

Surface Sizing Agents

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The discussion of the factors that influence surface sizing is intended here to show the variety of parameters, which all together affect the performance of the sizing agents. Each of them must be taken into account, especially when the performance of the sizing agent is not constant or satisfactory. The case studies of a variety of sizing agents are given here for nearly every special application in paper and board making. Products from anionic to cationic and from solution to emulsion types are available.

INTRODUCTION

Sizing mechanisms

The fibre web produced on paper manufacture without additional additives consists of hydrophilic fibres, that make up a capillary system with cavities of different sizes and shapes between the fibres. Due to both capillarity and the hydrophilic nature of the fibre web the sheet of paper is very absorbent. Hence, depending on the further processing (e.g. coating, printing, gluing, siliconizing) or the later purpose intended (e.g. xerox paper, inkjet paper), it is necessary to influence the absorbency of the paper to a specific degree.

For this it is necessary to achieve a controlled reduction of liquid pick-up (water, ink, oil, fat etc.) into the fibre matrix by reducing the interfacial energy of the fibre surface.

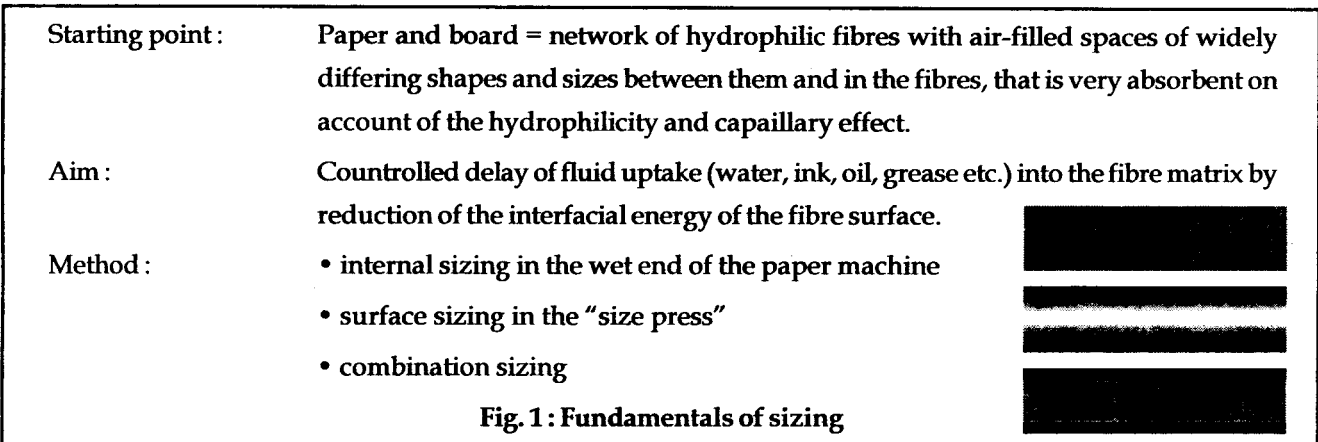
Nowadays two basically different procedures are available to attain a hydrophobic paper, paperboard or cardboard; internal and surface sizing. Their application is dependent on the demands made on the product and the construction of the particular paper or board machine. Both techniques can be used alone or in combination.

Internal sizing (Figure 1-1) is carried out in the wet end of the paper machine, where size is added to the fibre

suspension before sheet formation and without any additional unit apart from dosing equipment. This brings about sizing over the cross-section of the paper sheet.

Surface sizing (Fig.1) is carried out by means of a special unit in the drying section of the paper machine. Here the already formed and dried paper sheet is treated in an application device, generally called size press, with a formulation composed of hydrophobizing substances (size) and starch, generating not only hydrophoby but also surface strength due to polymeric structure of starch and sizing agents. The sizing is generally limited to a surface region of the paper, which acts as a protective layer preventing penetration of water into the hydrophilic interior of the sheet.

It is also possible to combine the two techniques (Fig. 1), in order to control the hydrophobization precisely over the cross-section of the sheet in the case of very high quality products. Thus, for example, in some papers for inkjet printing, the internal sizing provides a protective layer that prevents the ink penetrating through and enhancing colour brilliance. The surface sizing effects a balanced hydrophobic/hydrophilic surface, which takes up the ink in a controlled manner and guarantees good edge sharpness.



In the case of rosin sizing the mechanism of sizing depends on the fixing of the rosin particle at the fibre by complex formation with the aluminium ion (Fig. 2).

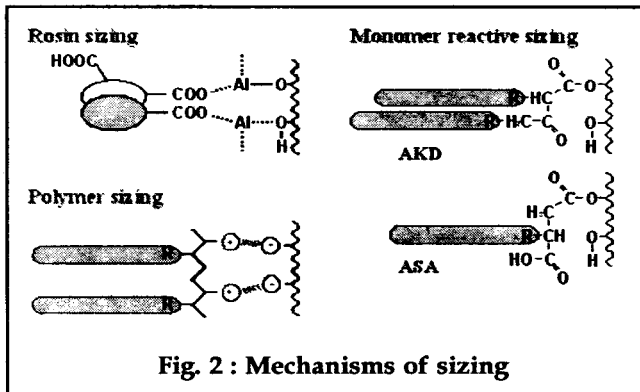


Fig. 2 : Mechanisms of sizing

In the case of monomeric reactive sizes - AKD and ASA - the formation of a beta-keto ester or a succinic acid half ester respectively with chemical bonding to the fibre as the mechanism of sizing has been discussed (cf. Fig. 2).

Modern polymer sizing agents, that are now used in surface sizing, undergo very strong dipole-dipole and van der Waals interactions with the cellulose (cf. Fig. 2 bottom).

It is a common feature of all mechanisms that the sizing components contain both hydrophilic and hydrophobic regions. The attachment and fixing to the fibre surface is brought about by the hydrophilic part of the molecule with high fibre affinity. The sizing effect is provided by the alignment of the hydrophobic side chains away from the surface.

Fig. 3 : Advantages of surface sizing

Advantages of surface sizing

The advantages of surface sizing are listed in Figure When we compare internal and surface sizing, some significant arguments crystallize out, which speak for surface sizing.

Polymeric surface sizing agents are generally applied, together with starch solutions, so that the internal and surface strength of the paper increases. The yield of the surface sizing agent is 100 %. It is possible to control the degree of sizing over a wide range during surface sizing, whereby the sizing costs fall at higher basis weights.

Suitable surface sizing agents are available for almost

all paper qualities, that make it possible to achieve special effects and to endow papers with appropriate performance and optimum properties for further application.

Classification of surface sizing agents

The various types of polymer sizing agents can be classified according to their charge characteristics (Fig. 4).

Fig. 4 : Types of polymer sizing agents

The cationic sizes are generally stabilized with protonated or quaternized amino groups. Their high affinity for anionic substrates means that their effectivity is assured, even in papers with high concentrations of anionic interfering substances, e.g. in the case of recycling and wood-containing papers.

The anionic types are polymers that are generally modified by carboxyl and/or sulphonic acid groups. The first generation of surface sizing agents were styrene-maleic anhydride copolymers. In order to fix these polymers on to the basis paper, it is necessary for aluminium ions to be present. The presence of aluminium is not necessary for more recently developed anionic products. The compatibility with optical brighteners or alkali metal salt solutions, e.g. sodium chloride and sodium sulphate, are important factors for the application of anionic products for fine papers, particularly the so-called total office papers.

Amphoteric polymer sizing agents contain both cationic and anionic groups. The charge characteristics are pH-dependent, they are cationic in behaviour under acid conditions and anionic under alkaline conditions. A consequence of this behaviour is high stability over a wide pH range and good compatibility with different kinds of additives.

Depending on the manufacturing process, the cationic and anionic types are available as polymer solutions or polymer dispersions; amphoteric products are currently only available in the form of dispersions.

The BK Giulini product range (Fig. 5) includes cationic, anionic and amphoteric types. The cationic types are cationic polymer solutions, based on pure methacrylate copolymers.

Group of compounds	Application	Charge	Qualification	Packing
styrene methacrylate	surface	anionic	BgVV, RAL, nordt swan	tank truck, container, drum
styrene acrylate	surface	anionic	FDA, BgVV, RAL, nordt swan	tank truck, container, drum
styrene acrylate	surface	amphoteric	FDA, BgVV, RAL, nordt swan	tank truck, container, drum
styrene acrylate	surface	amphoteric	FDA, BgVV, RAL, nordt swan	tank truck, container, drum
styrene acrylate	surface + mass	cationic	FDA, BgVV, RAL, nordt swan	tank truck, container, drum
styrene acrylate	surface	cationic	FDA, BgVV	tank truck, container, drum
styrene acrylate	surface + mass	cationic	FDA, BgVV, RAL, nordt swan	tank truck, container, drum
acrylate	surface	cationic	FDA, BgVV, RAL, nordt swan	tank truck, container, drum
acrylate	surface + mass	cationic	RAL, nordt swan	tank truck, container, drum
polymer size formulation	surface + mass	cationic	FDA, BgVV, RAL, nordt swan	tank truck, container, drum
polymer size formulation	surface + mass	cationic	FDA, BgVV, RAL, nordt swan	tank truck, container, drum

Fig. 5 : Compounds produced

In contrast, the cationic dispersions are styrene-acrylate and methacrylate copolymers.

The anionic products are styrene-acrylate and styrene-methacrylate copolymers, whereby are dispersions and is a polymer solution.

The amphoteric dispersions, are based on styrene-acrylate copolymers.

The amphoteric contain AKD wax and so combine two different synthetic sizing agents.

The majority of polymer sizing agents are products of polymerisation. Polycondensates, based on polyamide resins or polyaddition products, such as polyurethanes, only play a minor role in the sizing agent market.

Principles of synthesis and raw materials

Unsaturated olefinic monomers are the basic raw materials for the manufacture of the polymerisate. The range of monomers available is large so that application-orientated polymer design is feasible.

As already described at the start, hydrophilic and hydrophobic components, that is monomers, are required for the development of surface sizing agents.

Hydrophilic monomers

The hydrophilic monomers, used to achieve water solubility and to adjust high fibre affinity, can be cationic and, hence, basic, or they can be anionic and, hence, acidic in nature. Non-ionic hydrophilic polymers play scarcely any role.

The nitrogen-containing cationic monomers (Fig. 6) are generally the acrylate or methacrylate esters of alkylated amino alcohols, whereby the homologous amides could also be of interest. The nitrogen is protonated under acid

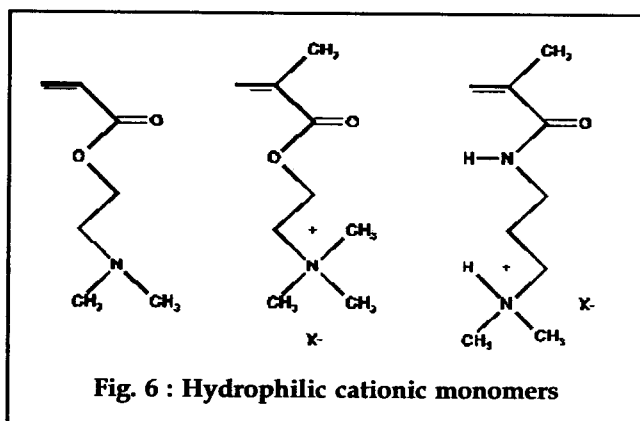


Fig. 6 : Hydrophilic cationic monomers

conditions, whereby it is possible to increase the cation activity by quaternizing the amino groups.

The anionic monomers (Fig. 7) are unsaturated olefinic carboxylic acids, e.g. acrylic acid, methacrylic acid and maleic acid. Water solubility is obtained by the addition of alkalis so that they are converted to the carboxylate form. The pH and electrolyte stability of the product can be increased by the use of sulphonic acid monomer derivatives.

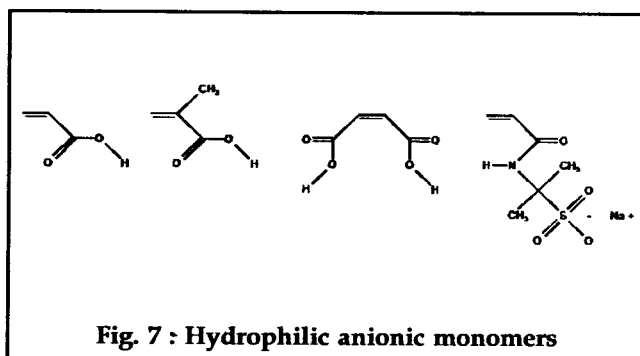
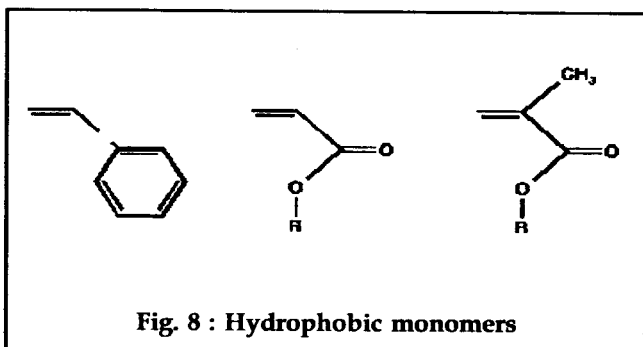


Fig. 7 : Hydrophilic anionic monomers

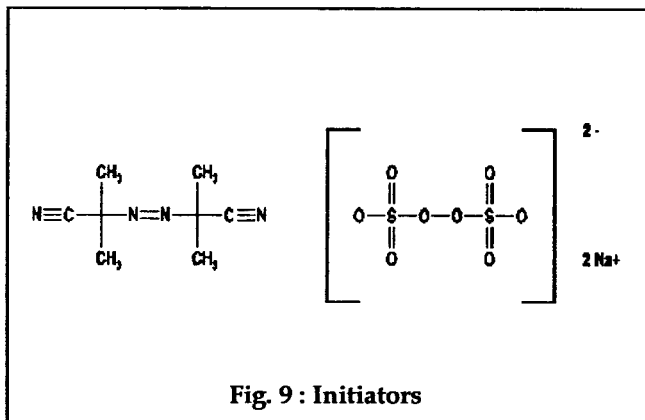


Hydrophobic monomers

The hydrophobic monomers (Fig. 8) generally used are styrene, acrylate and methacrylate esters. Styrene plays an important role here. Methacrylate and acrylate esters are available with a selection of various side chains. These range from the short-chain methyl residue of methyl methacrylate to the long-chain stearyl acrylates.

These monomers can be used to adjust important parameters, e.g. the glass transition temperature. Monomers with short side chains generally lead to hard polymers; monomers with long side chains are soft products with low glass transition temperatures, because they are internally plasticized.

The flexible side groups, with high orientation capacity, are of importance. This is evident when it is considered that butadiene, a monomer without side groups, does not have any importance as a co-monomer in the synthesis of polymer sizing agents.



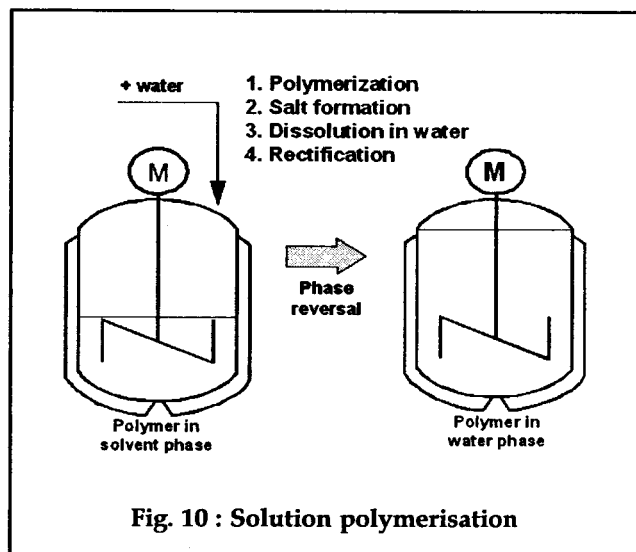
Initiators

Polymers are produced by radical polymerisation of the monomers. The radical formation is provided by so-called initiators (Fig. 9). In general, these substances decompose thermally and the free radicals produced initiate a radical-chain reaction.

There are solvent-soluble types, such as azobisisobutyronitrile, and water-soluble types, such as sodium peroxodisulphate. These different types find application as a function of the polymerisation technique.

Synthesis principle of solution polymerisation

Polymer solutions are produced in batches, by solution polymerisation (Fig. 10). The various monomers are dissolved in a solvent and heated. Polymerisation is started by the addition of an initiator soluble in the solvent. This takes place with a very high conversion so that a degree of polymerisation of more than 99% is reached. The polymer resin remains homogeneous in the solvent phase.



The viscosity of the resulting resin melt is very high. The reaction is stopped, at this point, by salt formation. Cationic polymers are treated with an acid, e.g. acetic acid, anionic polymers with an alkali, e.g. caustic-soda solution. Water is added after neutralization and a phase inversion occurs. The polymer passes from the solvent phase into the water phase.

Finally, the solvent is rectified and prepared for use in the next batch so that it remains in the process.

The polymers dissolved colloiddally in the aqueous phase behave as polyelectrolytes. They have a characteristic dependence of viscosity and molecular weight. This also applies to our PERGLUTIN types, that are optimised with respect to active ingredient content, viscosity, molecular weight and sizing effect.

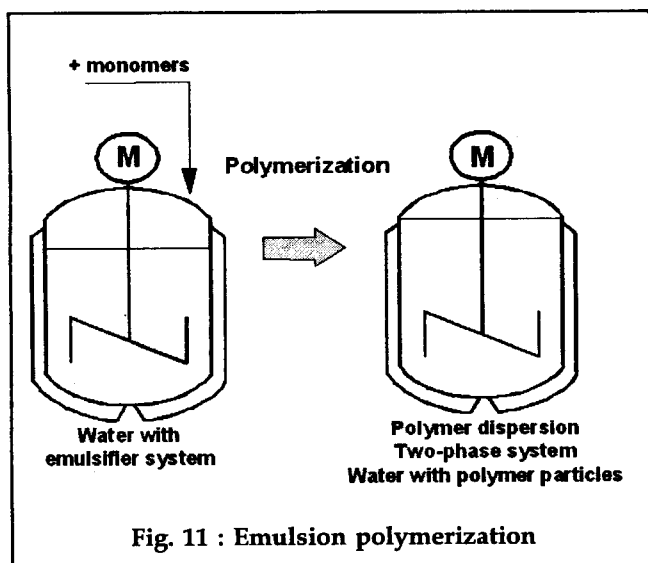
Synthesis principle of emulsion polymerization

In contrast to polymer solutions, the polymer dispersions are prepared by emulsion polymerization, a typical two-phase reaction system. The continuous phase is water, the monomers and the resulting polymer particles are the discontinuous phase. An emulsifier system is necessary in order to stabilize the monomer droplets and the polymer particles (Fig. 11).

The polymerization process can be separated into three steps:

Step 1

The water-soluble initiator decomposes and free radicals



are formed. The water solubility of the monomers is minimal and the reaction with the water-soluble radicals begins in the aqueous phase. The polymers formed are not water-soluble but are immediately stabilized by the micelles of the emulsifier system. Particle formation takes place during this step.

Step 2

The monomers diffuse from the monomer droplets to the polymer particles, where polymerization takes place. The polymer particles grow in the second step. The reaction is controlled by monomer diffusion through the water phase.

Step 3

The monomer concentration drops drastically and polymerization stops. If an excess of initiator is used, high monomer conversion is obtained with a degree of

polymerization of more than 99.99%

If commercial surfactants, such as are used in the manufacture of standard lattices, are employed, the dispersions obtained do not possess any sizing effect. The emulsifier systems used for our surface sizing agents are special developments, that lead to very stable products with high fibre affinity that is a prerequisite for the very good sizing effect.

Parameters for the description of polymer sizing agents

Now let us turn to some parameters for the description of polymers (Fig. 12).

The hardness of the polymers is described by the values of the glass transition temperature (T_g) and the minimum film-forming temperature (MFT). Polymers with a glass transition temperature above 30°C are usually described as being hard, those with a lower glass transition temperature as soft.

MFT and T_g are related to each other, whereby the minimum film-forming temperature lies below the glass transition temperature, because water in the systems acts as plasticiser during the drying process.

The CEQ is the molecular weight of the repeating unit in the polymer chain bearing a charge. The higher the value, the fewer charges are present and vice versa.

The CD is usually referred to the active substance, so that only limited comparisons can be made without knowledge of the solids content.

The charge activity, which is usually quoted for polyacrylamides, can only be given if the polymer composition is known.

While charge equivalent weight and charge density can be determined by polyelectrolyte titration, it is not possible to determine the cation/anion activity of

T_g Glass transition temperature	↔ Transition of the amorphous polymer into the liquid phase
MFT Minimum film-forming temperature	↔ $T > \text{MFT}$: homogeneous transparent film ↔ $\text{MFT} < T_g$, since the water and solvent serve as plasticizers in the case of polymer solutions and dispersions
CEQ Charge equivalent weight	↔ Charge carriers are repeated throughout the polymer chain. The CEQ gives the molar mass of the repeat unit in the polymer, which contains a charge carrier ↔ Dimensions: g (active substance)/mol (charge) ↔ Small charge equivalent Δ more charge units
CD Charge density	↔ Information concerning the molar charge in the polymer ↔ Dimensions: meq (charge)/g (commercial product)
CA Charge activity	↔ Molar proportion of cationic or anionic monomers ↔ Dimensions: mol%

Fig. 12 : Parameters describing the polymers

polymers of an unknown composition.

Overview of polymer sizing agents

The cationic types

The schematic diagram, Fig. 13, of our cationic polymer solutions illustrates the principle of their structure differ significantly because of the use of different side chains along the polymer chain. Although the charge equivalent weight of all products is very similar, you can see that the charge density along the polymer chain and, hence, the cation activity increases appreciably.

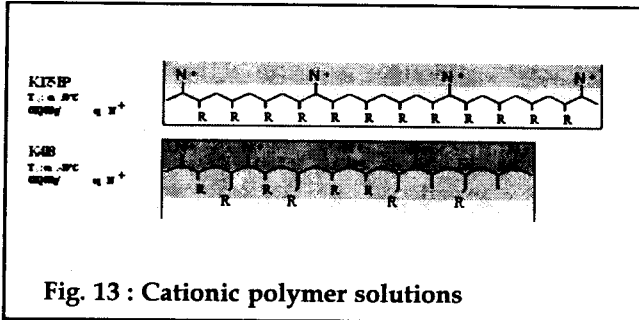


Fig. 13 : Cationic polymer solutions

One consequence of this is that the glass transition temperature and, hence, also the minimum film-forming temperature are reduced. Very good retention properties are obtained with the high cation activity so this product can also be used for internal sizing.

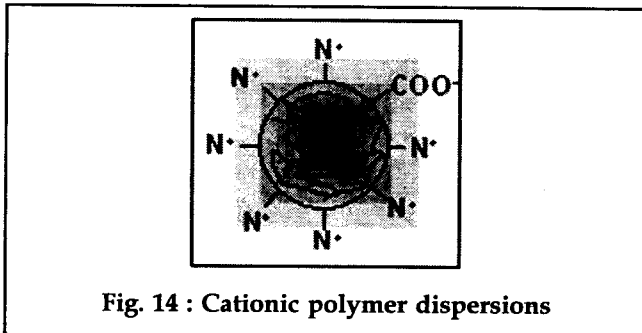


Fig. 14 : Cationic polymer dispersions

The cationic polymer dispersions and have charge equivalent weights of 1300 to 1400 g/eq cationic groups, which are relatively high for polymer dispersions. This means that they can be used very successfully as internal sizing agents as well as in size press applications.

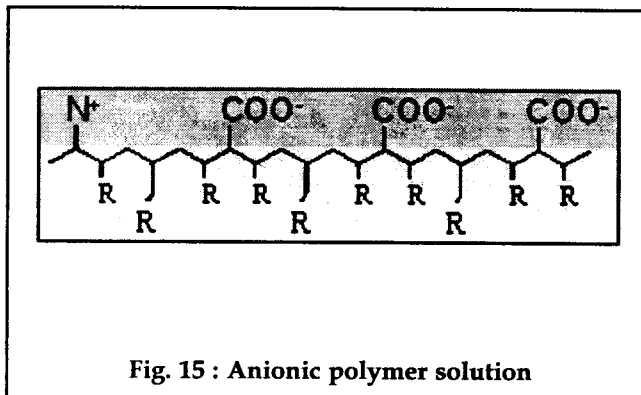


Fig. 15 : Anionic polymer solution

The anionic types

The next Fig. 15 shows the scheme for our anionic erglutin solution type. PERGLUTIN® A 200 is a polymer solution with a relatively high anionic charge density.

It has a high fibre affinity because of the special monomer composition, so that it is also independent of the aluminium ions in the base paper.

(Fig. 16) shows polymer dispersions with a high glass transition temperature and a relatively low charge density. The emulsifier system makes it possible to stabilize this very finely dispersed product successfully and to endow the system with the necessary fibre affinity.

The polymer dispersions have a very high molecular weight in comparison to the polymer solutions. This is also a reason for the limitation of the number of carboxylic groups in polymer dispersions. If the carboxyl content is increased, over a certain limit, an alkali-soluble product, with the character of a thickener, is obtained.

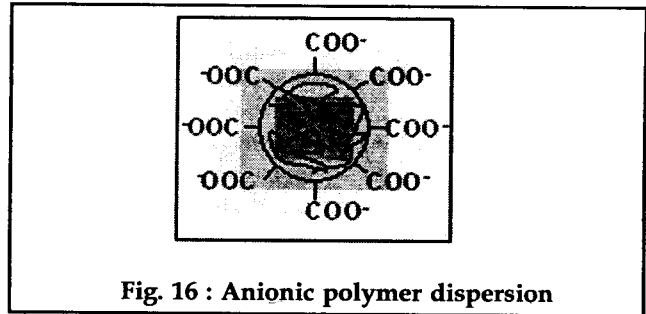


Fig. 16 : Anionic polymer dispersion

The amphoteric types

These are typical amphoteric products. Both anionic and cationic monomers are employed for their manufacture in a multistage process. It has very good stability and is compatible with almost all paper additives. It has a charge equivalent weight of 1500 g/eq for anionic and 1800 g/eq for cationic groups, which is a factor of 5 and 3 respectively higher than so that the amphoteric character is appreciably greater here.

Amphoteric products can even be included in size press systems, with high concentrations of anionic interfering substances, without problem.

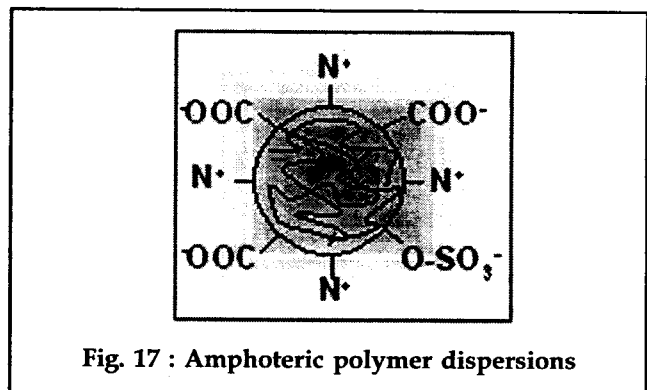


Fig. 17 : Amphoteric polymer dispersions

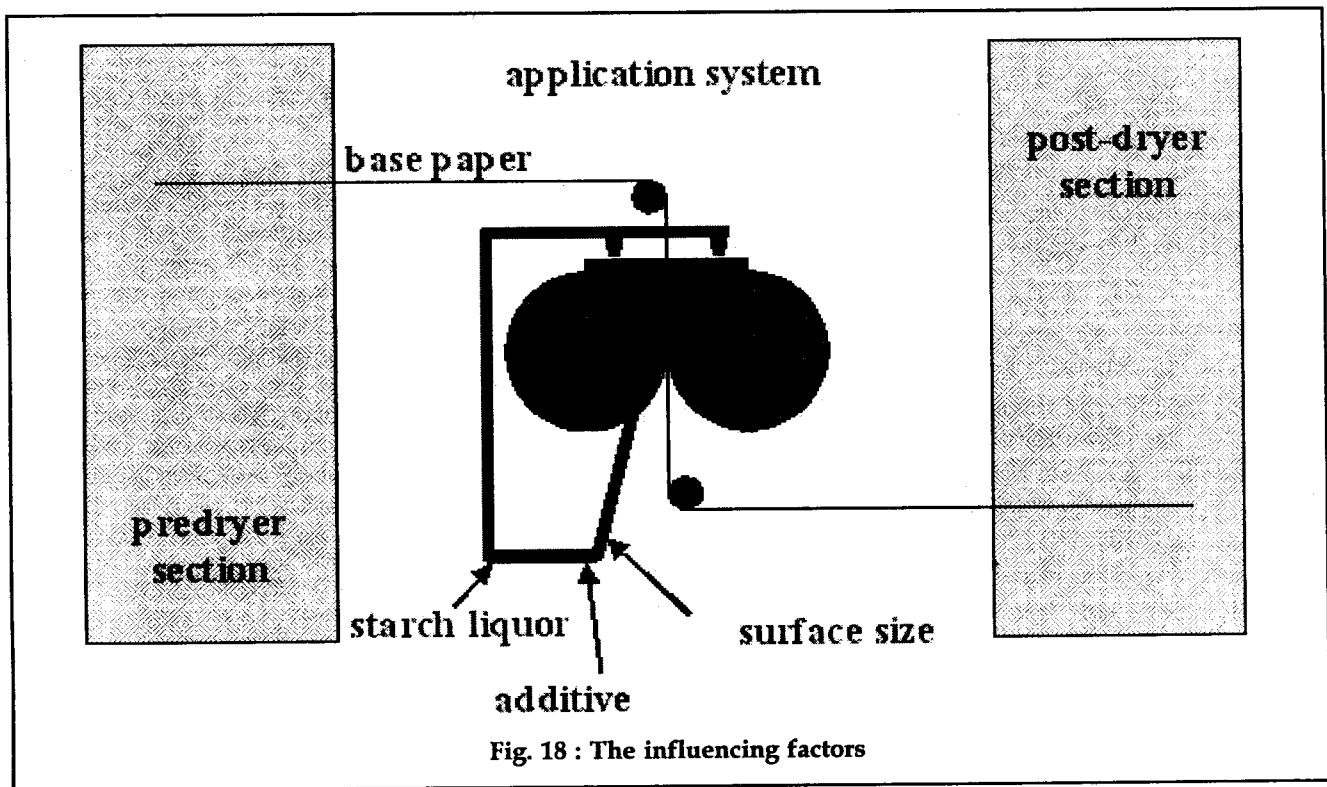


Fig. 18 : The influencing factors

The factors that influence surface sizing

This chapter is intended to give a broad overview of the factors that influence surface sizing. Based on this it will explain how these factors affect the result of sizing, the running of the machine and the paper quality.

If we consider the participants in surface sizing (cf. Figure 1-18) the following parameters require further discussion:

- base paper
- application unit ("size press")
- starch liquor
- additives
- surface size

These parameters never act separately and, hence, interact with each other in many cases. The resulting interactions can be both synergistic and antagonistic in nature.

In order to discuss the influence of the parameters logically, we will follow the paper sheet on its way through the paper machine and describe the effects chronologically.

Since customers and users of surface sizes are confronted with these problems every day, some topics, that you will certainly find trivial in nature, will be mentioned but only dealt with very briefly. Topics, that are the subject of frequent questions, will be dealt with in more detail.

The influence factor base paper

As one may be certainly aware, the raw paper, as the basic material, has a large influence on surface sizing.

Pulp

Normally, already at the pulper a special type of surface sizing is determined by the utilized pulp system, since the raw material has already been selected for a definite application.

In general, it may be said that every fibre system is suitable for sizing with any type of surface size - that means with anionic, cationic or amphoteric polymer sizes. Here we are not yet considering the economics of sizing.

This general statement applies particularly when wood- and/or recycled waste paper-containing fibre systems are considered. Cationic sizes generally have the best effect on these raw papers and that is why this type is used for economic reasons.

What has been said also applies to virgin fibre systems. However, these fibre systems are nowadays primarily used to manufacture brilliantly white paper grades, which are generally also treated with optical brighteners. Since for reasons of cost the brightener is added in the size press and the brighteners used are anionic, the choice of sizing agent is limited to anionic or amphoteric sizes, that do not interfere with optical brighteners.

In the following example (Figure 1-19) an anionic and a cationic polymer size dispersion in combination with enzymatically degraded potato starch were compared

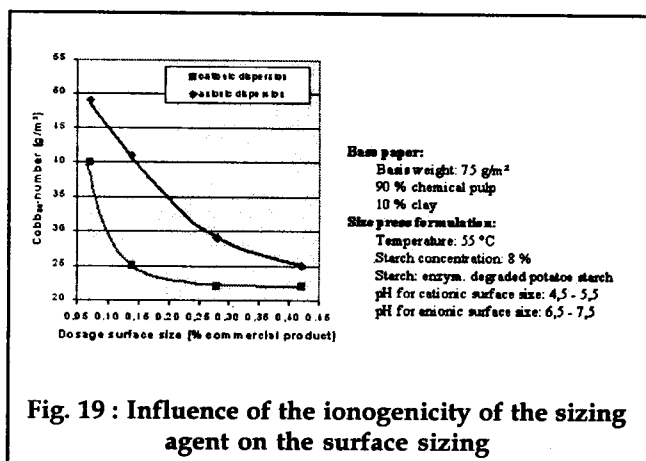


Fig. 19 : Influence of the ionogenicity of the sizing agent on the surface sizing

in a laboratory test on unsized, uncoated paper. The white, uncoated paper was used as the reference. Each size type was applied in the pH range, that is best for that type. Over the whole concentration range better sizing values were obtained with the cationic size.

The cationic sizes contain protonated or quaternized amino groups as charge carriers. On account of their cationic charge, these types possess a high affinity for anionic substrates, thus, ensuring high effectivity even on papers containing large quantities of anionic interfering substances. Because of their high fibre affinity, these cationic types are more effective sizing agents under optimal application conditions than the remaining types.

Moisture

The moisture content or moisture profile of the base paper is a second important property. The moisture content of the base paper has a great influence on its absorbency in the size press. Hence, it is necessary to avoid an uneven temperature profile in the longitudinal and transverse directions of the paper web.

For this reason the residual moisture content of the paper is frequently reduced to 2 % in the predryer section in order to ensure an even moisture profile. This way guarantees a very uniform pick-up capacity of the paper.

In addition, the moisture content of the raw paper determines its absorption behaviour. The higher the residual moisture the greater the absorption tendency. This moisture in hot base paper is present in the form of vapour. When this paper enters the size press pond at ca. 50 - 60 °C there is a spontaneous cooling of this vapour, that is associated with a reduction in volume, which then causes the size press formulation to be sucked up into the sheet.

A dry paper is required if it is desired to keep the majority of the size press formulation on the paper surface.

Hence, in some cases the predryer section can be the limiting factor, if it becomes necessary to reduce the speed of the machine in order to maintain this high degree of initial drying.

Presizing

When the paper machine is running particularly slowly the presizing of a raw paper can also affect the surface sizing.

However, the prerequisite for this is, that the internal sizing was carried out with a sizing agent, whose hydrophobic effect has already fully developed while leaving the predryer section. This is generally the case for rosin-based sizes. For most reactive size types and synthetic polymer sizes a developed sizing is unlikely, so that an effect is scarcely detectable in these cases. This property is deliberately exploited for some paper grades, where a hard internal presizing is carried out with AKD, but which only takes effect after leaving the paper machine. This brings about a massive barrier effect in the paper mass combined with a surface coating, whose hydrophobic/hydrophilic balance can be specifically controlled.

Strongly cationic mass additives

Just as the pulp has an influence on the base paper substrate and, hence, on the surface sizing, mass additives can also influence the surface sizing.

Here we think particularly of the strongly cationic additives, such as cationic starches, cationic fixing and retention agents or also dispersed cationic fillers.

The use of large quantities of these cationic paper additives, alone or together, can lead to a reversal of the charge, which means a positive zeta potential when the headbox is reached. For this reason such a base paper is more economically treated with an anionic surface size than with a cationic one.

The application unit as an influence factor

Type of applicator

The type of application unit - from the conventional size press to the speedsizer - has an influence on surface sizing, since there are differences in the physical limits with respect to the viscosity of the size press formulation and in the coating characteristics. These differences express themselves in the paper machine velocities, that can be reached, and in the penetration of the size press formulation. The varying penetrations, in turn, lead to differing sizing profiles over the cross-section of the paper sheet.

We will not go any deeper into the topic of size press units in this contribution. The interested reader is referred to the original literature.

Size press circulation

The size press circulation (Figure 1-20) with all its parameters is of fundamental importance for the optimal efficacy of the surface size.

Thus, a poor starch preparation can have a negative effect on the surface sizing. Starch-degrading substances, such as peroxides, when present in excess,

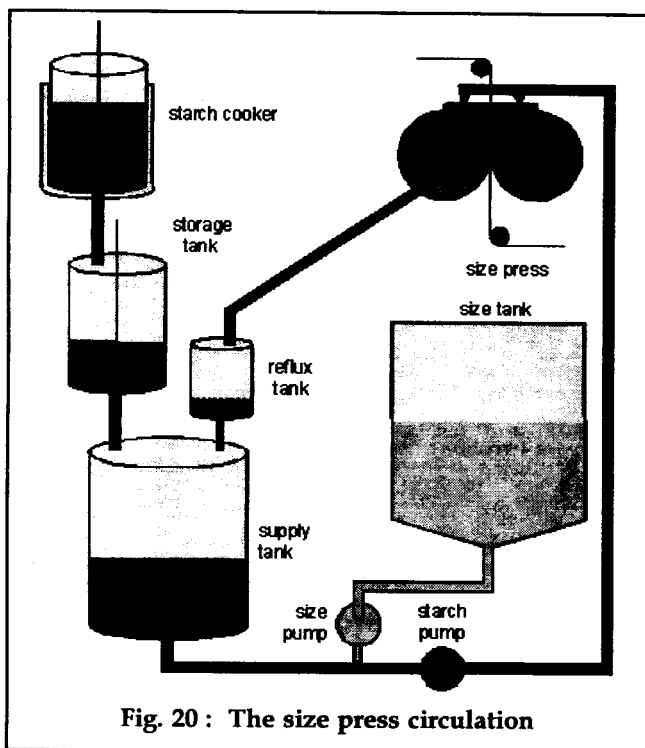


Fig. 20 : The size press circulation

not only result in excessively degraded starch, they can also participate in reactions involving oxidation of the surface size or other additives of the size press circulation. Finally, this can lead to interferences, such as inadequate sizing effect, variations in sizing or deposition on the applicator rolls of the size press.

In addition, care should be taken to avoid areas in the size press circulation with a high air entrainment, e.g. waterfalls and cascades or pumps that are not air-tight, because air is sucked into the size press formulation and foaming is promoted hereby. Countermeasures, that have proven themselves, are simple changes such as, for example, the back flow of the size press liquor below the liquid surface of supply tank and the use of air-tight pumps. If such process-technical changes do not prevent foaming, then the foam should be controlled by means of a suitable antifoam. Here care should be taken to ensure that the antifoam is compatible with the size press formulation and does not have a detrimental effect on the sizing.

Finally, the point of addition of the surface sizing agent should be selected carefully. The size should be preferably dosed into the size press feeding pipe continuously and as close before the size press as possible. An optimal solution would be to add the size into the starch line between the supply tank and the starch pump, since the pump ensures good mixing with the starch liquor and the size becomes available at the size press after a very short residence time. Points of addition at the supply tank or storage tank along with a batch-wise addition should be absolutely avoided. Long-term storage at high temperatures can lead to a loss of activity by thermal change.

Influence factor starch liquor

The starch liquor is an extremely important parameter for surface sizing since the application of the surface size is carried out almost exclusively in direct combination with a starch liquor.

Considering this parameter of surface sizing, you will find out that this important parameter has several degrees of freedom.

Water

The water used for the preparation of the starch liquor and afterwards for the size press formulation is of great importance in many paper mills.

Currently, while attempts are being made to reduce the specific water consumption even more, the question is often posed concerning an alternative to the fresh water, that has been exclusively used until now.

However, this parameter is an extremely sensitive influence factor for sizing. The size press formulation generally contains 88 - 94 % water and, thus, water makes up the majority of the formulation. Therefore, great care must be taken to ensure that this component is high-quality and pure.

Hence, impurities and interfering substances must be excluded. Treated water from the paper machine circulation is generally unsuitable, even if it appears optically clean. There are always dissolved substances, either from the paper manufacture or in the form of electrolytes, which were added for the water treatment process. These substances always have a detrimental effect on the efficiency of the size press formulation, since they enter into undesired reactions with the surface sizing agent or with the paper surface.

New developed products might allow the utilisation of clarified circuit water in the future.

Starch

Potato, wheat and maize starches are mainly used for paper manufacture in Western Europe. Very small quantities of tapioca starch and modified starch derivatives are also used. The consumption of the different starches varies seasonally, to a certain degree,

- Starch types:**
- Potatoe starch contains ca. 0.3 % phosphate, traces of protein and no lipid
 - Maize starch contains ca. 0.1 % phosphate, ca. 0.5 % protein and ca. 0.9 % lipid
 - Wheat starch contains ca. 0.2 % phosphate, ca. 0.3 % protein and ca. 0.2 % lipid
 - Other: e.g. tapioca starch, cationic starches

Fig. 21 : Size press starches

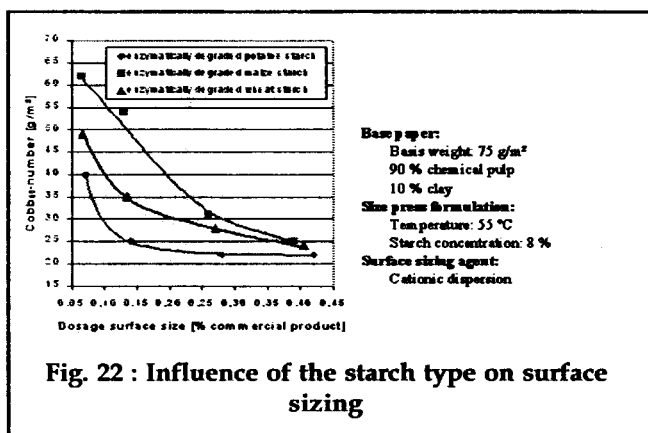
according to harvest and price, but the larger proportion remains potato starch.

Naturally, due to their various sources, starches of different properties are obtained depending on the raw material.

For instance, the protein content is of particular importance for application as a surface starch. Proteins have a detrimental effect, in particular, during the enzymatic degradation of starch, since they can lead to precipitation of protein and, hence, to blockage of strainers and sludge formation as well.

For this reason, it is not surprising that the type of starch strongly influences the surface sizing in the same way.

The following example presents the results of a laboratory test (Fig. 22), where different starches were



used for surface sizing of the same paper grade. All other parameters were kept as constant as possible.

As can be seen, potato starch gives the best sizing values over the whole concentration range. This effect is particularly marked in the low application region. The wheat starch and, even more, the maize starch act appreciably worse in combination with the surface sizing agent used. The effect is very marked in this case and the differences are usually not so drastic as presented here.

Nevertheless, the tendency shown has been confirmed in various mill trials. Hence, this influencing factor should always be taken into account, for example when considering a change to another type of starch for economical reasons. Therefore, it is always necessary to compare the overall costs of sizing, including the sizing agent, and not merely the cost difference of the starches.

In the same way the influence on sizing, particularly in the case of a modified starch, must be considered. Nowadays, cationic starches are being more frequently used in the size press formulation for various reasons (e.g. relief of the process water re-circulation system when broke is re-used, printability). These cationic starches have an influence on the surface sizing, as so far as they are not chemically tolerated without problems by all types of sizes. Medium and highly cationic

starches, in particular, can undergo incompatibility reactions with anionic surface sizes, which hinder sizing.

Starch degradation methods

In order to use native starch for surface sizing it is – as we all know – necessary to degrade the starch. Starch degradation is a chemical modification of the starch, where the chain length of the starch molecule is reduced and, thus, the viscosity of the starch solution. From the chemical viewpoint, this molecular degradation of the starch is a depolymerisation reaction.

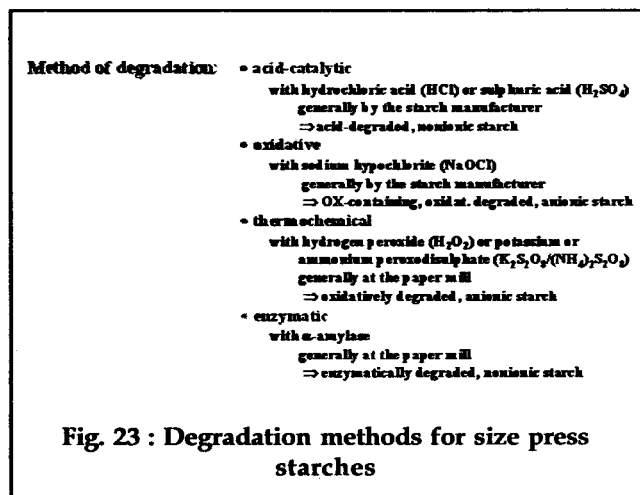


Fig.23 lists the various degradation methods. Nowadays, the thermochemical or enzymatic degradation is usually applied in paper mills.

The thermochemical degradation is carried out by depolymerising the gelatinised and dissolved starch with an oxidizing agents, such as hydrogen peroxide (H₂O₂) or persulphates (K₂S₂O₈/(NH₄)₂S₂O₈) at 120 - 150 °C. These chemicals form hydroxyl radicals, which act as hydrolytic decomposers during starch cooking. Iron or copper sulphate act as catalysts and accelerate the reaction. In practice, the reaction is carried out in such a manner, that the oxidizing agent has all been consumed when the period of reaction is complete. These starch solutions possess a low tendency to retrograde, which is attributed, amongst other things, to the low proportion of carbonyl and carboxyl groups, that have been formed during the depolymerisation process.

Enzymatic degradation is based on the α-amylase-catalysed hydrolysis of the native starch molecules. The enzyme α-amylase is a protein molecule obtained from bacteria, but it is only active under definite conditions. Thus, enzymatic degradation requires the gelatinised and colloidal dissolved starch that is obtained at 80 - 85°C under neutral conditions (pH 6 - 7). The addition of Ca²⁺ or M²⁺ ions promotes the reaction. Since the enzyme acts as a catalyst and is not consumed during the reaction, it is absolutely necessary to inactivate the enzyme, when the desired degree of degradation has been achieved, in order to prevent further degradation

down to sugar. The enzyme can be inactivated by acidification with sulphuric or formic acid, by the addition of heavy metal salts, such as zinc sulphate ($ZnSO_4$) or copper sulphate ($CuSO_4$), complexing with EDTA, oxidation e.g. with perborate, or simply by heating and denaturing the protein at 100 - 130 °C. The last mode of stopping the reaction has the advantage that no additional substances are added and that the pH is not altered. Enzymatically degraded starches are distinguished from thermochemically degraded starches by a lower tendency to retrogradation.

The following test series was intended to investigate the influence of the mode of degradation on the sizing effect.

The same base paper and conditions, as constant as possible, were employed for all the trials.

Fig.24 shows, using a commercially available, cationic polymer dispersion as an example, that when the same starch is used as starting material, the sizing can vary markedly as a function of the starch degradation method.

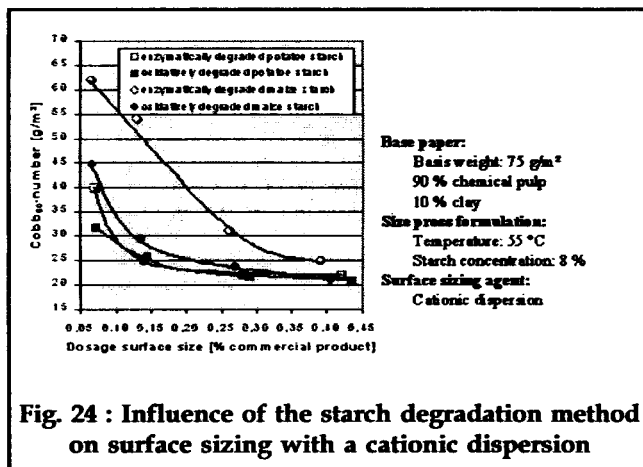


Fig. 24 : Influence of the starch degradation method on surface sizing with a cationic dispersion

Both potato starch and maize starch reveal the same tendency. The oxidatively degraded starches lead to better results, i.e. to higher sizing values, in combination with the same quantity of surface size. These differences are predominately marked in the lower dosage range.

The following Fig. 25 shows the results obtained with an anionic polymer size dispersion.

This investigation confirms again that better results are obtained with oxidatively degraded starches, particularly when low amounts of surface sizing agent are added.

In addition, these investigations underpin the results already described before. As demonstrated there on the basis of another example, the efficacy of a polymer size is affected by the type of starch used. Even in combination with this anionic polymer size the potato starch exhibits a better synergy than the maize starch.

With respect to oxidative starch degradation it should also be mentioned that this degradation can be more

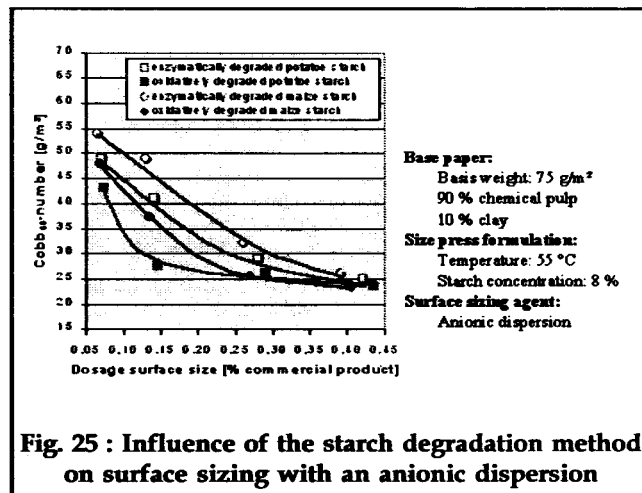


Fig. 25 : Influence of the starch degradation method on surface sizing with an anionic dispersion

critical than, for example, enzymatic degradation. Since the oxidizing agent is not destroyed at the end of the oxidative degradation, any excess oxidizing agent added, that is not consumed during the reaction, can be introduced into the size press circulation. This residual oxidizing agent still possesses an oxidative potential and can oxidize and, thus, destroy any organic ingredient in the size press formulation including the polymer sizing agent. In addition, oxidized starch degradation products can be produced, which can, as anionic interfering substances, hinder sizing.

The viscosity of the starch liquor

The viscosity of the starch liquor plays a significant role in the surface treatment, since this influences the uptake and penetration of the starch.

Thus, on account of the differing penetration of the starch, large differences were found in the paper strength in spite of the same amount of starch being taken up, independent of the mode of application (size press, film press). Starch solutions of higher viscosity (i.e., higher concentration or higher molecular weight) remain more on the surface and provide better surface strength, however, their contribution to the internal strength is less.

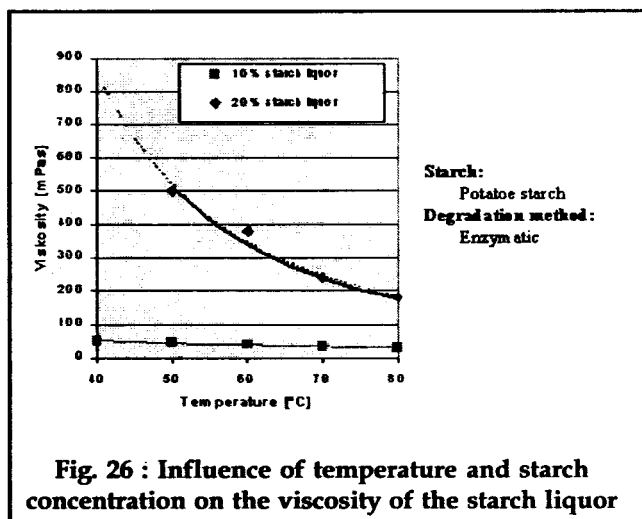


Fig. 26 : Influence of temperature and starch concentration on the viscosity of the starch liquor

The viscosity of the starch liquor is an additive parameter made up of the degree of degradation of the starch, the concentration and the temperature.

For physical reasons there is an upper limit to the viscosity, which is defined by the application equipment. For example, if the viscosity is too high, there can be an undesired nip rejection (rolling of the starch liquor in the size press). This means that it is not possible to apply undegraded native starch. The starch must be degraded as already described before application in the size press.

As already described above, since the viscosity of the starch liquor influences penetration, this parameter also has an effect on sizing. Therefore, an excessively degraded starch can lead to a poor sizing result, when the surface sizing agent and degraded starch together penetrate too deeply into the paper matrix.

The pH of the starch liquor

Under normal conditions, the pH can only cause problems if it is deliberately altered by the addition of acid or base.

Usually, surface sizing agents are designed in the way, that they set up their optimal pH themselves.

Thus, for example, cationic surface sizes are generally adjusted to an acidic pH range, so that, on their addition, the pH of the starch liquor is automatically shifted into the optimal range. However, if a size press formulation, with a cationic size, is intentionally adjusted to an alkaline pH, then the surface size molecules can become unstable causing their effectivity to be drastically reduced.

This pH dependence is illustrated in Fig. 27 using two different cationic size types. As can be seen, in this example, surface size B begins to lose activity from a pH of about 5, while type A can be used up to a pH of 6 with good results.

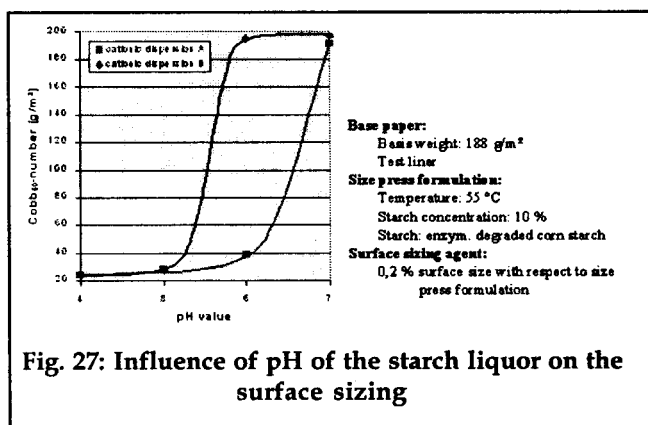


Fig. 27: Influence of pH of the starch liquor on the surface sizing

Hence, the surface sizes used should be adapted to the operating conditions in the size press (acid, neutral or alkaline).

If it is necessary, for other reasons, to use a sizing agent of a different type, then the pH of the starch liquor must

be adjusted appropriately before application.

In order to avoid misunderstandings, it should be remarked here that it is of course possible to treat a base paper from an acidic stock with a neutral or slightly alkaline size press formulation and an anionic sizing agent. In practice, it is found that even very acidic base paper can generally be sized more simply with an anionic surface size, yielding significantly lower Cobb values.

Influence factor additives

Nowadays, additives for achieving particular paper properties are frequently applied simultaneously with the starch and surface sizing agent.

Pigments/optical brighteners

In order to improve or standardize the optical quality of the final product, both in the field of graphic paper and board, colours are added.

In the field of graphic papers optical brighteners are added to increase whiteness. The paper industry uses anionic brighteners almost exclusively for reasons of price. Since they are of anionic nature, these additives naturally influence surface sizing, in that they limit the degrees of freedom with respect to the type of size. This is because anionic optical brighteners are not compatible with cationic surface sizes. If they are used together, a sticky precipitate is generally produced and the brightener is quenched resulting in a loss of efficacy of the sizing agent.

In a similar manner, basic and cationic dye stuffs, such as are used in liner production, are not compatible with anionic surface sizes.

Hence, such additives play a decisive role in the selection of the correct size type.

Neutral salts

It is necessary to increase the conductivity of paper intended for use in copier or laser printers. This is generally done by adding neutral salts to the size press formulation.

These neutral salts (NaCl , Na_2SO_4) increase the electrolyte content of the size press formulation and can, under certain circumstances, exert a negative influence on the surface sizing. This is because synthetic polymer sizes are so-called polyelectrolytes, that are also stabilized by their charge. Increasing the electrolyte content of the surrounding medium can have an adverse effect on the stability of the sizes, leading to precipitation and, thus, loss of size associated with sticky deposits on the rolls of the size press and in the size press reflux tank.

On the other hand, there are phosphate-based additives that can increase the stability of the size press formulation, on account of their dispersive and stabilizing properties. In addition, under optimal

conditions, such additives to the size press formulation can also increase the effect of the optical brightener and, thus, have a positive effect on the whiteness of uncoated paper.

Pigments

The demand for high quality papers, that can be polychrome printed with inkjet printers, frequently leads, nowadays, to a request to apply pigments in the size press. In particular, the use of calcium carbonate-pigmented size press formulations is of interest here, since the first results indicate a mechanically improved surface with better printing properties.

When applying such pigmented size press formulations, as with all other additives, the principal concern is compatibility with the surface sizing agent.

Pigment slurries have to be initially dispersed for transport and storage. The dispersing agents used are naturally charged. Thus, for example, the use of a cationically dispersed pigment slurry in connection with an anionic surface size can lead to a loss in efficacy. In the worst case, this loss of efficacy is accompanied by precipitation of sizing agent and pigment causing deposits in the size press.

In the same way, the use of cationic size types can lead to problems. The optimal effect of these sizes is obtained at acid pH, hence, they are already adjusted, so that the starch liquor is acidified when they are added. This means that calcium carbonate is decomposed to CO₂ with the generation of gas and, thus, with the production of foam.

Finally, the rheology of a pigmented size press formulation must also be considered.

Lipophobic agents

Lipophobic agents are used to make paper products oil- and grease-repellent. Since these lipophobic agents do not generally possess any hydrophobizing properties, it is necessary to use these products in combination with a surface sizing agent, in special papers that need to provide both.

For reasons of cost and because of the fixing, such products are usually added to the size press. Hence, depending on the paper machine and the product requirements, it can be necessary to apply surface size and lipophilising agent together in the size press.

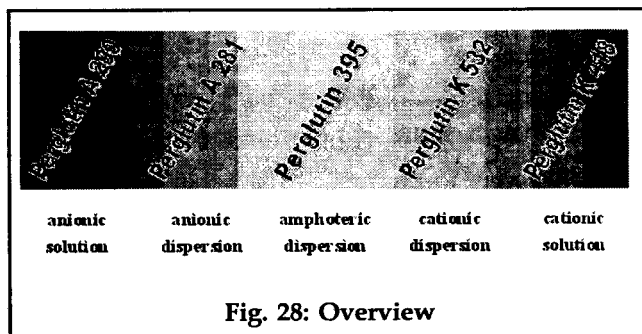
Since such products are generally applied in the upper pH range, the choice of sizing agents is limited to those sizes that are stable for application in this pH range.

Influence factor surface sizing agent

The sizing agent is intended to bring about a hydrophobic coating of the fibre surface. This lowers the interfacial energy of the fibre material, the fibres are wetted less when exposed to moisture and the penetration of the moisture into the fibre web is delayed. However, the sizing agent must not contribute to the

wet strength of the paper or board so that there is no problem in reprocessing the broke.

The various types of surface sizing agents can be classified according to their charge characteristics (Fig. 28). The product range varies from highly cationic solution via amphoteric dispersion to highly anionic solution.



Here the basic rule is that the solution polymers have a higher charge density than the dispersion types. Accordingly the charge density of our anionic and cationic surface sizes increases with the transition from dispersion type to solution.

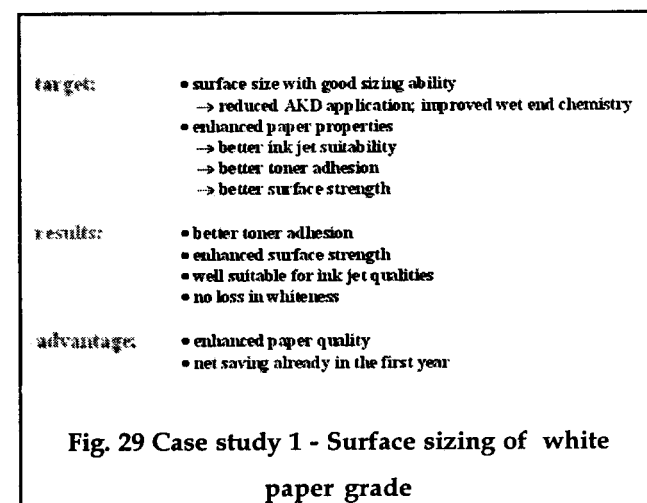
For the field of surface sizing BK Giulini offers a broad range of polymer sizing agents. Thus, the customer is offered a wide range of high quality products that can be used for various applications and to solve almost all problems concerning surface sizing.

Plant trials

In the following 4 case studies are presented which show some interesting applications of our products in paper and board manufacturing.

1-6.1 Case study 1 - Surface sizing of white paper grade

The first case study involves a customer producing a white paper grade. To make his paper more suitable as total office paper and especially to reduce the AKD content in the copy paper grades, trials were carried out to introduce our anionic surface sizing agent. The targets are given in Fig 29.



As shown in Fig. 30, the change-over resulted in a better toner adhesion (the higher the figure the better the toner adhesion) and therefore a higher suitability for copy machines. The ink jet printability was comparable or a little better compared with the competitors product and the nearly same as before. But surface strength was enhanced considerably as show by the Taber abrasion tests.

Result summary

To illustrate this, the following Fig.31 shows the tests samples after the Taber abrasion test.

As can be seen, the surface of the paper treated with shows less abrasion than the other paper samples.

Case study 2 - Surface sizing of test liner

The next case study shows a technical application of our new cationic sizing agent PERGLUTIN K 532 on a test liner. This product has become in the meantime one of the best accepted sizing agents mainly for liner production and works on some of the world's biggest paper machines.

As shown in Fig. 32, the target was to optimise the surface sizing with respect to a more constant sizing performance.

The size press used is a film press (OptiDoser type) for one-sided sizing.

As diagrammed in Fig.33, the change-over resulted in very constant sizing at a 35 % lower dosage level. This means for the customer a safer production with respect to board quality. A further advantage is a cost saving for sizing in a range of 16 %.

Additionally, during the change-over period we optimised the size press formulation by the addition of our size press defamer. As could be seen during the trial, small air bubbles were already contained in the freshly prepared starch solution. These air bubbles were still stable in size press circulation and resulted in small voids on the sized surface. High Cobb values resulted because of stike-throughs at these voids. This problem was solved by introducing 0.16 % of commercial with respect to the surface sizing agent.

Case study 3 - Internal sizing for improved newsprint paper

This case study a producer of newsprint paper had problems with dusting and picking of his paper in the printing office and with register differences especially on multi colour offset printing systems.

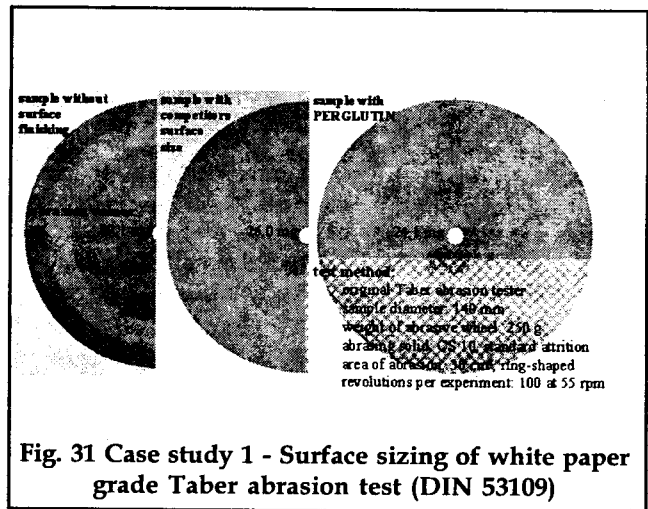


Fig. 31 Case study 1 - Surface sizing of white paper grade Taber abrasion test (DIN 53109)

No.	surface sizing agent		pH value	temp.	Cobb ₆₀ immediate 2h in RR	whitening R447+ PE	toner adhesion GT [1-6]	printing tests		Taber abrasion [m d]
	name	concentration [g/l]						consumption [% HW]	HP DeskJet 550 C [1-6]	
	untreated base paper				17	103	3	1	4	99,1
0	base paper with starch		6,32	55	33	106				
1	competitor	3,0	0,10	6,34	53,0	21	4	2	5-6	26,0
2	PERGLUTIN A 235	3,0	0,10	6,29	53,9	21	5	2	5-6	24,1

base paper:
80 % SF; 20 % LF; 20 % PCC
basis weight: 80 g/m²

starch:
enzym. degr. com starch
concentration = 11 %
viscosity = 18 mPas

size press additives:
0.4 % OBA
neutral salt

Fig. 30 Case study 1 -Surface sizing of white paper grade

target:

- surface size with good sizing ability
→ reduced consumption; cost saving

results:

- reduction of surface size consumption of ca. 35 %
- very constant sizing
- reduction of air in the size press circulation by combination with our defoamer CONTRASPUM T 50 (0.16 % with respect to surface size)

advantage:

- cost saving of ca. 16 %

Fig. 32 : Case study 2 - Surface sizing of test liner

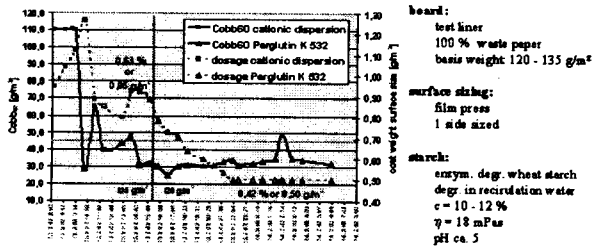


Fig. 33 : Case study 2 - Surface sizing of test liner

The dimension of the paper must be stable within the printing period, which will take place in the first two seconds in the printing machine. Thus the target is to reduce the wet stretch of the paper in the first seconds after wetting.

As can be seen, the wet stretch is reduced significantly in the production of newsprint paper.

The enhanced surface strength was reported by the printing house, due to significantly fewer deposits on the rubber blanket.

problem:

- dusting and picking of newsprint paper in the printing office
- register difference

target:

- use of PERGLUTIN 450/280
→ use of the hydrophobic action to reduce water take-up
→ use of the binder action to strengthen the surface properties

results:

- enhanced surface strength (less dusting and picking)
- good printability (reduced wet strain)

Fig. 34 : Case study 3 - Internal sizing for improved newsprint paper

To solve the problems we introduced our special sizing agent. This product combines two components; one component with binding properties to enhance the paper strength and a second component with an excellent sizing effect. The binding efficiency is used to reduce the picking and dusting, the sizing efficiency to reduce register difference.

The effects needed in the print house are very small, so that a special measurement technique has to be used.

Fig.35 shows the results measured with a wet stretch dynamics analyser.

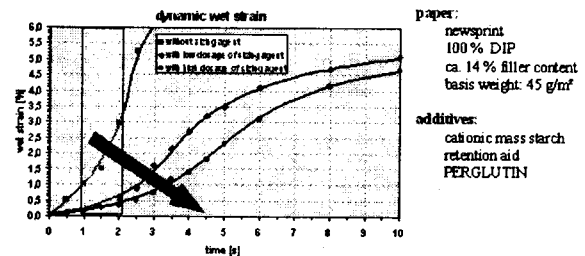


Fig. 35 : Case study 3- Internal sizing for improved newsprint paper