New Age Fixing Agents: Challenges and Effectiveness

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The fixing agent plays a vital role in charge neutralization which has a strong bearing on the properties both at the wet end & the dry-end. Retention (FPR & FPAR), drainage. picking(at the press), fluffing, linting and surface strength are the major properties that are effected by the charge levels at the head-box. This has a direct bearing on the efficacy of fibre/fine utilization, yield & Effluent clarity. The microbiological activity is directly proportional to the fibre/fine/ash content in the Back water as it acts as a food/nutrient for them. The topic focuses on the need for fixation(Charge neutralization), HOWs and WHYs related with it

INTRODUCTION

The continuing advances in closing water loops during paper production, the reduced proportion of fresh water and the increased use of used paper from recycling all produce disadvantages as well as undeniable advantages for paper producers. The advantages of reduced fibre and filler losses, improved dewatering due to higher loop temperatures and lower costs for waste water treatment are in opposition to the disadvantage of increased buildup of interfering substances in water loops. This negatively influences the runnability of paper machines as well as paper quality.

In order to fully develop the advantages, on the one hand, and aviod the disadvantages, on the other, increased demands, among other things, are placed on the paper process chemicals especially in the wet end of a paper machine. Therefore two methods for detecting interfering substances (laser-optical particle counter and impinging jet apparatus) will be presented. The use of fixing agents has long presented itself as an alternative or effective supplement to the separate treatment of water loops using micro flotation techniques: by using suitable fixing agents. Interfering substances are bound to fibres, fines and fillers and discharged with the paper, thereby removing interfering substances from the paper machine loops.

Sources of possible interfering substances and their classification

Knowledge of the type and origin of interfering substances as well as their chemical nature is very important in the development of effective fixing agents that remove the load of interfering substances introduced into the water loops while at the come time freeing process chemicals such as retention agents from acting as fixing agents.

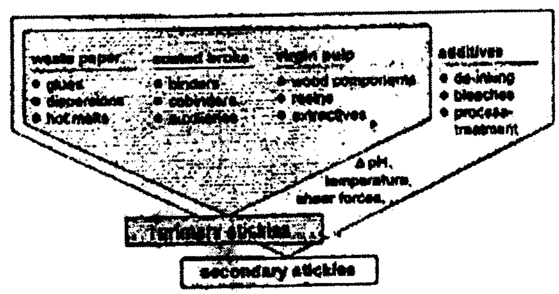


Fig. 1 Sources of detrimental substances

Interfering substances come from many sources and are determined by the raw materials used, the fresh water introduced and chemical additives [1,2]. Besides resins and resin components, principally extract substances such as lignins, lignin sulfonates and hemicelluloses are introduced by the new fibre used and as a result of the digestion conditions used in production. Used paper is contaminated with substances from previous paper manufacturing and converting processes such as dispersions and glues. Binder and cobinder components from paper coating processes are introduced into the loop primarily by the use of coated broke, but also by the introduction of used paper as a raw materials source.

Definition of interfering substance classes

- Pitch deposits consist exclusively of resin or resin components, while white pitch deposits are formed from binder and coating color components resulting from the introduction of coated broke.

The term stickies is used for sticky deposits in the form of organic complexes created by the agglomeration of interfering substances from used paper which interact with each other. All sticky deposits that are exclusively introduced through the raw materials are designated as primary stickies.

Sticky contamination which only occurs as a result of additives, such as those required for the production of highly converted paper qualities (e.g. polyvinyl acetate and polyvinyl alcohol for the production of sticky labels adhesive tapes and envelopes), are designated as secondary stickies. Their formation is encouraged by de-inking chemicals, surface-active substances such as soaps, surfactants and fatty acids, bleaching chemicals such as water glass, as well as alkaline production conditions, sharp pH changes and the occurrence of shear forces and temperature fluctuations.

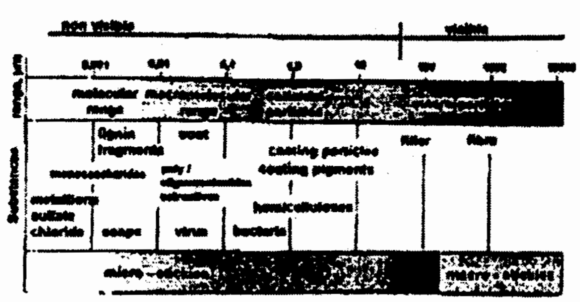


Fig. 1 Distribution of detrimental substances

The size distribution of interfering substances is also highly important for ensuring the effective treatment of interfering substances. A rough distinction is made between macro stickies, for particle sizes larger than 150 µm, and micro stickies, for sticky contaminants with a size distribution from 1 µm to 150 µm. As representative examples, decomposed starch components, hemicelluloses, lignins and bacteria are presented in Fig. 2.

Loop cleaning methods

The loss of effectiveness of process chemicals in the wet end of a paper machine due to the increasing load of interfering substances in closed water loops can be compensated with higher dosing amounts. However, this is accompanied by significantly increasing costs as well as, for the most part, increasing amounts of deposits in the form of secondary stickies that can form through the interaction of process chemicals with interfering substances via the formation of polyelectrolytic complexes. To restore the optimal effectiveness of the process chemicals [3], one can, in principal, proceed in three ways:

- Isolation of the interfering substances using mechanical separation

  ⟶ sorting and filtration techniques
- chemical treatment of the interfering substance loads

  ⟶ fixing agents
- combined mechanical/chemical application

  ⟶ dissolved air flotation

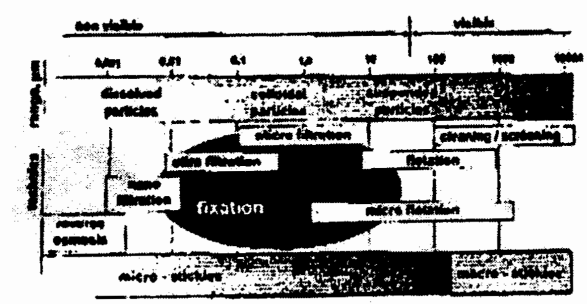


Fig. 3 Treatment of detrimental substances

Separation techniques such as cleaner and sorting systems operate on the basis of particle size and successfully separate interfering substance components to approx. 50 µm from the material streams (compare Fig. 3). Over time, they have become a component in the preparation of every substance and are being continually improved. The use of filtration systems for cleaning process water is a much less used technique. Depending on particle size. filter systems with pore sizes between 1 µm and 1 µm are used. In addition to high costs, the drastic increase in filtration area as particle sizes become smaller and the filter material requirements needed for treating sharply increasing waste water volumes have up to now been the limiting factors for the large-scale introduction of these techniques.

Flotation cells can remove sticky particles from the macro sticky region, even though it is originally intended to remove ink particles. The introduction of microflotation cells represents the first technique for the separate treating of waste water. The use of chemicals such as polyaluminum chloride, polyamine and polyethyleneimine allows colloidal and partially dissolved interfering substances in the size range between 5 mm and 1 mm to be precipitated in flotation cells, with the agglomeration of the microflocs being achieved in a subsequent step by using polyacrylamide (PAM). They allow particles in the range of 2 µm to 1 µm to be successfully flocculated and, in a subsequent step, floated [4]. In all cases, concentration of the flotation residues and disposal of the sludges is necessary, likewise representing a considerable expenditure.

- Reduction of turbidity, COD and cationic demand
- Neutralization of anionic substances
- Reduction of stickies and white pitch

- Adsorption of lipophilic / hydrophobic contaminats
- Repression of agglomation characteristic

- No formation of secondary stickies with process chemicals
- Long-term fixing of interfering substances
- Support of retention, promotion of sizing, etc.

Fig. 4 Fixing agents requirements

Using fixing agents to treat interfering substances has proven to be a recognized alternative and supplement to the flotation process, allowing various loads of interfering substances to be fixed to fibres, fines and fillers and discharged with the paper. Depending on the type'and modification of the chemicals used, the effective range of fixing agents reaches from approx. 1 mm to 50 µm (Fig. 3). Advantages such as the targeted treatment of individual interfering substances, reduced sludge accumulation, control of the runnability and productivity of paper machines while at the same time economizing on technology are obvious.

Fixing agent requirements

The following fixing agent requirements result from the complexity of the problems caused by the different interfering substances:

The currently available fixing agents differ in their chemistry and molecular structure and vary in molecular weight and charge density. Their main task is the fixing of anionic dissolved and colloidal interfering substances [5].

A highly cationic fixing agent, for example, neutralizes polyanionic interfering substances by formating a polyelectrolytic complex with surplus positive charges of the fixing agent fixing them to the fibres or fillers and discharge them with the paper [6,7].

Non-ionic hydrophobic or sticky interfering substances, which are substantially involved in the formation of secondary stickies, must likewise be discharged. In this regard, the fixing to the fibres must result in a type of long-term fixing (irreversible fixing) [8] In which the fixing agent used may, alone or through Interaction with other process chemicals, generate no secondary stickies.

As far as possible, fixing should take place while avoiding the agglomeration of white pitch and sticky particles to large aggregates, since this is the only

Summary parameters

- Determination of cationic demand (PCD-measurement)
- Turbidity measurements (optical method)
- COD - determination (oxidation process)
- Precipitating methods
- Extraction processes

- IR spektroscopy
- ▶ Laser-optical particle counting
- ▶ Impinging jet apparatus

Fig. 5 Detection methods

Models for detrimental substances

- Lignin sulfonates / Lignins
- Humic acids
- Wood extract models
- Water glass / sodium silicate

▶ Models for hydrophobic substances

Fig. 6 Substances models

way to continue to ensure a reduction in the tendency towards deposits and avoidance of breakage.

Interfering substance detection methods

The detection of interfering substances and knowledge of their composition on the one hand, and the development of effective, specifically acting fixing agents and their targeted use on the other, require reliable detection methods for the different interfering substances. The currently available methods exclusively provide summary parameters:

Until now, only cationic demand and turbidity have been measured online in the - machine loops. All other test methods are far more time intensive and can, therefore, only be carried out on a laboratory scale. Their use is, however, essential for the development of specifically acting, performance optimized fixing agents [10]. Thus, practical interfering substance models for use on a laboratory scale are made available for dissolved anionic interfering substances and their targeted treatment with fixing agents :

For the majority of Interfering substances, which have no or only a small anionic charge. fixing mediated exclusively by the charge mechanism using cationic fixing agents is often not sufficient. Therefore new modified cationic polymers have been developed that can interact with lipophilic/hydrophobic interfering substances which tend strongly towards homoflocculation. With this type of fixing agent, the focus of attention is no longer on high cationic charge but on a type of adsorption mechanism between fixing agent and hydrophobic interfering substance. The polyelectrolytic complex taking form (interfering substance / fixing agent complex) is irreversibly bound to the fibres by the total remaining residual cationic charge, so that discharge with the paper can take place. When used appropriately. the advanced laser-optical particle counting method [11,12] can

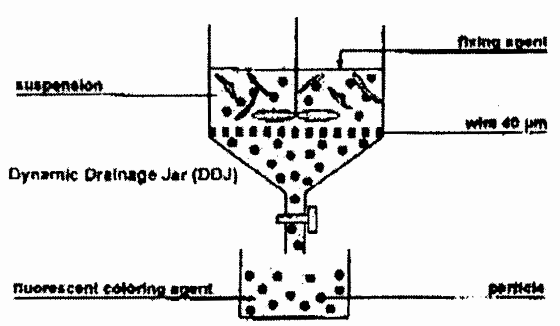


Fig. 9 Isolation of free particles

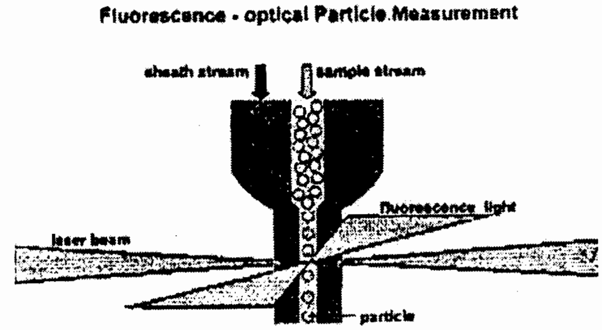


Fig. 10 Detecting of hydrophobic particles

serve as a detection method for detecting and measuring not only resin but also hydrophobic interfering substances such as white pitch and stickies.

Laser-optical measurement of pitch particles

All pitch particles not fixed to fibres are Isolated in a dynamic drainage jar (Fig. 9), The pitch particles collected in the filtrate are then dyed with a fluorescent coloring agent and transferred to a fluorescence-optical analyzer (Fig. 10).

Laser light exciting the coloring agent applied to the pitch particles results in the emission of fluorescent light which is detected in a photo multiplied. Every light pulse emitted by single particle are detected and counted.

- The lower the intensity of the collected fluorescent light. the smaller the number of free pitch particles found in the filtrate, and the better the fixing agent used and, naturally, vice versa.

In addition to the number of pitch particles, the size of the interfering substance particles may also be measured using the intensity of the reflected fluorescent light. Information on particle volume is derived from the number of particles detected and their diameters, so that a decrease in volume (parallel to a decrease in the particle count) gives information about the agglomeration characteristics: Fixing of hydrophobic interfering substances from the liquid phase only takes place if, in addition to a reduction of the particle count, a reduction in the particle volume is also observed (no agglomeration of hydrophobic interfering substances to macro stickies).

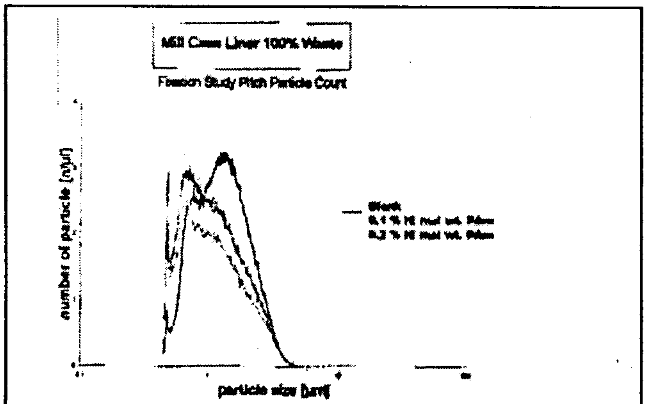
- reduction of particle volume = fixing of
  Interfering substances without
  agglomeration.

= no build-up of macro stickies, no deposits

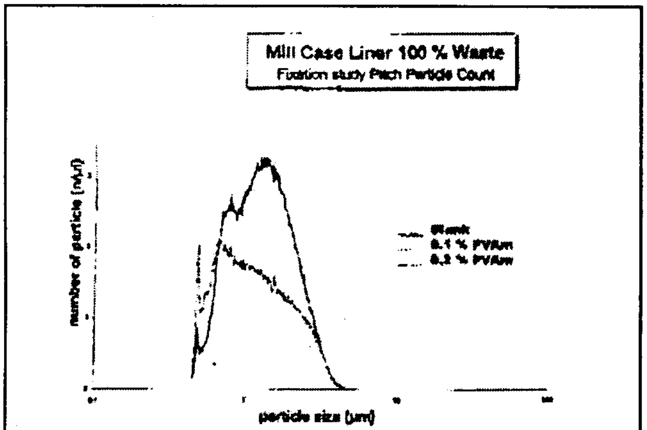
Identification of suitable fixing agents

Currently, 3 white-pitch models comparable to practical substance systems are available for testing the suitability of fixing agents. Model 1 consists of pitch particles based on acrylate polymers, while model 2 is constructed using styrene butadiene polymers. Extremely hydrophobic pitch particles are available using model 3, which makes use of acrylonitrile and butadiene monomers. All of the monomers listed are once again found In coating colors, binders and sizing agents and other additives which enter the paper machine loop through used paper and coated waste. Additional models based on vinyl acetate, vinyl alcohol or hot melts are currently in development. with reproducibility being very difficult due to stickiness or a strong tendency to homoflocculation [13b]. In order to properly detect these contaminants, test methods that deal specifically with the detection of stickiness and its consequences are currently in development.

As previously indicated, the efficiency of modified cationic polymers as fixing agents may be determined using these interfering substance models. Main criteria for success in fixation are reduction in Cationic Demand, improvement in turbidity levels, Enhancement of filler retention and its distribution, support of RDA system and optimization of other process chemicals etc. For all above to achieve. it is important that right chemical is chosen for the desired purpose. There are number of chemistries available like Polyamine. PolyDADMAC, Polyethyleneimine (PEI) and newly developed Polyvinylamine (PVAm). Following figures show the fixation efficiency achieved by using polyamine and polyvinylamine in a mill using 100% waste. As is quite evident. the use of Polyvinylamine considerably reduces the number of pitch particles (explained later) and outperforms Polyamine based chemistry.



Pitch particle count with use of PAm



Pitch particle count with use of PVAm

Pitch particle count with use of PVAm

A good fixing agent should be able to provide the following:

- Neutralization of anionic trash
- Prevention of white pitch
- Sticky control
- Reduction / elimination of deposits
- Positive influence on drainage
- Positive influence on retention (filler/fines)
- Increase in paper m/c runnability / productivity

Consequently, pre-treatment with suitable fixing agents can be a suitable measure for solving the interfering substance problem in closed water loops, without further investment in machinery. In addition cationic process chemicals such as retention agents are freed from acting as fixing agents, and are restored to their full effectiveness. The new fixing

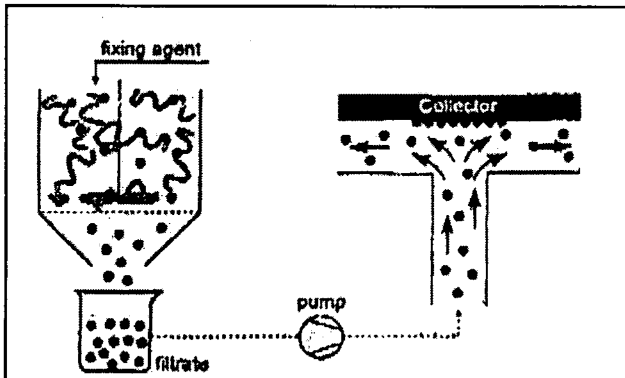


Fig. 12 Schematic diagram of the Impinging Jet apparatus

agents allow a wide spectrum of particle sizes to be dealt with. More R&D work is needed for the solution of all interfering substance problems caused directly or indirectly by hydrophobic and, above all, sticky contaminants.

In order to quantify the deposition tendency of non fixed white pitch particles, the filtrate is pumped through the impinging jet cell which is depicted schematically in Fig. 12. Some of the particles collide with the collector plate and they will stay there if the colloidal interactions between the particle and the collector plate are strong enough, Various different materials can be selected for the collector plate. For practical reasons, however, it makes sense to employ materials that are used in the wet end of the paper machine such as metals and plastics. For the investigations described in this paper, polyester was used. When we used a collector plate made from glass, it allowed us to view the formation of the deposits in situ and from the outside of the cell using a microscope.

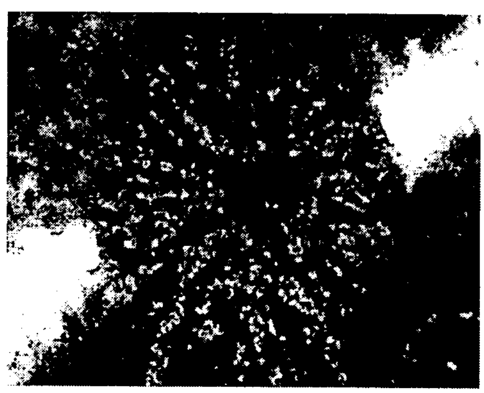


Fig. 13 White pitch deposits on glass

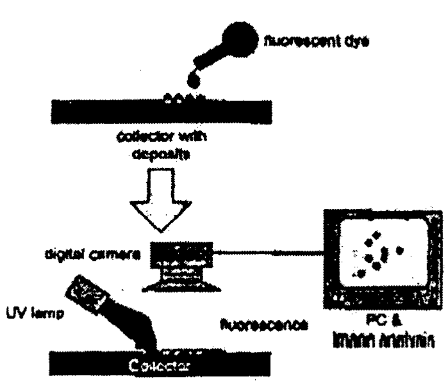


Fig. 14 Deposit qualification

The illustration (fig. 13) shows the central area of the cell with a diameter of 2mm. This roughly corresponds to the diameter of the inlet tube of the impinging jet cell. Deposits are formed mainly in this central area, because the velocity of the particles in the vertical direction is particularly high. The number of particles flowing through the impinging jet cell within a particular unit of time depends on the pumping speed and the concentration of white pitch particles in the filtrate. For a fixed pumping speed the typical particle flow is between 100.000 and 1.000,000 particles per minute. Only a fraction of these particles are deposite on the surface of the collector plate. The proportion deposited on the plate is a measure for the tendency of single white pitch particles to deposit on the collector plate. In order to quantify the deposits the following two step procedure was applied:

1. Measure the amount of white pitch deposited on the central area of the collector plate over a defined period of time. This quantity can be assessed by measuring the percentage of the central area that has been covered by white pitch deposits.
2. Take the result from step 1 and divide it by the concentration of white pitch particles in the filtrate. This quantity has been determined from the first part of the filtrate using the particle counter.

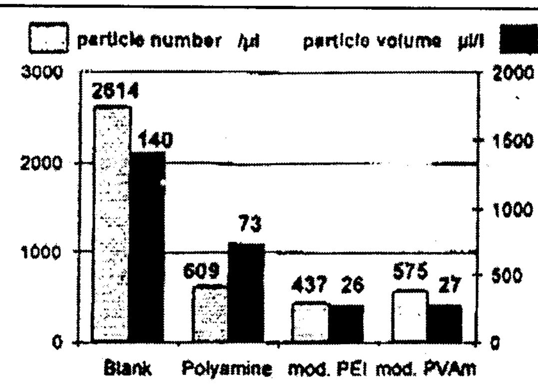


Fig. 15 White pitch particles number and volume.

This new quantity is named "deposition tendency". In order to evaluate the performance of a fixation agent, one should balance the change of deposition tendency against the change of white pitch concentration after fixation treatment.

Because the collector plate of the impinging jet cell is not usually transparent, it has to be removed from the cell after a certain time to allow the deposits to be measured. The plate is sprayed with a lipophilic

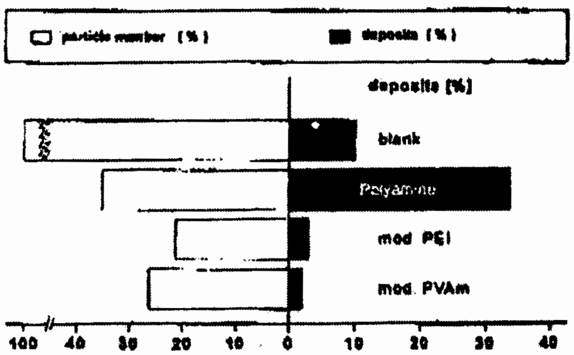


Fig. 16 Number of particles and amount of deposite

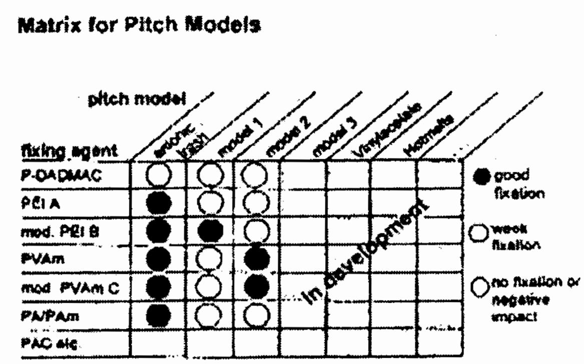


Fig. 17 Matrix fo fixing agent performance

fluorescent dye (Fig. 14). which has a high affinity for the hydrophobic deposits. This treatment results in a high contrast between the deposits and the substrate when the plate is illuminated with UV light. The contrasting areas are viewed through a microscope and scanned with a digital camera. Finally the digital image is evaluated using a PC and a special sorftware for image analysis. The formation of white pitch aggregates induced by cationic polymers can be explained in terms of a simple mechanistic model. The key parameter in this model is the adhesive and cohesive strength of heteroflocs formed by white pitch particles and fibres after fixation treatment with a cationic polymer.

When the floc strength is small, shear forces can tear off the white pitch particle from the fibre surface. Taking into account the collision probabilities of particles and fibres under practical conditions (16), for a single particle, the process of fixation and tear off can occur up to several hundred times before free particles and fibres are finally separated by filtration.

For anionic white pitch particles, undergoing several successive fixation and tear off circles, we have observed a net transfer of cationic polymer from the fibre surface onto the particle surface. When the amount of transferred cationic polymer is high enough. this will lead to a destabilization of the particles. Eventually collisions between the destabilized particles will occur and they will form white pitch aggregates. Shear forces acting on the aggregates also increase with increasing aggregate size. There is a critical point at which the aggregates become too large to be fixed to the fibres. As a result, poor fixing performance is always observed in connection with the formation of large white pitch aggregates.

However, when the floc strength is high, the number of successive tear off and fixation cycles is rather limited. Accordingly the probability for destabilization and aggregate formation will be small and one will expect a good fixing performance.

Future prospects

In order to avoid deposits in paper machine loops, thereby improving the runnability of paper machines, among other things improved fixing agents are needed. Different interfering substance models, such as those presented here based on white pitch, can be a crucial factor in their development.

A matrix of different modified fixing agents based on different interfering substance models creates the possibility of developing new comprehensively acting fixing agents which meet the indicated requirements of paper makers.

CONCLUSION

In this article various alternatives for the treatment of interfering substances in paper machine loops have been discussed and the use of fixing agents has been stressed. The fixing agents presented here allow a wide range of anionic, dissolved and colloidal Interfering substances to be treated.

New fixing agents that significantly reduce the agglomeration tendency of hydrophobic interfering substances therefore effectively counteract the formation of primary and secondary stickies and free process chemicals from acting as fixing agents. In this way, a significant improvement in the runnability of a paper machine may be attained, together with an increase in productivity, Consequently, adjustment of process chemicals to the new environment makes efficiency increases possible without investments in additional chemicals or even machinery.