

The starch granules swell to many times their original volume and lose their typical granule structure. At the same time, the characteristic birefringence of the granules disappears as swelling progresses.

The amylose fraction of starch never completely dissolves, in the chemical/physical sense of the word, during boiling and gelatinization. It displays a tendency to create hydrogen bridges and to reorganize itself into linear bundles after some time.

This effect is called retrogradation, a process which results in the heated aqueous solution becoming opaque upon cooling. The amylose may be precipitated if the solution possesses low viscosity and is stored for a long period of time. At higher viscosities, rigid gels may be formed through which water can be partially released in a reversal of hydration. This process is called syneresis and is irreversible in most cases (see Figure 5).

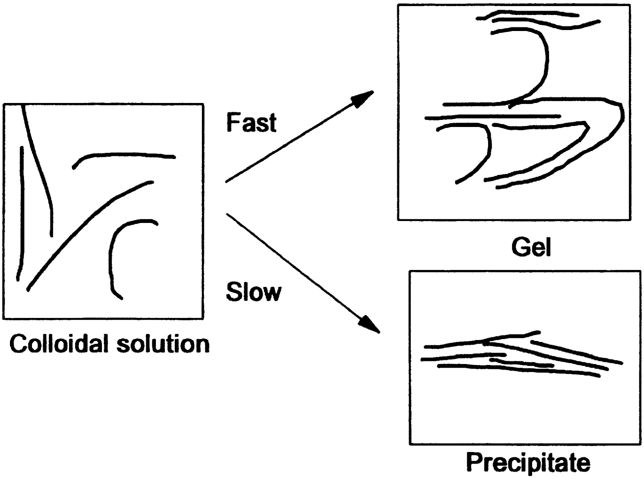


Fig. 5. Retrogradation of amylose

In addition to these changes the amylose in maize and wheat starch pastes sometimes forms crystalline complexes which may be precipitated in the form of small particles under specific conditions - long storage time, high temperature (above 70 °C) and low pH (< 7). This amylose precipitation takes place if the starch-lipid complexes are broken up (at cooking temperatures above 115 °C) and then reform. As potato starch contains no lipids this amylose precipitation can only take place in the presence of surface active substances.

These amylose particles look almost like ungelatinized starch granules in polarized light, but are larger and possess concentric rings in addition to the polarization crosses (Figure 6).

Amylopectin is more resistant to this aggregation effect owing to its branched structure. Correspondingly, its retrogradation tendency after boiling is less marked.

Amylopectin pastes retain their flow properties over a long period of time and any signs of slight retrogradation disappear after renewed heating.
In Table 2 the properties of regular (unmodified) starches which are of interest in paper manufacturing are listed.

STARCH MODIFICATION

Although pure native starch is used in the paper industry, it meets the physical demands of modern industrial processing only to a restricted extent. In many cases, the starch properties, such as binding or adhesive strength, water retention capacity, rheology or film formation properties, first have to be adapted to the special requirements of an application by physical or chemical modification.

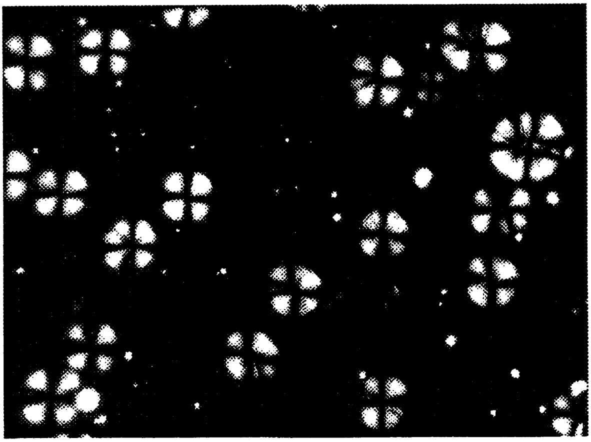


Fig.6. Retrograded amylose seen in polarised ligth

PHYSICALLY MODIFIED STARCH

It is possible to destroy the crystalline structure of starch granules by the influence of heat and mechanical shear forces,obtaining an amorphous material which dissolves easily in water to give a colloidal starch solution. Such starches are usually produced by roll drying or extrusion, followed by drying of the starch paste.

As a result of this additional treatment and the high amount of energy required to dry the hydrated starch, these products can be used economically only where starch cooking at the point of application is not possible.

CHEMICALLY MODIFIED STARCHES

Chemical modification of starch can be performed so that
- only the viscosity is reduced - degradation
- various chemical groups are introduced into the starch molecule - substitution
- the starch molecules are linked to each other - crosslinking.

It is also possible to combine any of these modification processes.

The viscosity of starch can be reduced by various degradation methods - acid degradation, oxidation, enzymatic degradation or by thermal treatment. Thermochemical degradation as used in the paper industry can be considered as either oxidation or as acid modification depending on the reaction conditions employed.

Acid-modified starch

If a starch suspension is treated with acid below its gelatinization temperature, partial degradation of the starch molecules results. However, the external form of the starch granules and their birefringent properties are not visibly influenced.

In this way, starches are obtained which form pastes with low hot viscosity compared to the original, i.e. at the same concentration. The fact that shorter chains are present facilitates macromolecular reorganization and the retrogradation tendency of the pastes is increased.

Owing to their high retrogradation tendency (see Figure 7), these starches find limited use in the paper industry, but are significant intermediate products in the manufacture of starch ethers and esters with different viscosities.

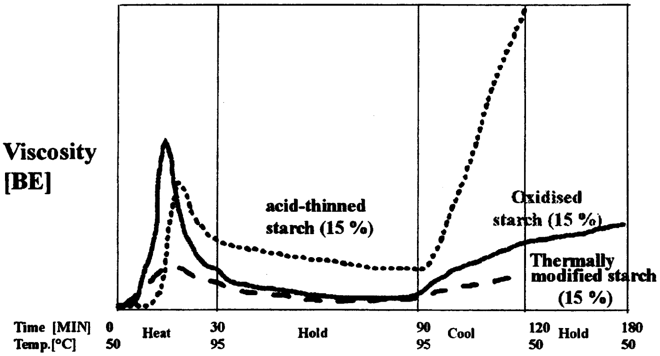


Fig. 7. Brabender curves of different modified starches

Enzymatically and thermochemically converted starch

Controlled reduction of the molecular weight, and thus of paste viscosity, can also be achieved by enzymatic or thermochemical degradation of the starch molecules. Thermochemical degradation is performed by high-temperature cooking at 130-150 °C, with addition of an oxidant such as potassium or ammonium persulphate, or hydrogen peroxide. In this process, chemical conversion takes place in the already dispersed cooked paste at high temperature, rather than on suspended granules below the gelatinization temperature.

These degradation steps are therefore not performed in the starch factory but in the paper mill. The addition level of oxidants can vary between 0.2 to 1.5 %.

Even though these degradation processes are chemically very similar, the resultant starch pastes have some significantly different physical properties.

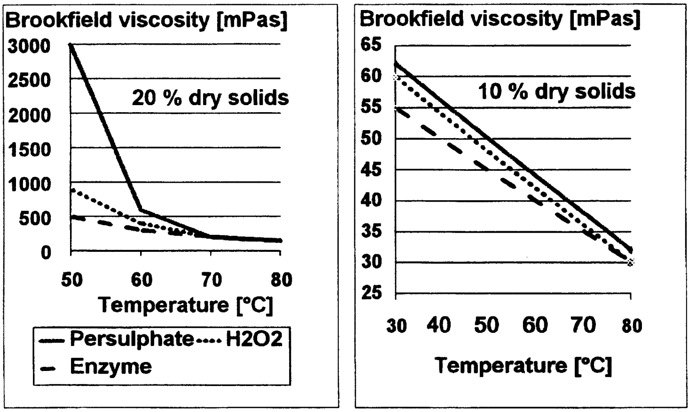


Fig. 8. Relation of viscosity and temperature for different in-mill converted starches

This is evident in the lower retrogradation tendency of thermochemically degraded starch pastes, which is caused on the one hand by degradation in solution or pasted condition, and on the other, by the carbonyl and carboxyl groups produced as a result of ring splitting.

An enzymatically degraded starch paste differs from a thermochemically degraded starch paste by its lower retrogradation tendency. Such differences can be seen at higher concentrations - as shown above in Figure 8, where the difference is small at 10%, but large at 20%.

This improved visco-stability of enzymatically degraded starch, compared to thermochemically degraded starch, is due to the higher

content of low-molecular starch fractions. A similar situation is seen when different oxidants are used in the thermochemical process.
The different levels of low- and high- molecular starch fractions are shown by molecular weight distribution curves, and Fig. 9 shows that a higher content of low-molecular starch is obtained with hydrogen peroxide than with persulphate.

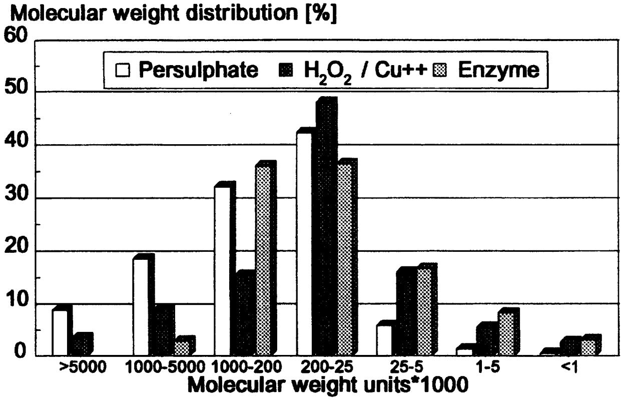


Fig. 9. Molecular weigth distribution of in-mill converted starches

Oxidised starch
Native starches can be depolymerized by the starch producer whilst the starch is still in the granular form, by treatment with one of several oxidants. Such starches yield low-viscosity pastes with a high solids content and high viscosity stability (see. Fig. 7).
In production of standard commercial oxidised starch, an alkaline hypochlorite solution, containing approximately 5% active chlorine, is slowly added to a starch slurry with a solids content of approx. 40%, while stirring vigorously. The acid formed in the reaction is neutralized with soda ash, and the reaction temperature is controlled either by cooling or by the rate of hypochlorite addition. It is impossible to avoid the formation of organic chlorine compounds under such reaction

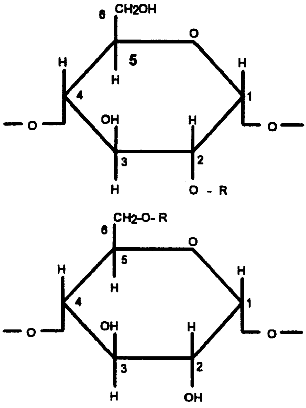
conditions. Oxidised potato starches contain 20 to 100 ppm of OX, (organic halides) and oxidised maize starches contain 60 to 400 ppm. Starches treated with hypochlorite give pastes with lower viscosity and higher transparency than the corresponding native starches. Retrogradation is reduced greatly by the carboxyl group content, with the result that the paste remains clear and liquid even after cooling.

Thermally modified starch

Thermally modified starches contain no OX. They are viscosity stable (see Fig. 7) and non-ionic. The stability of the starch paste is achieved because the macromolecules, which are hydrolysed at high temperature in the latter part of the process, undergo a *transglucosidic* arrangement. The amylose fragments are structured in such a way that amylpectin- like rearrangements occur.

Starch ether

The most important group of chemically modified starches is the starch ethers. A wide spectrum of ionic and non-ionic starches can be produced by reaction with correspondingly substituted epoxides, which are either used directly or are accessible in-situ from the corresponding chlorohydrins (Fig. 10).



REAGENT	FUNCTIONAL GROUP R
3-chloro-2-hydroxy-propyltrimethyl-ammonium chloride (CHPT)	Cationic quatenary ammonium chloride
Sodium monochloroacetate	Anionic carboxylmethyl starch
Propylsulphone	Anionic sulphonate starch
Calcium maleate	Anionic dicarboxylethyl starch

Ethylene oxide	Non-ionic hydroxyethyl starch
Propylene oxide	Hydroxypropyl starch
Epoxy propanol	Dihydroxypropyl starch

Fig. 10. Methods for production of starch ethers

Hydroxyalkyl starch

Non-ionic hydroxyalkyl starches with degrees of substitution (DS) between 0.01 and 0.10 can be obtained in aqueous solution by reaction with ethylene-, or prophylene-, oxide.

The alkyl substituents considerably reduce the tendency of hydrogen bridge formation and thus of retrogradation, with the result that the viscosity of the pastes is exceptionally stable in the event of cooling or during long periods of storage. At the same time, the pastes possess a high water retention capacity and good binding power. This, together with the considerable improvement in film-producing characteristics compared with native or oxidised starches, makes this type of starch derivative particularly suitable for surface applications where good film-forming characteristics are required. They also provide an effective barrier against organic solvents.

Ionic starch

Ionic starches can be divided into three different groups:

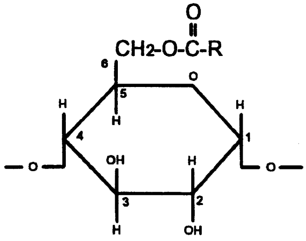
- Cationic starches
- Anionic starches
- Bi-ionic or amphoteric starches, i. e. they contain both cationic and anionic substituents.

Cationic starch

In order to incorporate cationic groups into the starch molecule, it is necessary to chemically activate the starch with respect to the cationization reagent. This is done in the aqueous starch slurry by adjusting the pH to 11.5-12.5 with alkali before adding a cationization reagent. A typical reagent is 3-cloro-2 (hydroxyprophyl)-trimethyl ammonium chloride (CHPT).

The higher the reaction temperature chosen, the faster the reaction progresses between starch and cationization reagent. At the same time, however, excessively high temperatures lead to non-uniform cationisation, and side reactions which give undesirable hydrolysis products. For this reason, a reaction temperature of 40-50 °C is maintained. In order to avoid partial gelatinisation of the starch granules under these pH and temperature conditions it is usually necessary to add gelatinisation inhibiting salts.

Owing to their cationic charge, the starches obtained possess high substantivity with respect to anionically charged fibers, fillers or pigments.



REAGENT	DERIVATIVE $\overset{O}{\overset{\|}{C}}\text{-R}$
Acetic anhydride	**Acetyl starch**
Inorganic phosphates	**Monophosphate starch**
Carbon disulphide	**Xanthane starch**
Urea	**Carbamate starch**
Sulphur trioxide/amine complex	**Sulphate starch**

Fig. 11. Methods for production of starch esters

Starch ester

Acetylation of granular starch in aqueous alkaline suspension is performed with acetic anhydride as the acetylation reagent. Esterification (see Fig. 11) can be combined with other modification methods such as cross-linking, acid degradation or oxidation in order to obtain products tailored to the specific application. They are significantly less stable with respect to chemical influences than the extremely stable starch ethers. For example an acetylated starch with an acetyl content of 1.8% will be completely saponified within 4 hours at pH 11.

Excellent visco-stability, easy gelatinisation, and thus problem-free handling during use and storage, as well as good film properties are characteristic of starch esters and ethers. The viscosity of all starch ethers and esters can be reduced to the desired level by hydrolysis or oxidation in the same manner described earlier for regular starches.

SURFACE APPLICATION METHODS

There are several methods for applying starch pastes, or starch based coatings, to paper. In this chapter only those of importance for the coating of starch will be described, and even then only in so far as these parameters influence the quality of application

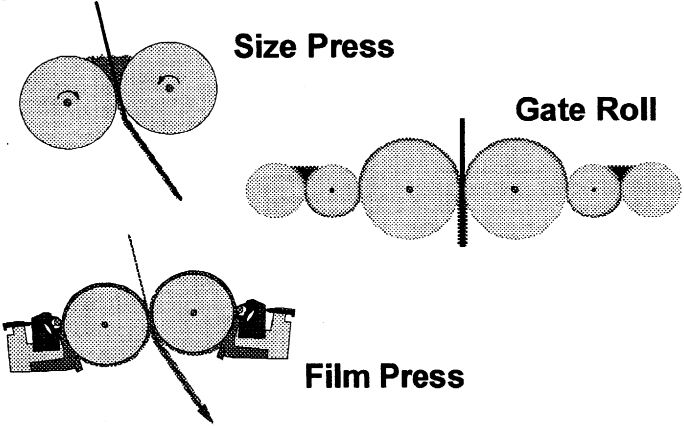


Fig. 12. Surface application methods

Size press application
The size press is the most common method of starch application. It consists of two rolls pressed together to form a nip, where a pond of low viscosity starch paste is formed (Figure 12). The passage of paper passes through this pond. Excess starch is squeezed off between the two rolls, which may have different diameters and be covered with materials of different hardness and surface tension.

The liquid in the size press nip is always in movement. The passage of paper and the rotation of the rolls inevitably gives rise to turbulence. (see Figure 13).

After entering the nip, the liquid can either be pressed into the paper or be ejected in the opposite direction to the paper travel. The turbulence in the size press pond will depend on the pond depth and width, the speed of the paper machine, and on the rheology of the size press liquid.

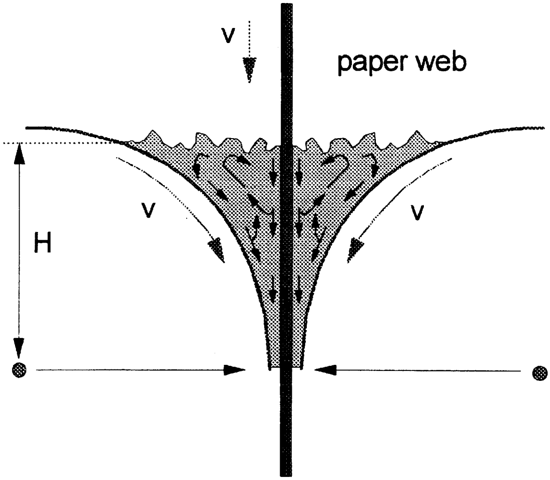


Fig. 13. Hydrodynamic forces in the size press nip

Now that these factors are better understood, it has become normal for machinery manufacturers to build size presses with larger and larger diameter rolls as papermachine speeds increase. Size press speeds up to 1200 m/min can be achieved today using a first, and normally softer, roll diameter of 1600 mm. The other roll would in such a case be smaller - approximately 1000 mm diameter. The hardness of the rolls would be approximately 20 and 0 P&J units respectively; and they would be mounted horizontally in order to build the greatest possible pond depth. The hardness of the rolls and the pressure between them determine the nip width, which in turn influences the penetration of the size press liquid into the paper. The size press rolls have to be pressed together firmly enough to overcome the hydraulic pressure which is built up by the liquid in the pond.

In spite of its widespread use, the size press nevertheless suffers from several important disadvantages:

- high energy requirement for after drying owing to the high fluid absorption
- turbulence in the nip pond at high speeds which may cause non-uniform coating
- the need to adjust the viscosity of the starch solution according to the hydrodynamic forces in the nip
- fibre swelling resulting from excessive water absorption into the sheet, causing increased roughness
- the running properties in the size press necessitate a certain minimum wet strength of the paper
- the fluid absorption in the size press varies depending on the moisture content of the incoming paper. In order to ensure a uniform moisture cross-profile drying to a moisture content of approximately 1-3% is necessary for graphic papers, and to approximately 7-12% for packaging grades.

Nevertheless, speeds of over 1000 m/min are achieved today using larger roll diameters (as described above) and low starch concentrations (3-5% solids content). However, it seems provisionally that the conventional size press has probably reached the end of its development.

Gate roll application

The use of coating equipment for direct or indirect starch application permits metering of the supplied starch, while avoiding some of the problems associated with turbulence. Premetering via roll systems - e.g. the gate roll coater (see Figure 12) - is possible but there is the disadvantage that uniform and reproducible premetering can be achieved only if the starch pastes have a relatively high viscosity. This is due to the hydrodynamic operating principle of the metering system and the streak formation owing to the film splitting.

In the case of a conventional starch paste this means solids contents of 15 - 20% will need to be used. This will also avoid too high a penetration into the sheet. Starch solids contents of 4 to 5% can be used if non-degraded starches of excellent viscosity stability, ie. unthinned starch ethers or esters, are used.

Disadvantages of this technology are as follows:

- the application weight depends entirely on premetering
- the equipment is technically complex owing to the large number of rolls
- the premetering rolls must be cambered and can be used only at a specific operating point
- it is difficult to avoid deposits on the rolls.

Film press application

In order to overcome the turbulence in the size press pond and the above mentioned problems, the blade metered size press was introduced in 1982. The further development of this application system led to what today is called the metered size press or film press (SPEED-SIZER, SYMSIZER, FILMPRESS, TWIN-HSM, GRIC (gate roll inverted coater)).
The size press rolls now are used as appplicator rolls (as in the gate roll system). A film is applied to one or both of these rolls by means of a jet or fountain applicator system. The film is metered by either a profiled rod, or a smooth rod in the case of coating colour application. Blade metering, which was how the technology first developed, is also still used.
The applicator rolls in a metered size press are much softer than those of a size press. The first rolls used for non-pigmented coating application have a hardness of 15 and 25 P&J, both with the same diameter of approximately 1250 mm. The hardness of the applicator rolls are lower for coating application. In the size press the paper can be run only in the downwards direction. However, in the metered size press the paper direction can be either up or down depending on the best positioning for different machines. Additionally, a new configuration of metered size press has been introduced to the market in which only one side of the paper is treated at a time, in separate units, like normal blade coating stations.

The metering element may consist of blades of either smooth or grooved rods. If premetering is performed with doctor blades, a film is applied to the roll with a premetering device similar to a short dwell blade coater, instead of by a rod premetering system (Fig.14). The film is transferred to the paper in the nip without pond formation, and pressed into the sheet even though the hydrodynamic pressure is low. Such metered size presses operate at speeds of up to 1300 m/min., and pilot systems have already reached 2200 m/min.

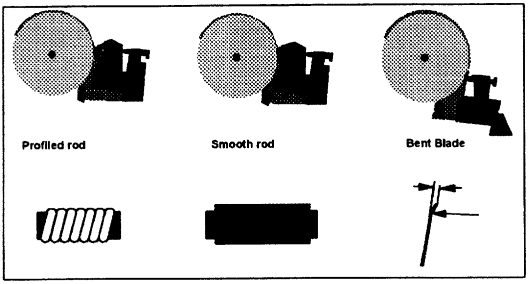


Fig. 14. Film press predosing systems

The main advantage of film press installations is the possibility of setting a defined application quantity at high paper machine speeds. In addition, the quantity of water which has to be evaporated in the after-drying assembly is considerably reduced (Figure 15). This leads to more favorable energy costs and improvements in running efficiency owing to the reduced tear sensitivity of the paper.

The metered size press is a very flexible piece of equipment. If the emphasis of starch coating is on strengthening the paper surface, this demand can be satisfied by the film press without having to reduce the paper machine speed to avoid splashing. If, on the other hand, the objective is more penetration through the whole thickness of the paper sheet, operation of a size press or metered size press in pond mode is necessary, particularly for high-grammage papers. Pond mode means that more starch is supplied by the premetering system than is absorbed by the paper, thus causing collection of the starch excess in the nip.

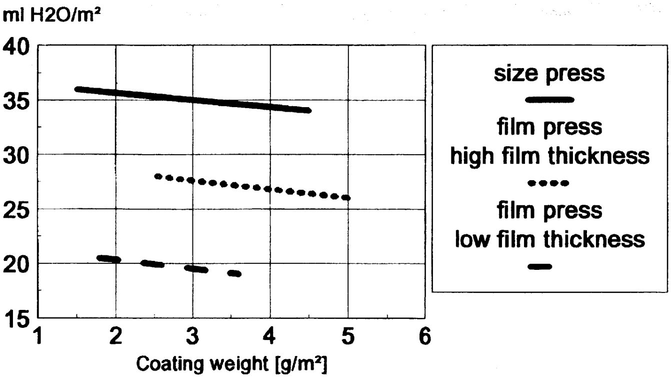


Fig. 15. Water quantity to be evaporated during drying is depending on both application weigth and application mode

Experience with the use of soft applicator rolls in the Liquid Application System (see next section) led to the introduction of the TWIN-HSM coater. Rubber hardnesses of 90 - 110 P&J are used on the applicator rolls and the wire-wound metering rolls are of large diameter (400 - 700mm). The starch or coating colour is applied through a combination of volumetric and hydrodynamic metering. This leads to a long service life for the rolls.

The web runs normally upwards to facilitate cleaning, allowing the circulating rate of the applied suspension to be reduced to around five times the rate of application to the web.

On each side, the coating is fed into the pond between the HSM roll and the transfer roll from a distributor pipe fitted with holes across the full machine width. The pipe itself is double-walled to allow for cooling, which encourages condensate moisture to form on its surface. This helps keep the pipe clean during operation.
The unit operates with a very low specific nip pressure, which, coupled with the soft rolls used, makes it possible to meter the starch or coating onto the surface of the paper.

If greater levels of starch penetration are required (for example, to improve internal bond) harder rolls and higher nip pressures can be used. The TWIN-HSM is in use today at speeds up to 750 m/min on recycled base at weights as low as 35 g/m^2. Speeds of 1400 m/min have been achieved on pilot installations coating wood-containing grades.

Liquid Application System (LAS)

Another application unit, more normally used to add water to the back side of one-sided coated paper to prevent curl, is the Liquid Application System (LAS). The LAS coater can also be used to add starch solutions of low viscosity. The LAS coater (Fig.16) uses a hydrophilic transfer roll, which is chromium plated and treated by a proprietary etching process. The treated roll can carry wet films 3-15 microns thick without slinging or spattering, at speeds up to 1700 m/min. Liquid is applied to the hydrophilic transfer roll by a resilient rubber-covered metering roll running in a supply pan. Varying the speed of the metering roll maintains a flooded nip to prevent air intrusion into the starch solution. Pressure in the metering/transfer roll nip is controlled to provide a uniform, unbroken film on the transfer roll. The hydrophilic transfer roll is run in the same direction as the web to apply the liquid film to the web, though with a speed differential between them to minimise film split pattern on

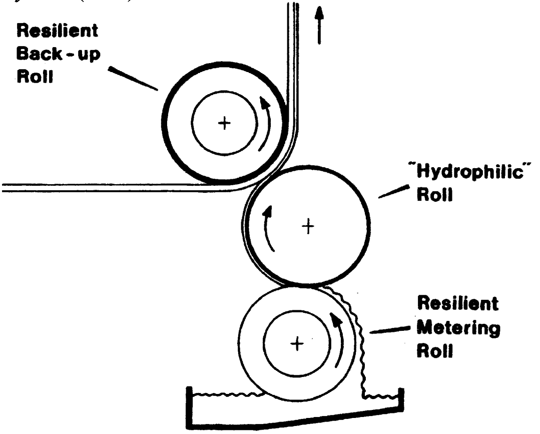


Fig. 16. Schematic view of the Liquid Application System

the sized sheet. Pick-up is controlled by varying transfer roll speed and the pressure between metering and transfer rolls. A resilient rubber-covered backing roll is used to assure uniform contact between the sheet and the hydrophilic transfer roll.

STARCH PROPERTIES REQUIRED FOR SIZE PRESS APPLICATION

The most important aim of starch application is improvement of mechanical strength, both at the surface and within the body of the sheet. This can be achieved by penetration of the sheet structure by the starch solution. The effect of the starch can be measured by means of one or more of the following parameters:

- tensile strength
- plybond strength
- pick resistance (Dennison wax, IGT)
- ring crush test
- flat crush test
- stiffness
- printability
- runnability

Surface application of starch thus primarily serves to improve certain paper properties. The economy of paper manufacture can be improved by optimizing the selection of the raw material used.

In order to improve the desired property it is necessary to understand the behaviour of starch during the size press treatment; and how different starch modifications influence both the runnability of the size press and the paper properties.

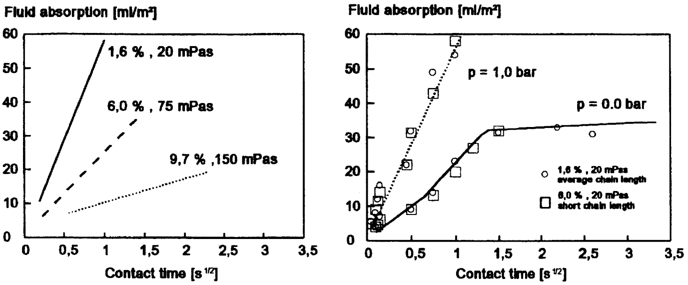
Starch data for two paper machines equipped with size presses are shown in Table 3 . Both machines produce wood-free uncoated paper. It can be seen that the liquid volume absorbed differs between the heaviest and the lightest quality by about 14%. The reason for this difference is the lower absorption capacity of the lighter paper.

Area Weight	g/m^2	45	60	80	100
Paper machine A					
Size press speed	m/min	>900	800	>650	
Starch concentration	° Bx	4	6	7	
Starch viscosity (50°C, 100 rpm)	mPa s	20	28	30	
Starch pick-up					
(solution)	ml/m^2	50	55	57	
(dry)	g/m^2	2	3,3	4	
Paper machine B					
Size press speed	m/min		>900	800	600
Starch concentration	°Bx		7	9	12
Starch viscosity (50°C 100 rpm)	mPa s		30	40	50
Starch pick-up					
(solution)	ml/m^2		43	44	50
(dry)	g/m^2		3	4	>6

Table 3. Typical size press conditions in modern paper machines

Influence of viscosity

The influence of starch viscosity together with subsequent absorption is shown in Figure 17. The forces which counteract fluid transport grow tremendously as the viscosity of the penetrating fluid increases. In this case the viscosities are set on the basis of the desired final dry pickup. However, it should be of no significance for the absorption rate whether the viscosity has been set on the basis of the dry content or the chain length. The amount of starch solution absorbed is determined solely by its viscosity.



(Remmer/Eklund)

Fig. 17. The influence of starch viscosity on starch absorption

However, there is some question as to how best to measure the viscosity of a starch paste. Brookfield viscosity, the normal measurement used in the paper industry, describes the size press behaviour of a known starch paste in an appropriate way. The viscosity of the starch solution should be measured with the Brookfield Viscometer at as high a concentration as possible, since low concentrations do not differentiate between starches well enough. The measurement however is sensitive enough to control the size press make-up system, even though it does not provide enough information to predict the effect of replacing one starch by another.

It seems to be evident that the molecular weight distribution of the starch plays a dominant role in this behaviour. The data in Figure 9 show that the chain length distribution of starches of similar viscosities can vary considerably. It seems to be logical that the lower molecular portions of the starch are more easily absorbed and that these portions also penetrate faster. This could be the explanation for the differences between research investigations and practical results from fast running paper machines, regarding the relationship between starch pick-up and viscosity level.

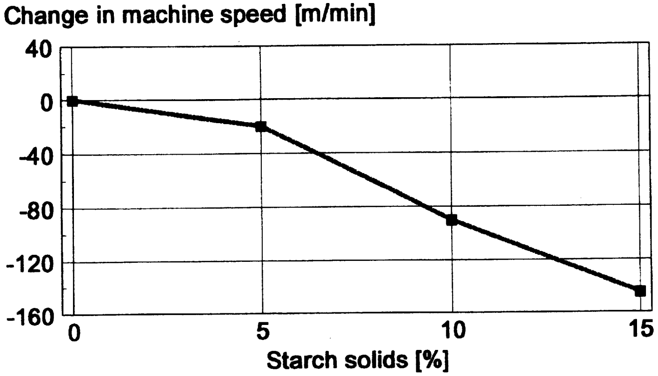


Fig. 18. Influence of starch solids in the size press on machine speed

The molecules in solutions of maize starch have a shorter structure than those of potato starch. This structure difference can be seen by pouring the starch solution from a beaker very slowly. A very fine filament can be formed with potato starch, while the maize breaks up into droplets. A Bohlin-rheometer can also detect this difference. The Bohlin-rheometer measures the starch viscosity at low shear rates and is a good tool for investigating starch pastes. The shorter structure of a maize starch solution leads in some size presses to a lower splashing tendency and to less misting during filmpress coating.

When the viscosity is increased from, say, 40 mPas to 80 mPas, measured at the same solids and temperature, the liquid pick-up in the size press can increase because of the increased hydraulic load. At speeds below 600 m/min and with small diameter size press rolls, however, the applied amount of liquid will decrease as the viscosity increases.

Influence of solids content

The starch pick-up increases almost linearly with the solids of the size press solution on fast running paper machines. This means that less water is added to the paper. However, less water to evaporate does not necessarily mean that steam consumption in the after drying section can be decreased. The opposite is often the case. More starch pick-up means that the applied water will be more difficult to evaporate. Therefore the steam consumption will rise or the machine speed will have to be reduced (see Figure 18). The water holding capacity of the starch is greater than that of the fibers.

Penetration

The penetration of starch depends on the following factors:

- viscosity of the starch paste or solution
- solids of the starch paste
- paper structure
- paper moisture
- fibre swelling behaviour
- linear pressure of the size press rolls
- hydrodynamic pressure of the size press liquid
- molecular weight distribution

These factors have not been investigated sufficiently thoroughly that the desired answers can be given. However, industrial experience gives enough information to understand the first four.

Both size press penetration and pick-up decrease when the moisture of the paper entering the size press is reduced from 10 towards 1%. The penetration depth of starch can be determined by microtome sectioning technique or by measuring different paper strength characteristics of the treated paper.

A low viscosity starch penetrates into the paper sheet more than a higher viscosity starch. This can be seen in the microtome sections shown in Fig. 19, and in the resulting surface strength figures in Fig. 20. The solids content of the starch influences the penetration behaviour only if the starch viscosity is drastically increased by increasing the solids content. This can be seen if the penetration of an acid modified starch

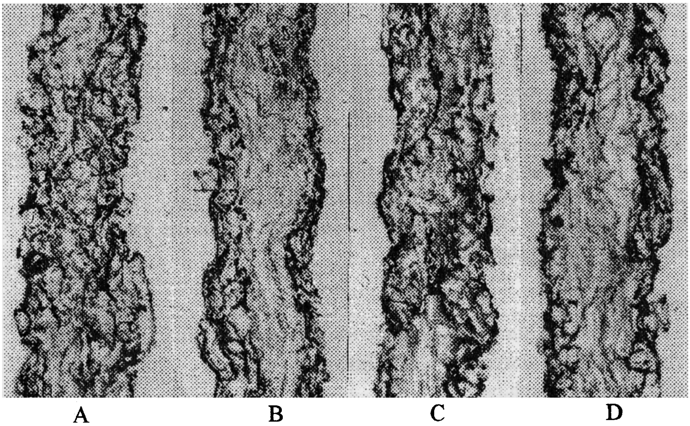


Fig. 19. Microtome sections of papers treated in the size press (A,B) and film press (C,D) with starch of low (A,C) or high (B,D) viscosity

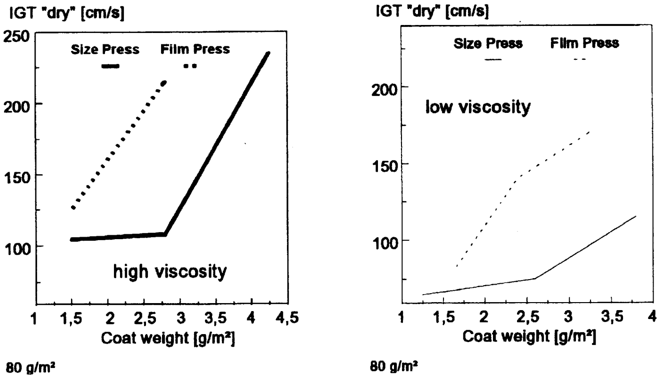


Fig. 20. Correlation of starch viscosity and achieved paper properties

which has high retrogradation tendency (set-back), is compared to that of an oxidised starch with lower set-back. At low solids (eg. 5%) there will be no difference, but at higher solids the acid modified starch will stay more on the surface of the paper, because its higher set-back viscosity will restrict penetration.

Influence of paper machine parameters

Size press pick-up increases as the speed of the papermachine is increased. This is caused by the increased hydraulic forces in the size press nip. The increased starch pick-up at higher speeds is however also dependent on:

- starch viscosity
- paper absorptivity
- size press roll diameter

and it is only possible to apply general rules.

As the hydraulic pressure increases with increased viscosity it should be expected that the pick-up would also increase. This is true for size presses with large rolls. The effect is even more pronounced if the nip load of the size press rolls is not too high at the same time. Papers of high weight (more than 100 g/m^2), with an open structure and made predominantly from fibres which do not swell quickly, show a higher coat weight increase as speed increases compared to closed papers with a limited absorption capacity.

Smaller diameter size press rolls and harder roll surfaces have higher linear pressures in the nip. These presses do not show so much influence of speed increase as those with bigger rolls or softer covers.

STARCH PROPERTIES REQUIRED FOR FILM PRESS APPLICATION

There are, as described above, in principle two main parameters which can be controlled during size press application:

- the solids content of the starch paste, and
- viscosity of the starch paste

Film press application adds another parameter to these two:

- the film thickness on the applicator rolls.

The main difference between size press and metered size press application of starch is the absence of the pond in the applicator roll/paper nip. That means that the hydraulic forces of the size press nip are not present in the film press system; or, if a „minipond" is present, they will be very low. The result of this is that the penetration of the applied liquid will be reduced compared to the size press. At the same time, the absence of a pond makes it possible to work with much higher viscosities on the metered size press.
The maximum possible film thickness is dependent on the absorptivity of the paper used; more aborbent papers can accommodate a thicker film on the applicator rolls before a pond, which causes splashing, is created.

Independent of the paper quality, savings in drying energy can be achieved when switching from size press to metered size press application.
However, it is true for both size press and metered size press application that the higher the concentration, the more starch is applied and hence the more difficult the sheet is to dry.

Differences in the dependence of applied weight on the solids content are difficult to detect when using two starches with completely different viscosities. There are, however, slight differences, as the film splitting effect when the paper leaves the applicator rolls is different. A film of a low viscosity starch applied at 10 % will be split so that approximately 90% is applied to the paper and 10 % returns to the metering rod. Higher starch viscosities can lead to a 70:30 % split in the divergent zone. A relationship between starch viscosity and the amount of liquid starch applied to a paper as a percentage of the amount of liquid applied to the applicator rolls (known as the transfer ratio) is shown in Figure 21.

The penetration behaviours of starches of different viscosities are different too. Starches of lower viscosities penetrate more. This is shown clearly in Figure 19 where results from applying starches of different viscosities to an 80 g/m^2 wood containing paper in both a size press and a metered size press are shown. The high viscosity starch (24% solids: 50°C: 1500 mPas) penetrates only partially in both metered size press and size press application, giving essentially the same result. On the other hand, the starch of much lower viscosity (110 mPas, measured at the same concentration and temperature) penetrates the paper completely when applied at the size press. Penetration after metered size press application is good too, however, because of the rapid swelling of the groundwood fibres and is only a little less than for the size press treated paper.

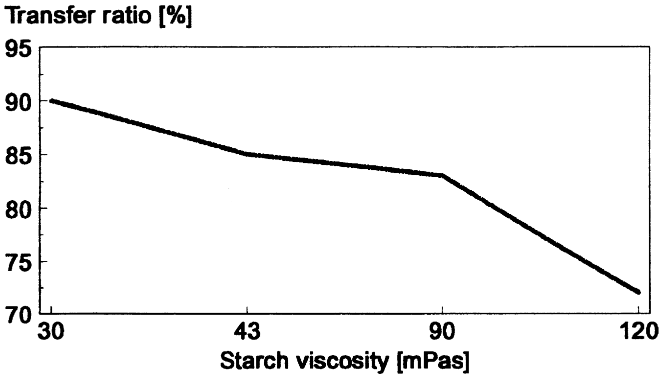


Fig. 21. The influence of starch viscosity on the transfer ratio

The physical testing of the papers described above produced the expected results. Slightly higher tear strength values are obtained with size press treatment than with metered size press. However, the results differ with respect to surface strength (see Figure 20). Here, the metered size press proves to be superior. The increased starch concentration in the layers close to the surface improves the the surface strength both for the low-viscosity and the high-viscosity starch solution.

Higher speeds are always possible with a metered size press than with a standard size press, while achieving comparable paper strength. However, more starch has to be applied if high penetration is required to achieve the desired properties. Low viscosity starches allow higher machine speeds than the high viscosity types.

STARCH PROPERTIES REQUIRED FOR BLADE APPLICATION

Starch application with on-machine short dwell coater units (SDTA) is not often carried out, though it can certainly be done.

Starch application weight is influenced only by the solids content of the starch solution and not by the starch viscosity or blade pressure of the SDTA. The solids content used in the industry for this type of application will vary between 3 and 10%.

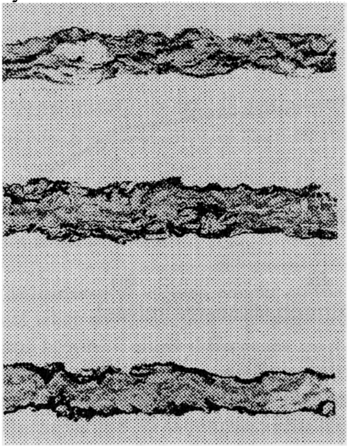


Fig. 22. Microtome sections of newsprint paper surface treated with starches of different solids (5% top, 10% middle, 15 %bottom)

Microtome sectioning of newsprint papers which had been surface treated with starch solutions of different solids, and with two starches of quite different viscosity, showed that penetration by the starch solution is only possible at low solids content. In Figure 22 it can be seen that a starch solution of high solids remains concentrated on the paper surface. Applied at, for example 5% solids, the starch viscosity does not influence the penetration. At higher solids (eg. 10%), the higher viscosity starch penetrates less than the low viscosity starch.

These findings demonstrate clearly how blade application of starch influences the technological properties of a paper :

- tensile strength increases with increased amount of applied starch Increased tensile strength does not necessarily lead to decreased Brecht-Imset tear values. Addition of high viscosity starch can increase the tear resistance of a newsprint paper, while low viscosity solutions seldom do. It is evident that the shear stress behaviour of fibre-to-fibre bonding in the sheet is less influenced the more the starch is kept on the paper surface.
- an increase of stiffness can be achieved with a pick-up of 0.5 g (ds)/m^2/side
- The surface strength increases at the same time with increased starch addition
- The tendency to linting and dusting will be reduced
- The gloss of calendered paper does not appear to be influenced by the starch treatment.
- Printing gloss, however, can be significantly improved. This will depend on how effectively a starch film can be formed on the paper's outer layer.

In summary then, surface treatment by blade with starch (or with CMC or other film formers, or with a lightly pigmented coating) can greatly improve surface strength and reduce linting and dusting. The loss of brightness and opacity must be compensated by the use of different pigments.

STARCH IN PIGMENT COATING

Starch is a very efficient material in coating colours both for binding pigment particles to each other and to the paper substrate, and for controlling rheology and water retention.

The amount of binder which is used in coatings depends to a large extent on the solids of the coating colour. In size press coating colours, which can range from 45% down to 15% solids, the binder quantity can be in the range of 25 to 100 parts based on 100 parts of the pigment used. The relationship between solids and binder amount is shown in Figure 23. At lower solids contents, starch will be used as the only binder; whereas in higher solids coating colours, other binders may also need to be used, depending on the purpose of the applied coating. If this coating layer is a pre-coat it can be assumed that 70 to 100% of the binder will be starch. The viscosity of a size press coating will normally be around 50 - 100 mPas at higher speeds, but can be increased to 400 mPas at lower speeds. The running conditions in the size press determine the range of solids content of the coating and the viscosity of the starch selected as binder.

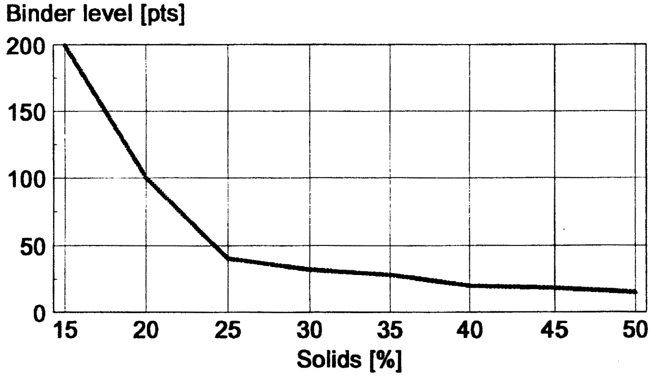


Fig. 23. Relationship of binder content and solids in coatings

A paper or board which is size press coated, even at lower solids content, has improved surface strength, and the surface will be closed to such an extent that the next coating can be applied with a significant reduction of latex binder.

A lower starch/latex ratio is used if the paper is to be offset printed directly after the size press- or film press coating. The ratio can be 50:50 or 30:70.

The starch quality used for size press pigmentation will normally be the same as the starch used for pigment-free application in a size press. Much wider ranges of solids content and viscosity are possible with metered size press application of coating colours than with a conventional size press. Solids levels up to 65% can be applied. It is natural that the viscosity of the starch used in a formulation of 65% dry solids is much lower than for when the solids level is in the normal size press range of 30%.

RELATION BETWEEN STARCH CHEMISTRY AND COATING COLOUR PROPERTIES

Starches, unlike latex binders which are dispersions of particles, are hydrocolloids and thus soluble in the aqueous phase.

Therefore they form three dimensional structures, whose architecture and stability influences important coating colour qualities like rheology and water retention.
Today many possibilities are available to engineer a starch with a specific property profile by raw material choice and different single step or even multiple step modification reactions.
All this not only influences the behaviour of the starch solution, such as viscosity level and stability, shear resistance and water retention, but also interactions with pigments, film forming and migration. The evaluation of the behaviour of a starch in a coating colour, and the final paper properties, needs an empirical laboratory evaluation and pilot plant confirmation for fine tuning.

Effect of Shear on Coating Colour Viscosity.

During application and dosing, the coating colour is subjected to different levels of shear depending on several parameters including the type of coater, machine speed and coatweight.
In order to estimate the runnability of a coating colour its rheological behaviour, under the shear conditions actually applied during the coating process, must be known. Using a combination of different types of rotational (Brookfield, Haake, Ferranti Shirley) and capillary viscometers a range of shear rates from $10 - 2 \cdot 10^6$ sec^{-1} can be covered. Comparing a thermally modified starch, oxidised starch and a CMC in a LWC colour for short dwell coater application the strong pseudoplasticity of CMC can be seen i.e. high low-shear and low high-shear viscosity. This behaviour has been described before and is

explained by the structure of the dissolved hydrocolloid molecule, as well as by pigment-hydrocolloid interactions . The starches give somewhat higher high-shear viscosity than the CMC (see Figure 24.).

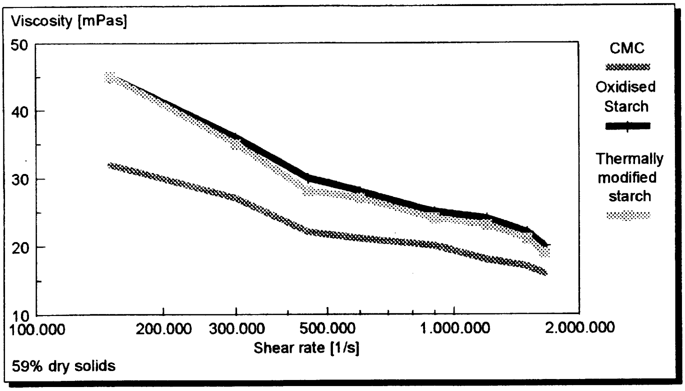


Fig. 24. The development of the coating colour viscosity during increased shear

But to draw immediately the conclusion that CMC must result in the best runnability in the coater due to its low high-shear viscosity would be premature since a high low-shear viscosity is not an advantage in short dwell coaters, and the influence of water retention, immobilization and runnability have to be taken into account at the same time.

As Fig. 25 shows, with the thermally modified starch the desired add-on is achieved at the same tube pressure on the short dwell coater as with oxidised starch. This means that the high-shear viscosity is indicative of the behaviour on the coater, but it is not the only factor involved.

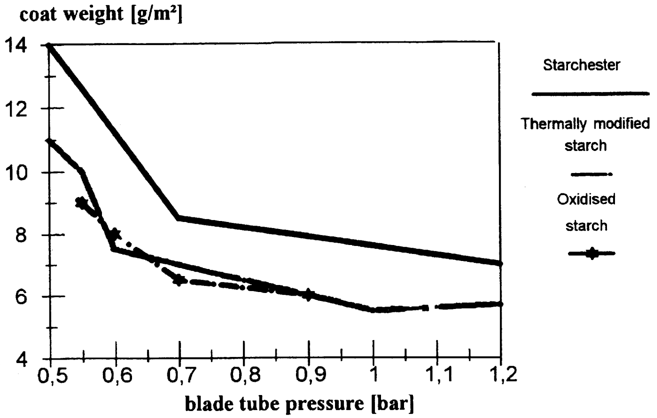


Fig. 25. The relationship of coat weigth and blade tube pressure in a short dwell coater

Water Retention and Immobilization

In addition to the control of coating colour rheology the cobinder also determines the resistance of the colour to release water. A too low water retention leads to an immobilization between applicator roll and blade. Dilatancy streaks under the blade can be the consequence.

A too high water retention prevents the formation of a thin "filter-cake" at the applied coating/base paper interface. This filter helps prevent pigments and other coating colour components from penetrating too deeply into the base sheet. A poor filter cake is unfavourable for coating hold-out and fibre coverage, especially at lower coatweights.

At the optimum, the coating colour solids remain constant, the blade tip runs under constant load in a mobile phase, the fibres do not swell too much and the coating immobilizes quickly enough to minimize binder migration.

It is difficult to find a meaningful laboratory evaluation technique of water retention capacity of coating colours. Today the method of pressure filtration,with variations, is most frequently used .

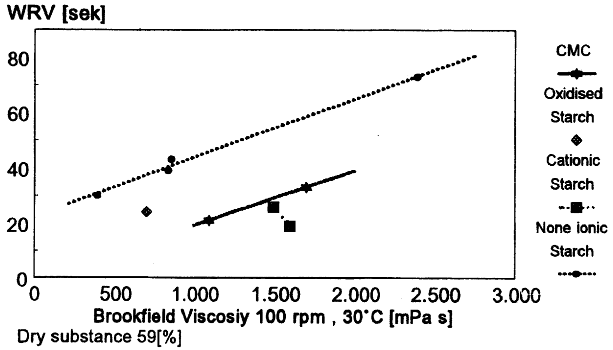


Fig. 26. Correlation of coating colour viscosity and water retention

By comparing non-ionic starches of different modification and molecular weight, to CMC types and cationic starches of different molecular weight, a clear correlation between coating colour viscosity (which depends on starch viscosity) and water retention for the non-ionic starches can be found (see Fig. 26). CMC as well as the oxidised (anionic) and cationic starches deviate from this pattern showing lower water retentions at comparable viscosities. This behaviour is explained by interactions with other components which are strongest among the cationic starches. By adjustment of cationic substitution and molecular weight it is possible to adjust to an optimal degree of pigment flocculation.

STARCH - LWC BLADE COATING

Blade coaters at the speeds of todays LWC coaters require quite elaborate coating colours. The cobinder plays an important role.
It should provide a high low-shear viscosity to allow skip free application of the coating colour at acceptable applicator roll speed. It

then has to hold onto its water strongly enough to prevent the coating colour from penetrating too deeply, and to leave sufficient wet film on the surface to allow the blade to run in a mobile phase (see Fig. 27).

This, together with a low high-shear viscosity, ensures that the desired coatweights can be achieved with low blade pressures and thus a minimal risk of breaks. Of course it should, in addition, lead to excellent printability results in conjunction with the synthetic binder .

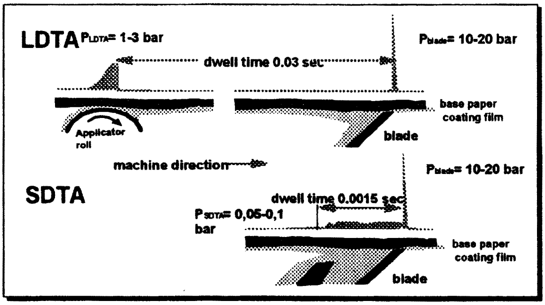


Fig. 27. Configuration during blade coating

To fulfil one or two of these requirements is relatively easy, but the combination of all of these elements is what makes guaranteed performance difficult.
With a low viscosity pigment it is not easy to achieve the necessary low-shear coating viscosity (for roll applicator blades) using only approximately 4 parts of starch and still have a stable non-thickening system without using "flocculation methods".

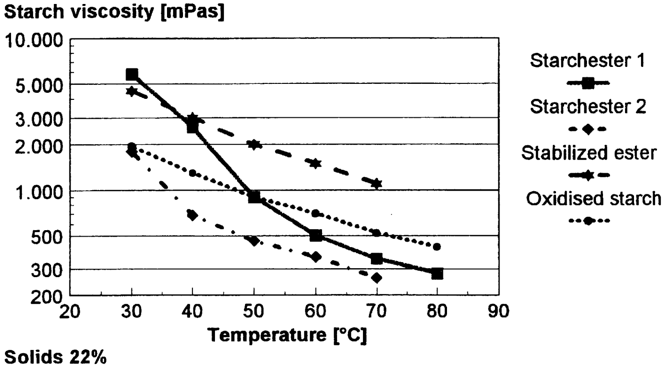


Fig. 28. Viscosity profiles of coating starches

As shown in fig. 28, using the normal techniques of hypochlorite oxidation or acetylation, viscosity stable starches can be produced, but only at rather low viscosities. An acetylated starch of „normal" degree of substitution (appr. 1,5 % acetyl level) with higher viscosity eg. as shown in Figure 28, is no longer stable enough. Larger substituents or many more of the smaller ones are needed in order to ensure the viscosity stability of the starch, and of the coating colour. At the same time such starches have to be optimized with respect to rheology.

In order to verify the high-shear viscosity measurements a pilot coater can be used. The dry coatweights, as depicted in Fig. 29, of course differ quantitatively from those achieved on paper, but give a good comparison of how different cobinders can influence the high-shear viscosity or necessary blade pressures during application. In this example the roll application blade coater was run at 1000 m/min without paper and the coating film, (at 61 % solids), metered under a range of conditions, was scraped off the backing roll to determine its volume.

For the acetylated starches with normal degree of substitution, the starch viscosity does not influence the high-shear viscosity and add-on. Less colour is applied for the oxidised starch - though its viscosity level is above that of the acetylated starch. The oxidised starch and CMC show practically identical behaviour. The best characteristic in this respect, however, is shown by a special stabilised starch ester that had the highest low-shear viscosity level. Plant trials have confirmed these findings.

The use of tailormade starches makes it possible to select the products to suit the demand of the coating process and the required paper properties.

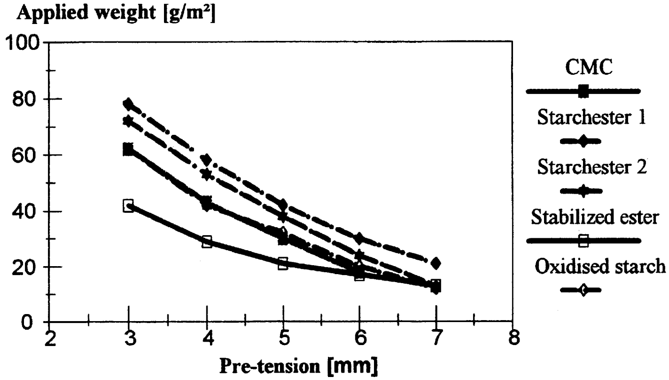


Fig. 29. Influence of blade pretension on coat weigth

Comparing a low viscosity cationic starch to a medium viscosity starch ether and CMC in a blade formulation shows that the cationic starch despite its low viscosity builds up a structure that leads to high viscosities, both under low- and high- shearing conditions. This is indicative of a strong starch-pigment interaction resulting in aggregates that are quite resistent to shearing.

These effects are more pronounced with clay than with calcium carbonate so that, by proper choice of pigment combination, degree of cationicity and molecular weight, a good control of coating immobilization and microstructure is possible. Hydroxypropyl starch of a much higher viscosity leads to coating structures that are much less dependent on the shear conditions. This can be explained by a much less associated and relatively rigid hydrocolloid molecule in solution.

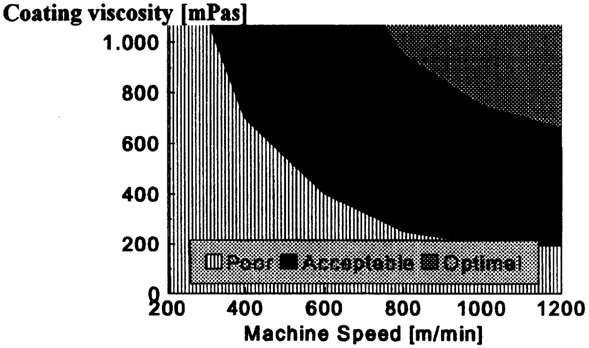


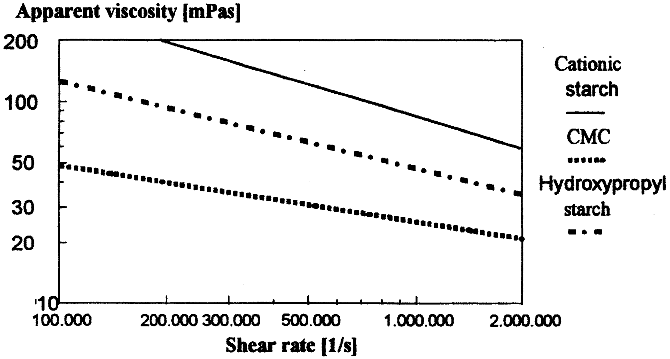
Fig. 30. Operational ranges of a 25 mm smooth rod in a film coater

STARCH - FILM PRESS COATING

For the production of pigmented commodity grades, with coatweights of 10 g/m^2 total or more, the smooth rod of 25 mm diameter seems to be an ideal premetering element. Ideal because it is cheap, easy to use (no/low wear), and due to the high effective pressure, it is able to level out cross-machine variations.

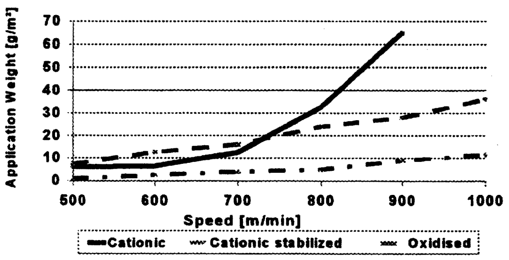
Generally speaking, the add-on improves as the Brookfield viscosity of the coating colour increases. At 1000 m/min for instance, a viscosity below 200 mPas is insufficient, between 200 - 750 mPas the results are satisfactory while for good results the range above 750 mPas is advisable. The lower the machine speed the higher the viscosity required (see Fig. 30).

However, the starch type has a strong influence on the hydrodynamic condition under a smooth rod. The influence of shearing on the apparent viscosity is shown in Fig. 31. Cationic starches, neutral starch ethers, oxidised and thermally converted starches develop very different viscosity levels as the shear rate is increased. This leads at the end to great differences of applied coatings as the film press speed is changed (see Fig.32).This confirms the previous findings that a cationic starch imparts a high high-shear viscosity to the coating colour. The stability of the cationic starch and of the subsequent coating colours can be achieved by the combination of cationic substituents and other bulky, non-ionic substituents.



59% solids

Fig. 31. Influence of shear rate on apparent viscosity



solids 50%; smooth rod diameter 25mm

Fig. 32. Influence of the starch type on the coat weigth add-on during machine speed changes

With respect to offset printability it is generally accepted that double modified starches can develop even more dry and wet binding strength than the hydroxypropyl starch, even though the latter is already very good in this respect. Such double modified starches lead to high printing gloss levels of double coated papers (film press/blade).

PROTEIN

INTRODUCTION

Soy protein consists of a polymer chain of amino acids, which has a variety of side groups (Fig. 33). These side groups are what makes the polymer sufficiently hydrophobic to be water insoluble, but hydrophilic enough to be solubilized with an alkali.(Fig. 34).
Soy protein polymers are the dominant cobinders for paperboard in the United States. They are used in approximately 2/3 of all coated board and in all coated board market segments. These polymers are not widely used in Europe, but when they are it tends to be more in the paper segment than in board.
The protein based starting material is extracted from soybeans. Soy polymers are, therefore, an environmentally friendly, naturally occuring material from a renewable world-wide resource. The functional behaviour of soy polymers in coating formulations depends not only upon their chain length and associated molecular weights, but most importantly upon their net negative charge.

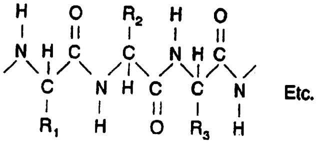
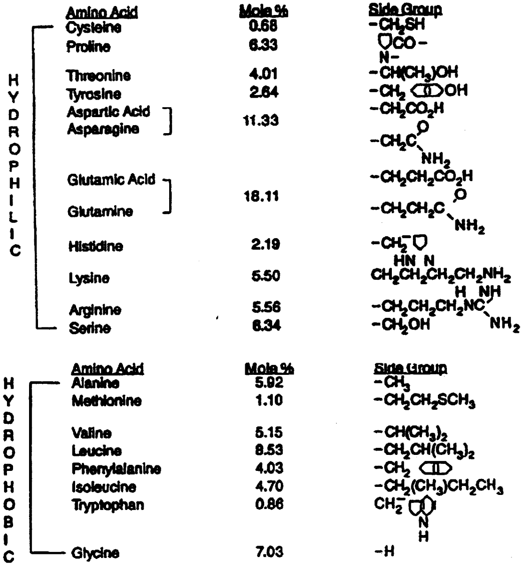


Fig. 33. Protein polymer

PRINCIPLE OF SOY POLYMER TECHNOLOGY

Soy proteins are obtained from soybeans by alkaline aqueous extraction after they have been crushed and the soybean oil removed.
The aqueous alkaline extract of the defatted soybeans contains soluble low molecular weight sugars together with soy protein in its native or globular form. This extract stream is then treated in a variety of processes to prepare the desired end product.



	Amino Acid	Mole %	Side Group
HYDROPHILIC	Cysteine	0.68	$-CH_2SH$
	Proline	6.33	CO- N-
	Threonine	4.01	$-CH(CH_3)OH$
	Tyrosine	2.64	$-CH_2$ OH
	Aspartic Acid	11.33	$-CH_2CO_2H$
	Asparagine		$-CH_2C(O)NH_2$
	Glutamic Acid	18.11	$-CH_2CH_2CO_2H$
	Glutamine		$-CH_2CH_2C(O)NH_2$
	Histidine	2.19	$-CH_2-$ HN N
	Lysine	5.50	$CH_2CH_2CH_2CH_2NH_2$
	Arginine	5.56	$-CH_2CH_2CH_2NHC(NH)NH_2$
	Serine	6.34	$-CH_2OH$

	Amino Acid	Mole %	Side Group
HYDROPHOBIC	Alanine	5.92	$-CH_3$
	Methionine	1.10	$-CH_2CH_2SCH_3$
	Valine	5.15	$-CH(CH_3)_2$
	Leucine	8.53	$-CH_2CH(CH_3)_2$
	Phenylalanine	4.03	$-CH_2$
	Isoleucine	4.70	$-CH_2(CH_3)CH_2CH_3$
	Tryptophan	0.86	CH_2- N H
	Glycine	7.03	$-H$

Fig. 34. Amino acid composition of soy protein

Soy Polymer Characteristics

The native soy protein is an associated polymer. The four major components are referred to as the 15S, 11S, 7S and 2S fractions. The major protein entities of these fractions are alpha, beta, and gamma conglycinine and glycinine. The approximate ratio of the sedimentation fractions in the extract is 15S -1 %, 11S -31 %, 7S - 52 %, 2S -16%

(see Fig. 35). Most of the 2S whey protein is lost during commercial isolation, and as a result, the standard commercial products are primarily 7S and 11S fractions.

The globular native protein is held in a tightly coiled structure by hydrogen and disulfide bonds (Fig. 36). Most of the hydrophobic side groups are located in the interior of the protein and the hydrophilic groups are exposed. The subunits are tightly coiled polymers made up of 20 amino acids characterized by different functions. The types and ratio of these amino acids differentiate the properties of the various commercial products. Based on the amino acid character of the soy polymer, it is amphoteric but while possessing both anionic and cationic charges it has a net anionic charge.

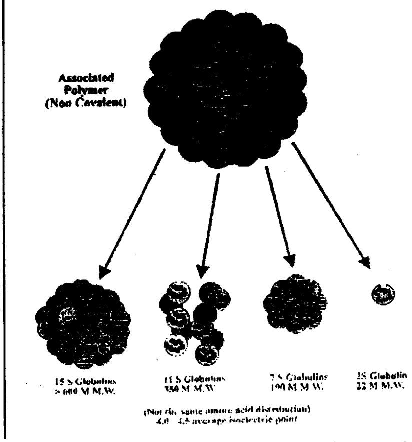


Fig. 35. Typical soy protein structure - sedimentation fraction

The even distribution of anionic and cationic sites promotes interaction of the subunits resulting in a high associated molecular weight. This in turn translates to a high solution viscosity.

Various chemical reactants can be added to the extracts of the processing streams to chemically modify the protein. This treatment also improves the functionality of the protein, not only as a coating modifier, but also as a coating dispersant. The modified soy proteins are precipitated by acidic neutralisation to the general isoelectric point of the

protein. Soluble sugars and processing salts are typically removed when the precipitated protein is concentrated and separated. The dried purified proteins are ground and packaged as protein polymers.
The various types of modification procedures are:

Hydrolysis

- Acid
- Base

Disulfide Bond Cleavage

- Reducing Agent
- Oxidizing Agent

Fluidizing Agent

- Urea
- Dicy

Derivatization

- Carboxylation
- Hydroxyethylation

Enyzme Modification

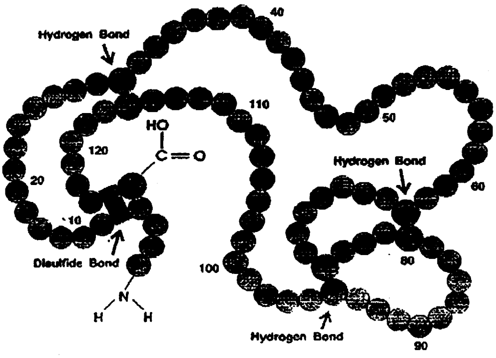


Fig. 36. The coiled protein structure is caused by hydrogen and disulfide bonds

As is typical for condensation polymers, the modified soy polymers have modest molecular weights generally in the 150-400 M.M.W. range.

Hydrolyzed soy protein still remains globular in nature. These molecules are amphoteric containing both cationic (amines) and anionic (carboxylic acids) characteristics. One way to characterize the degree of cationicity is to measure the moles of amines and carboxylic acids of the product . The difference between the number of moles of carboxylic acids on the polymer and the number of moles of amines gives the net negative charge(Fig. 37).

	Moles/10^5GM.
Amino ($-NH_2$)	116
Carboxyl (–COOH)	130
Hydroxyl (–OH)	56
Phenyl (–⌬ OH)	23
Sulfhydryl (–SH)	6

Fig. 37. Functional side chains

All soy polymer products used in the coating industry have more anionic entities than cationic, but some still are relatively high in cationicity. By chemical modification the cationic groups can be reduced and the acid groups increased giving a greater net negative charge.

Soy polymers are available with a range of net negative charges and associated molecular weights so that the best product for a given application can be selected.

Controlled alkaline heat treatment of the protein solution breaks down the globular native protein into smaller units, which results in a more uniform structure with improved functionality as a paper coating modifier.

Soy proteins can be thermo-chemically modified to alter the protein sub-structures and functionality. Such chemical processing allows the native protein globular structures to unfold and reassociate mostly by hydrophobic/hydrophilic regions. This exposes more hydrophilic anionic groups and changes the packing characteristics, thus reducing the self association tendency and solution viscosity. More hydrophilic anionic or acidic groups are liberated during caustic treatment due to the breakdown of the glutamine and asparagine sidechains to glutamic and aspartic acids.

The unhydrolyzed protein can be made more anionically charged by carboxylation . There are then still significant numbers of basic groups left on the protein even though many have been modified. Solution viscosities may vary owing to the different anionic charges. The higher anionic charge causes more dissociation of subunits, effectively lowering the associated molecular weight in solution.The viscosity of these products can still be high because of protein association.Partial hydrolysis, leading to a lower solution viscosity,and chemical modification , to give an increase in anionic character, will lead to a mid-low viscosity product of mid-low adsorbance.
An extended thermal chemical modification which is linked with carboxylation can lead to products of low viscosity and with a highly anionic character. These products can function in many respects as secondary dispersants as well as binders.

The charge of the protein polymers offered to the industry as coating binders are typically in the range shown below:

Soy Polymer Types	NetNegativeCharge
• Native Unhydrolyzed	- 14
• Caustic Treated	- 38
• Unhydrolyzed Carboxylated	- 55
• Partial Thermal-Chemically Treated Carboxylated	-58
• Extended Thermo-Chemically Treated	- 62

SOY PROTEIN INTERACTION WITH PIGMENTS

The functional behaviour of the polymer is dependent on its chain length, its associated molecular weight and its net anionic charge. These unique features provide several benefits in the coating formulation.
The reactivity of the soy polymer with various pigments (e.g. clays) can be controlled to optimize the performance and runnability of the coating formulations containing these soy polymers.
The cationic moieties interact with the anionic moieties on the pigment particles. The degree of cationic charge, as already described, can be

chemically engineered, controlling the degree of interaction with the clay.

The large numbers of cationic sites are extremely reactive to kaolin surfaces. The cationic groups reduce the effect of dispersants on clay slurries causing structuring, and what is classically referred to as „protein shock". Even though the proteins are attached to the clay surface, they are still very reactive with one another causing high coating viscosities and irregular pigment packing. Clay coatings containing native soy protein tend to dewater very quickly due to the porous pigment packing structure.

Associative forces between the recognized protein bodies, which are reduced during caustic treatment of the soy protein, also lower the solution viscosity and pigment interaction, resulting in loss of coating viscosity. These products are less attracted to the pigment particle surface and produce less shock, allowing more uniform pigment packing of the coating.

Pigment interaction is dependent on the anionic groups of the protein, but the structural orientation of the charged sites and average molecular weight also have a significant influence on the protein-pigment interaction.

THE PREPARATION OF SOY POLYMER; ISOLATED SOY PROTEIN AND CASEIN COATINGS

The cooking (when necessary) of these proteinaceous materials requires heat and temperatures in the range of 40° to 70° C. Because of the moderate temperatures involved, hot water and direct or indirect steam can be used. Alkali, preferably ammonium hydroxide, is used to solubilize these normally water-insoluble materials. The general procedure is to slurry the selected material in an appropriate amount of water to 10-25% solids, depending on the product, being sure to allow for condesate dilution if live steam is used. The temperature is adjusted to approximately 60° C.

The time needed for dispersing depends on the class of material selected, -soy polymers the fastest, then isolated soy proteins, and casein the slowest. The soy polymers disperse readily within 1-2 minutes, isolated soy proteins may require 5-10 minutes, and normally 30 minutes is required for the slightly more hydrophobic casein. An appropriate amount of alkali, 5-20%, 26° Be, ammonium hydroxide, or 2-5% sodium hydroxide, based on protein solids, is added to obtain a final pH of 8.5-9.0. To achieve the expected performance from a coated substrate to be offset printed, ammonium hydroxide, a fugitive alkali, and a crosslinker should be used to achieve the required level of wet rub resistance and wet pick. After adequate dispersion, termperature, and alkali have been selected, the material is cooked for approximately 30 minutes to achieve final solubilization. These materials, normally supplied in a dry form, only need to be solubilized, unlike starch which requires higher temperatures, at least briefly, to effect gelatinisation. The more soluble soy polymers can be dissolved at pH 8.5 minimum, while casein normally requires pH of 9.5-10.0 minimum. It is these considerations that lead to the selection of approximately 60°C and pH 8.5-9.0 as typical conditions for solubilization.

No general statement can be made regarding the concentration which can be successfully prepared. Some higher molecular weight unmodified materials are limited by the viscosity of the final solution to 10% solids. Other products in commercial use are being prepared at 25 % solids.

PREPARATION OF COATING COLOUR

Generally, the pigment dispersion is optimally prepared and the protein solution is added to the pigment slurry in a controlled manner. Finally, the latex binder is added, followed by any other additives which may be required. In some cases, the pigment dispersion is added to the protein solution, but depending on the rate of addition and the level of agitation and shear, this may present difficulties in handling and affect the performance of the coating.

Addition of Prepared Coating Modifier

Historically, proteinaceous materials were limited in use and suffered in reputation because of spoilage and too great an interaction with the pigment. A high level of pigment and protein interaction can lead to high viscosity build-up and flocculation or protein shock, which will limit performance and runnability. When working with coatings having above 50 % solids content, considerable trouble with protein shock may be

encountered when the casein or isolated (not modified) soy protein solution is first added to the pigment slurry. When the first 1 or 2 % of casein or isolated soy protein is added, there is a considerable increase in viscosity and some pigment agglomeration. It may take a while for this to break down before the rest of the protein can be added.
Although the balance of charge on the polymer is anionic, it is the high number of cationic sites which causes the severe interaction of casein and isolated soy with pigments, particularly clays of all types. Yet it is the interaction with the pigment that provides many of the beneficial properties of protein binders. If the interaction could be controlled, their utility would be greatly enhanced. That is one of the major breakthroughs achieved with the chemically engineered soy polymers. With soy polymers, less care is needed during mixing, higher levels can be used in the formulation, higher solids formulations can be used, and less „protein shock" is encountered.

TYPICAL FORMULATIONS

Soy polymers are more forgiving and generally can be used at higher levels, if needed, than the more cationic isolated soy proteins or casein, and generally can be run at higher solids and faster speeds
The wide variety of applicator types as well as coating formulation ingredients prevents one from giving specific typical formulations.

The following general comments can be made, however:

- In higher solids rod and blade formulations, 3-4 part of protein will provide the appropriate benefits of structuring, improved runnability, binder migration control, and water retention.
- In lower solids air knife or ultra-lightweight coatings, 6-8 parts of protein are typically used, giving similar benefits.
- Ammoniacal salts are most frequently used for offset coatings so that adequate wet pick and wet rub are achieved, but sodium salts are also commercially used.

Ammoniacal or sodium salts are used for rotogravure coatings where water sensitivity is not an issue.

SUMMARY

The soy protein - pigment interaction is the major mechanism controlling the functionality of soy protein in a coating formulation. It has significant impact on the immobilization of the coating, the coating structure and on the subsequent coated sheet properties:

- Due to this interaction coating immobilization can be achieved rapidly, helping to improve binder migration control and reduce the mottling tendency.
- The soy protein - pigment interaction also provides a coating structure with high void volume, which consequently improves fibre coverage. Pore size and pore distribution vary with the modification of the soy proteins, but the creation of this "interaction" coating structure gives controlled pore size and uniform pore distribution, helping to improve the final coated sheet properties, such as printability (ink receptivity) and glueability.

Soy proteins with various degrees of chemical modifications are commercially used for this purpose.

Soy proteins of the new generation are modified to be used in low or high solid coatings without compromising the rheological properties. Chemical modification of the proteins also helps control water retention of the subsequent coating formulations.

LATEX

INRODUCTION

A latex is a dispersion of finely divided particles of polymer in water. 1,6 mio tons (calculated as dry) of synthetic latex were sold in Western Europe in 1993, for all industrial applications. Styrene-butadiene (SB) latex made up 36 % of this tonnage, and styrene-acrylates (SA) latex 25 %. (see Fig.38). 460 000 tonnes (dry basis), equivalent to 920. 000 tonnes of commercial product at typically 50% solids, were used in the paper industry:

70 % SB-latex
16 % SA-latex.

Latices are primarily used in paper coating formulations to yield improved coating strength, sheet gloss, ink gloss and printability.

Macroscopically, latices are liquid white milky substances, and they have high adhesive properties. This adhesiveness, or stickiness, of latex provides the binding strength that is desired in many paper coating applications. Microscopically, latices are composed of spherical polymer particles suspended in water.
Typically, a latex is 50 - 55 weight % polymer solids concentration. Typical latex particle sizes range from 100 to 300 nm.

The impact of this particle size range is not fully appreciated until one realizes that a standard latex of 50 weight % polymer solids with an average particle size of 200 nm contains 10, 000, 000,000 particles per cubic centimeter.

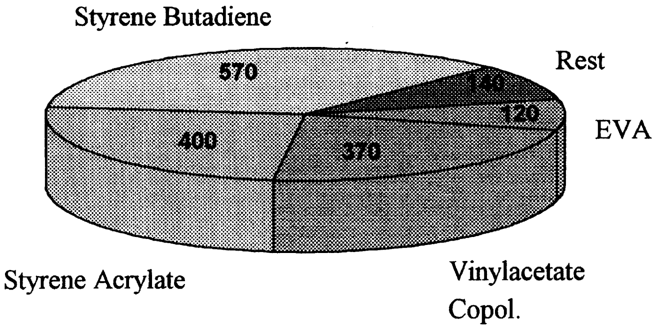


Fig. 38 Consumption of latex in 1993 (in 1000 tonnes)

The latex manufacturer can control polymer particle composition and size, molecular weight and degree of crosslinking.
Latices for paper coating are produced by an emulsion polymerization process. The initial development of emulsion polymerization occurred over the period from 1930 to 1950, in an effort to find a replacement for natural rubber.
An emulsion polymerization system is very complex and involves many colloidal phases, several monomers, modifiers, surfactants and initiators.To perform an emulsion polymerization, monomers are first

suspended as an emulsion of droplets in water, aided by an emulsifying agent. Reaction is usually initiated by water soluble free radical initiators, such as sodium or potassium persulfate. The rate of polymerization is directly affected by temperature, monomer concentration, the number of free radicals present and emulsifier concentration. Emulsion polymerizations are amenable to both batch, semi-batch and continuous reactor systems.

PRINCIPLES OF LATEX TECHNOLOGY

Monomers

The monomers used for the polymerisation process are chemicals of low molecular weight with reactive groups which are positioned to enable radical polymerisation to take place. The polymer structure which is created is very much dependent on the reaction conditions.
Polymers which are built up by the use of one type of monomer only, are called homopolymers. When two or more monomers are polymerized , they form co-polymers.
The copolymerisation process is not possible between all monomer combinations. Typical monomer combinations are:

- styrene / butadiene
- styrene / acrylic ester
- acrylic ester / methacrylic ester
- vinylacetate / acrylic ester
- vinylchloride / vinylidenechloride
- vinylchloride / acrylic ester

Often a combination of three monomers may be polymerisized, the third monomer can then contain a double bond and a functional group. Monomers with a suitable functional group include acrylic acid, methacrylic acid, acrylamide, methacrylamide, methylolacrylamide. Only small qantities of these monomers are required to be built into the polymer structure, nevertheless they are very important and have considerable influence on the properties of the final polymer.
Styrene polymers yield hard inflexible thermoplastic materials, while butadiene polymers are usually soft and flexible. When these two monomers are copolymerized over a wide range of styrene-butadiene (S/B) ratios, polymers with a wide range of properties are produced.

Vinyl acetate latices, readily made by homopolymerization, yield polymers that are hard and resinous. However, vinyl acetate copolymers can also be made to produce a wide range of properties.

Monomer	Contribution	Tg°C
Styrene	Stiffness, Gloss	+ 100
Acrylonitrile	Stiffness, Solvent-Resistance	+ 100
Methyl-Methacrylate	Stiffness, Gloss, UV-Stability	+ 105
Vinyl Acetate	Porosity	+ 30
Butyl-Acrylate	Binding, Flexibility, UV-Resistance	- 50
Butadiene	Binding, Flexibility	-100

Fig. 39. Contribution of latex monomers to latex film and paper coating properties

Acrylic monomers are easily homopolymerized and can readily be copolymerized to form products with a large range of physical and end-use properties. Methyl acrylate produces a tough, soft, rubbery polymer that is almost tack free, whereas butyl acrylate polymers are soft, plastic and tacky.
The contribution of the different monomers to the latex film characteristics or to the coated paper is summerized in Fig. 39.

Polymerisation
The polymerisation process can briefly be divided in three steps:

- Initiation and starting reaction
- Chain growth, this is the real polymerisation process
- Termination of chain growth, i.e. through the reaction of two polymer radicals with each other.

There are appr. 20 different process parameters which can be independently adjusted during the polymerisation process

Modifiers

The surface of a latex particle is often modified by incorporating small amounts (0-10%) of vinyl acids, vinyl hydroxyl monomers, unsaturated amines and amides. Examples of these modifiers are acrylic acid , itaconic acid, fumaric acid, 2-hydroxyethyl acrylate, methacrylic acid and acrylamide.

These modifiers add functionality to the polymer providing reactive sites to increase adhesion and enhance curing reactions in latex films. Modifiers also increase the colloidal stability of latex particles, helping prevent coagulation. The addition of only small amounts of modifiers greatly influences latex properties and stability.

Initiators

The most important initiators for emulsion polymerization are the inorganic salts of persulfuric acid, such as sodium or potassium persulfate. In all cases, radical initiators for emulsion polymerization are water soluble to ensure that polymerization occurs in the latex particles rather than the monomer emulsion droplets.

Surfactants and Colloidal Stability

Surfactants are used in latex systems to give colloidal stability to the polymer latex particles and thereby avoid agglomeration. A surfactant molecule is composed of a hydrophobic part, called the tail, and a hydrophilic part, called the head. Based on the charge carried by the head, surfactants are classified into several categories. Cationic and anionic surfactants are electrostatic stabilizers using charge to provide stabilization.

Another category of surfactants are polyelectrolytes. Polyelectrolytes combine both electrostatic and steric features to ensure colloidal stabilization.

Latex, like all colloidal systems, are thermodynamically unstable and tend to coagulate. This instability results from the tendency of the small latex particles to decrease the large specific surface and excess surface energy by agglomeration. Latices can be stabilized by either electrostatic repulsion between latex particles or by steric stabilization using nonionic macromolecules.

Steric stabilization is created by the presence of long-chain molecules at the interface between latex particles. The most effective steric stabilizers are copolymers that are composed of two portions. One portion, insoluble in the aqueous phase, becomes anchored to the latex particle surface. This anchoring can occur chemically or physically. The second portion of the stabilizer is soluble in the aqueous phase and imparts stability.

Surfactants are added to stabilize the latex particles during polymerization and are also added to ensure the stability of the final latex product.

LATEX CHARACTERIZATION

The polymer dispersions formed during the emulsion polymerisation process are two component systems. The dispersion medium is water, in which the polymers are finely distributed. The water contains also small quantities of solubles in the form of low molecular weight components, which were added during the polymerisation (emulsifying agents, inorganic salts,etc.). Additionally antifoamers and biocides may have been added after polymerisation to improve the storage and application properties of the dispersions.

Solids Content

The solids content of a dispersion is made up by the polymer, the polymerisation chemicals and any non-volatile additives. The non-polymeric components are very much different from one polymer to another. In some polymers this can be as much as 8 %, however, it will be normally considerably lower, especially in carboxylated polymer dispersions.

pH- Value

The pH-value of a polymer dispersion can influence its stability. Alkali adjusted dispersions will be generally of improved chemical or mechanical stability.

Surface Energy

Surface energy, or surface tension, is an important parameter of a latex coating . Surface tension is critical for the adhesion between the coating and substrate.It is mainly dependent on the total surface area of polymer particles, and on the type and quantity of surface active substances. The surface active chemicals are normally only available in small quantities in the water phase; the main portion is adsorbed by the latex-particles.
The surface tension after film formation is also an important factor affecting the wettability and printability of latex coated paper. Its measurement can be related to particle composition, particle size, polymer chain mobility and surface modification of the latex. A low surface tension means that the film is more water soluble.

Particle Size

Measurement of particle size and particle size distribution is necessary to characterize any latex. Accurate knowledge of the particle size and particle size distribution is critical because physical properties such as high-shear viscosity, low-shear viscosity, pick strength and sheet gloss are directly affected.
Polymer dispersions contain normally spheric particles of different diameter. The different methods used to determine this property lead to very different results which are only meaningful if details of the method are known. As a general rule polymer dispersions used for coating binders are mainly monodisperse systems and a typical particle size distribution in the range of 100 to 300 nm.

Latex Polymer Composition

Infrared spectroscopy is the most commonly used tool for determining the composition of a latex . Specific infrared frequencies are associated with molecular vibrations and rotations of certain chemical functional groups. By quantifying well known group frequencies, followed by computer calculation, bulk composition can be estimated to within about 5%.

Gel Content

The gel content is described as the amount of crosslinked units or insoluble polymer.The latex is treated with a solvent and the insoluble part of the product is used to characterize the gel-content of the latex. The interpretation of figures for the gel content is only meaningful if the solvent and the composition of the latex is known.

Glass Transition Temperature (Tg)

The glass transition temperature (Tg) is the temperature below which polymer chains no longer have freedom of motion and are subsequently frozen into a configuration that resists bond deformation. The physical state of the polymer below the Tg is called the glassy state. Upon heating, the polymer undergoes a transition from the hard glassy state to a soft rubbery state. This is the glass transition temperature (Tg).

Tg can be measured by thermal analysis technique - Differential Scanning Calorimetry (DSC). This technique characterizes thermal transitions in both polymeric and non-polymeric materials. The approach involves simultaneously heating two aluminum pans in a thermostatically controlled holder. The polymeric sample is enclosed in one of the pans; the second pan remains empty. The difference in the rate of increase in temperature, as measured by thermocouples connected to both pans, indicates energy absorption or release from the sample. The temperature range and the rate of measurement is defined by the material being analyzed. Routine DSC analysis can be accomplished in less than 20 minutes. Other data accessible with this technique include crystalline melting point, residual monomer analysis and polymer phase compatibility.

Glass transition temperature is an important parameter that can be related to the composition, the heat capacity (Cp), as well as the structure of the polymer particle (crosslinking). Tg provides a realistic comparison between different polymers.

Minimum Film Formation Temperature (MFFT)

The minimum film formation temperature (MFFT) is the minimum temperature at which a latex will form a continuos film. This property is characteristic for each particular latex and can be measured fairly reproducibly. MFFT is measured using a thermal bar as the substrate. The bar is heated at one end and cooled at the other. Just below the MFFT there is a distinct point where hazing is observed in the dried film; further down the bar „cracking“ takes place. The MFFT is approximated to be slightly above the hazy area. Estimation of the MFFT is critical to ensure that proper processing and drying conditions are chosen for developing a latex film.

The film forming temperature can be decreased by the addition of a softening agent. A temporary softening can be an advantage for many applications in order to faclitate film formation; a volatile softening agent will then lead to a hard film, which will soften only at higher temperature.

INFLUENCE OF PAPER CHARACTERISTICS THROUGH LATEX ADDITION

The different latices are used in the first place as a „binder", thereafter to influence the paper surface characteristics, such as gloss and surface microporosity, and to influence the calendering process. Latices will additionally influence the rheology and stability of the coating clolour. The development of latex process technology during the last 5 years has opened up many possibilities for controlling coated paper production and for engineering specific products. The physical measurements of latex dispersions and latex film properties are still important quality criteria for any single latex product. However, it is still very difficult to draw firm conclusions from these determinations or monomer compositions to be able to predict the influence of the latex on the coating colour performance and susequent paper properties.

In the following paragraphs an attempt is made to link the influence of latex properties on coated paper and board properties. However, this systematic aproach can be valid only if the process conditions during modification do not appreciably change.

Requirements for different paper and board grades, together with some latex control parameters are listed in Fig. 40.

Monomer Ratio

The influence of the monomers is shown in Fig.41 where it becomes clear that paper gloss can be improved considerably if the styrene content of the latex is increased from 50% to 70 %. At the same time, however, the binding efficiency of the latex, shown here as pick rating and wet rub, is also affected. The dry pick strength of the paper goes through a maximum at appr. 60 %, and as the wet rub of the paper decreases at higher styrene levels it is obvious that the styrene content has to be carefully considered during latex engineering.

Application	Requirement	Some Control Parameters
Art Paper	Printability, Gloss	Monomer Chemistry, Tg
Standard Sheet Off-Set	Strength	Tg, PS
Standard Web Off-Set	Blistering Resistance	Gel Content
LWC Off-Set	Strength	Tg, PS
LWC Roto	Surface Smoothness	Solebinder Approach
Filmcoated Papers	Runnability	Latex Stability
Mat Papers	Ink Abrasion Resistance	Monomer Chemistry
Graphical Board	Gloss Light Stability	Tg Monomer Chemistry
Food Packaging Board	Odour Regulatory Compliance	Residual Monomers Chemistry

Fig. 40. Important latex requirements in different applications

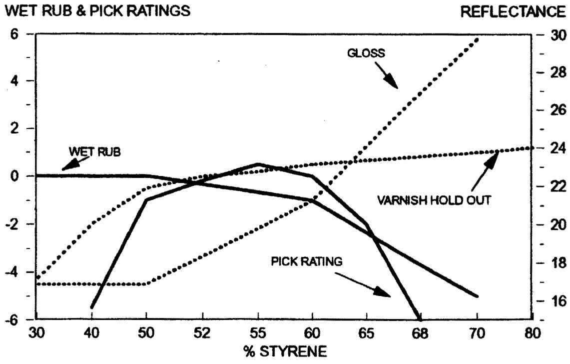


Fig. 41. The influence of styrene content on the latex performance

The stiffness of the latex film increases with increasing styrene content, until it passes through a maximum, similar to coating stiffness.
It is essential to bear in mind that monomer types and their degree of crosslinking or gel-content are just as important as monomer ratios.

Gel Content

The gel content of the latex affects the following paper properties:

- blistering temperature
- dry pick
- porosity

The more linear polymers give higher porosity and such latices are therefore better suited for web offset papers where blistering could be a problem. Higher porosity however also leads to a reduction in print gloss. As seen earlier both the dry and wet pick resistance of the paper surface seem to go through an optimum as the gel content increase.

Carboxylation

The degree of carboxylation of a SB-latex influences the product performance as follows :

- increased polymer strength at the expense of elasticity
- elevated temperature range of elasticity
- increased hardness and abrasion resistance
- enhanced wetting
- enhanced resistance to hydrocarbon solvents
- improved adhesion to many substrates
  - divalent metals
  - melamine (and urea) formaldehyde resins
- improved range of crosslinking reactants
- improved colloidal stability of the latex

The effect of carboxylation on coating colour viscosity is shown in Fig. 42. Coating colour viscosity increases as the carboxylation level increases.This is due to interaction of the carboxylic groups with other coating colour components. The coating colour structure which is built up leads to higher viscosities, as long as no shear is introduced to the system.

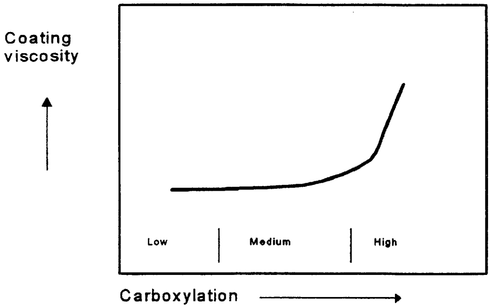


Fig. 42. The effect of carboxylation on coating viscosity

If the viscosity is created through an interaction of carboxylic groups, as described above, the viscosity will break down very quickly once shear is introduced. The high-shear viscosity will then be low and will permit low blade pressures to be used. On the other hand it might prove difficult to achieve the necesary coat weight in a film press coater operating with smooth rods.

Particle Size

The particle size of the latex influences not only the rheological behaviour of the coating colour, but also the paper surface properties as shown in Fig. 43. The particle size of a modern European latex binder will be in the range of 110 to 160 nm, however within this narrow range there is still an influence on paper gloss, printing ink gloss, surface strength and blistering resistance.

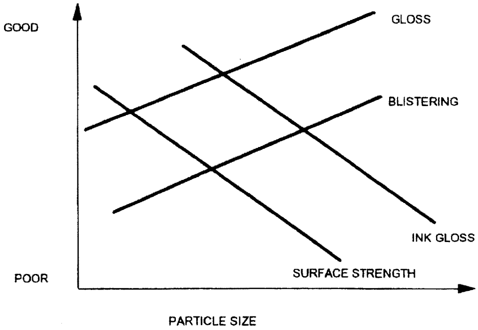


Fig. 43. The effect of particle size on paper properties

SUMMARY

The latex producer today can engineer polymer dispersions to suit not only one paper mill, but the needs of several individual products within that mill; a measure of the detailed relationship between polymer properties and paper characteristics.

CONCLUSION

The first step for sucess in the development of a new coating application system or a new coating is to define the targets for the production and the paper quality.

In selecting the binder for the coating colours it is important to take advantage of the properties of the different binders both in respect to their interactions with pigments and the required paper properties. An optimal binder combination with respect to economy and technology can be obtained by combining the atributes of the binders.

It is important to carry out the optimisation of the binders with the actual pigments to be used in the production. Only then the study of the coating colour rheolgy in the laboratories can be of help for the later pilot plant and production trials.
The most secure analysis of a possible binder system will be found when the paper producer organise a cooperation with between their binder suppliers.

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LITERATURE

Several books and articles have been consulted during the preparation of this paper. With the permission of authors and their companies I have reproduced some parts of their work in its original form.

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Transcription of Discussion

A Review of Starches and Binders used in Papermaking and Coating

Dr Nils-Olaf Bergh, Senior Adviser, Cerestar, Germany

Professor Jacques Silvy, Universidade la Beira Interior, Portugal

In your experiments did you notice that the roughness of the paper sheet influenced the process in the film press application?

Nils-Olaf Bergh

Yes.

Jacques Silvy

In which way?

Nils-Olaf Bergh

In the way that the higher the roughness and absorptivity is the higher film thickness you can use. Or said in an opposite way it is more difficult to use low film thickness so you need to use lower solid content in the paper then you have high paper roughness.

Paul Kolosick, Consultant, Union Camp, USA

You mentioned that the linear polymers increased porosity and I was wondering if by increasing porosity do you mean actually increasing the flow through the sheet or the opposite. Would you speculate on the mechanism?

Nils-Olaf Bergh

What I meant was by increasing the porosity that the blistering resistancy would change so that the water vapour is more easily removed in the drying section and so at the same time the printing ink absorption will be higher. That was what I meant.

Paul Kolosick

Could you speculate on the mechanism of linear chains improving that?

Nils-Olaf Bergh

If there is some latex manufacturer among us I hope he can help me to solve that problem, I cannot do that.