Sizing-Concepts and Technology For Effective Gains

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Today we appear to be on the brink of entering an era of new levels of sizing process and control, still without doubt, rosin sizing is the industry standard. Although the process of conventional sizing is over 170 years old, yet most articles and patents giving clear understanding of the entire process and control parameters have been confirmed only in last two decades. Simultaneously the invention of alkaline sizing, a method to manufacture paper that would not become yellow or brittle, was made in late 50's.

This report reviews the latest developments and understanding for both rosin and reactive sizing processes.

BASIS FOR ROSIN SIZING :

The purpose of rosin sizing is the prevention of water spreading on the paper surface. The wash burn's equation for the spreading of water reveals that the factors influencing the spreading are :

y — water surface tension.
μ — viscosity of water.
γ — capillar radius.
e — capillar length.
ϕ — contact angle.

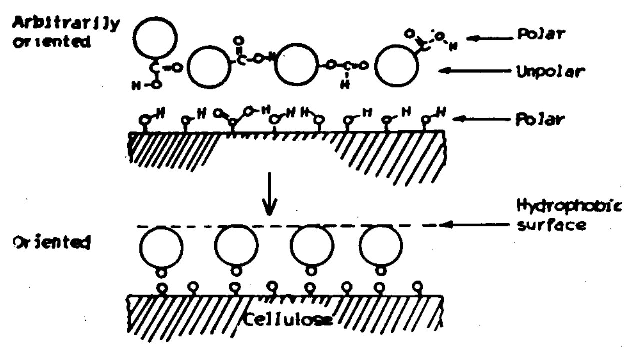
WASHUBURN'S EQUATION :

$$\frac{dl}{dt} = \frac{y}{\mu} \quad \frac{r}{\varrho} \cos\emptyset \qquad (1)$$

Water surface tension and viscosity, cannot be affected by treating the paper. The capillary radius and length are determined by factors like fiberous raw material, beating degree, pressing of paper and simply the basis weight, factors that have to be chosen without considering the spreading of water on paper...... Left, then is the contact angle which thus is the only parameter that can be purposely affected in order to reduce the wettability of paper. Thus the fiber surface have to be modified chemically in order to reduce their free energy[1] and thus their affinity to water.

The principle of rosin sizing is the introduction of unpolar chemical compound to the fiber surface. For getting this sizing material (unpolar chemicals) be fixed on the paper surface, it should have a binding part. This binding part being polar will also have affinity to water. The problem thus is to fix the sizing material to the paper surface in such a way that the hydropillic polar part points towards the paper surface, not towards the moistening water.

The figure 1 given below presents the phenomenon.



Rosin (Abietic Acid) thus holds the required double characteristic, one polar hydrophillic and other unpolar hydrophobic part. To work efficiently as a sizing medium they have to be fixed and remain in position on the paper. This requirement can be achieved by the addition of papermaker's Alum.

EFFECT OF DRYING ON ROSIN SIZING :

For the proper orientation of the ionically precipitated[2, 3] and electrostatically[4] fixed size precipitate, drying procedure plays a critical role.

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When depositing onto the fiber, the sizing particles will be some what swollen and hydrated. Polar groups on the particle surfaces will orient towards the surrounding water. If dried at room temperature, the particles will gradually lose their bound water, without proper reorientation. If so, some sizing molecules may end up with their hydrophilic part pointing outwards, and will reduce sizing efficiency.

Higher temperature levels provide following advantages.

1. Better ability for reorientation.
2. At sintering temperature, during drying the spreading of material is eased[5].
3. Higher temperature causes polymerization reactions enhancing binding of rosin particles
4. The very impotant aspect is that higher temperature eases the ability of the polar groups to reorient towards the paper surface (Fig. 2). The hottest dryer should be reached when the fiber consistency has increased beyond 42%. However, the necessary temperature profile varies for different sizes[6].

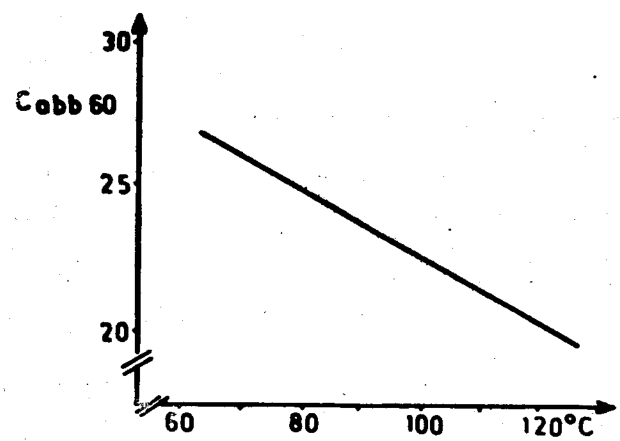

Fig. 2 Final Temperatnre at drying

ROSIN SOAP/ROSIN DISPERSIONS :

A better understanding of sizing development has led to replace the conventional soap type rosin sizes with the dispersed sized in modern mills.

Somesignificant draw back of soap type sizes are :—

(a) Soap type size reduces the paper strength
(b) They form large clusters of their precipitates, therefore, size distribution on the fibers is not very uniform. This tendency become more aggrevated when stock contains large amounts of Ca^{++} and Mg^{++} ions or recycled alum.
(c) Sintering temperature of soap type sizes is high, ranging from about 120°C to 250°C which is difficult to attain on normal dryers.

However, dispersion sizes consist of emulsified free rosin particles, ranging in size from 0.1 µm to several um.[7] The free rosin cannot react with alum, if added to paper stock[4]. The size particles are retained either by bridging with the adsorbed alumina or with cationic retention aid. The size particles are retatively free to relocate during the web consolidation on the dryers. During paper dryer the size melts thoroughly (as it has lower sintering temp.) and redistribute over the exposed fiber surface to form the aluminium rosinate[6]. This occurs when the fiber bonds have been largely established. Thus the delay in reaction with alum results in less interference with fiber bonding and produces a better oriented, low energy film[4,8] which covers the fiber surface more uniformly. Similarly wax sizes improve rosin sizing at relatively low dosage levels, cause of lowering the sintering point of the size providing once again a better orientation and formation of a more hydrophobic film.

ALKALINE SIZE :

A lot of efforts has been put into the work of developing new methods for making the paper hydrophobic. There are several reasons for this like (i) remedy to the problem of yellowing and embrittling of rosin sized paper, (ii) significant and interesting chemical market and (iii) considerable market for neutrally sized paper.

Over the past decades the following benefits observed on alkaline papermaking using cellulose reactive size have been computed.

1. Improved strength. [9]
2. Utilization of calcium corbonate filter.[10]
3. Reduced energy consumption.[11]
4. Reduced effluent loadings.[12]
5 Improved productivity.[13]
6. Improved sizing
7. Less corrosion to papermaking system.[14]

BASIS OF CELLULOSE REACTIVE SIZING :

Reactive sizes were introduced to paper industry more-than three decade back in 1950's. These sizes are synthetic, non-ionic organic compounds. They are made compatible with papermaking fiber by emulsifying with stabilizers and disperants. They form covalent bond with cellulose which is extremely resistant to hydrolysis[15]. Alum is not needed for sizing development, and infact, it often interferes with the reaction. Thus these sizes are usually used at neutral to slightly alkaline pH in alum free systems.

Utilization of cationic stabilizers gives theemulsified particles a net positive charge, which provides an electrostatic retention mechanism similar to that of rosin size precipitate[16]. Once the emulsion particle is retained, it must be redistributed over the fiber surface. However unlike rosin size precipitate, the synthetic size is retained as large particles and then spread down to molecular dimensions prior to reaction with cellulose. This occurs only during pressing and drying operations. This distribution is very uniform and effective and thus provide very highly efficient sizing. Lastly, the reaction with cellulose takes place and sizing is obtained, since in case of alkaline sizing every step must occur sequentially from retention in wet end, to distribution during pressing, initial drying and final reaction during drying, it is very sensitive to variables in papermaking process.

CHEMISTRY OF CELLULOSE REACTIVE SIZING :

All reactive sizes have a hydrophobic and a reactive group which reacts with cellulose and forms a a size material. The hydrophobic group determines the physical properties of size, such as melting point, solubility, reactivity in water and ease of emulsification. Whereas the reactive group is the heart of reactive size. Its properties relates to the rate of reaction with cellulose and stability of the emulsion. Some of the most commonly cellulose reactive sizes are depicted in Table-1.

There is always a competition between reaction of the size with cellulose . hydroxyl group and reaction with water. Reaction with water gives an ineffective size product. Thus papermaker has to make stable emulsions, insensitive to water, that would convert to a highly reactive form only after the sheet moisture reduced below a predetermined level and then react quickly with cellulose[17].

TABLE-I : CHEMICAL FUNCTIONALITIES OF COMMON CELLULOSE — REACTIVE SIZING SYSTEMS

Water resistant functionality	Cellulose Reaction Group	Size complex
Stearic Acid	Acid chloride or acid sulphate	Aluminium stearate
Alkylated succinic acid	Anhydride	Alky succinic anhydride.
Stearic Acid	Anhydride	Distearic Anhydride
Styrene copolymer	Anhydride	Styrene anhydride
Stearic Acid	Alkylated Ketene	Alkylketene dimer.

Three commercially known synthetic sizes are Alkyl Ketene Dimer, stearic Anhydride and Alkenyl succinic Anhydride having reactivity in the increasing order and have corresponding cure time in decreasing order i e. Alkenyl sccinic anhydride is most reactive and has lowest curing time under alkaline conditions.

Ketene Dimers is easily emulsifiable solid, with low melting point (40–45°). Alkyl Ketene dimers are believed to react with cellulose hydroxyl groups to form β Ketoesters (Fig. 3) with ring opening occuring at acyl-oxygen bond[18]. Because of its low reactivity with water it forms stable emulsified product. However, the low rate of cure poses problem when on machine sizing is required.

Fig 3. (A) Proposed reaction between AKD and and cellulose (B) end form of the β ketoester, showing internal H–bond.

The stearic anhydride is also a solid with somewhat higher m.p. than AKD and thus is more reactive, which makes its emulsification difficult and emulsified product with limited shelf life. Sizing reaction is more rapid than with A. K. D. Since the hydrolysis product of this acid is a free acid, alum can be used to fix this unreacted material to cellulose. They are primarily used in bleached boards.

Alkenyl succinic Anhydride is the most reactive synthetic size. It differs from the earlier two in being a liquid. Because of its high reactivity emulsion activity is lost in a matter of hours, therefore emulsion must be prepared at site.

EFFECTS OF REACTIVE SIZING ON PAPER PROPERTIES :

The most evident paper property which differs from rosin sized sheet is that the alkaline sized paper feels more slippery. Paisle et al have quoted 30% lower coefficient of friction and 20% lower slide angle for paperboard manufactured with alkaline size in comparison io rosin sized[14].

Bryson reports that 1–1½% higher moisture content level is possible in clay filled sheet before calender blackening is visible[9], which gives smoother denser and softer sheet. At the same time productivity increase is obvious.

Alkaline sized sheet with $CaCO_3$ can have 8–15 points higher brightness and a matter appearance than a shiny look in comparison to a clay filled sheet.

EFFECTS ON PROCESS :

Alkaline sizing can lead to some advantages, some disadvantages too. As mentioned earlier reaction of reactive sizes with water leads to an hydrolysed product which reduces sizing efficiency. This hydrolysis also give rise to machine operation problem especially press picking. Formation of hydrolysed product is directly dependent on the reactivity of sizing agent and the retention.

Usage of cationic retention aid is the good remedy for the problem. They improve the sizing development time and retention also. Mechanically a flooded doctor blade for cleaning the roll surface has also been suggested.

While changing system for Alkaline sizing from conventional acid. The size deposits are cleaned out, and can cause holes and wet breaks. An alkaline boil out before a trial will usually help.

Tne energy necessary to develop a certain strength is lower by about 10% for an alkaline system. Rid-dell has given the economics of alkaline/acid system[19] and has reported the benefits in two ways :

(1) By direct power reduction to the refiner.

(2) By possible substitution of lower strength lower cost fibers to reduce material cost, which is particularly useful to a country like India where, the quality of raw matererial is poor.

The filter content can also be increased in some products to lower the cost of production.

Alum is a very offensive ingredient utilized in conventional rosin sizing system which hydrolyses water, can be very corrosive. This situation as well as salt build-up on suction rolls can be eliminated by alkaline sizing, which also add to the savings.

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