Effect of Acidic and Neutral Sizing on the Strength and Printability of Indigenous Pulps

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ABSTRACT

Sizing of pulp blends of mixed hardwoods and bamboo, mixed agricultural residues and jute the common furnish components of Indian large and medium sized mills were studied using fortified rosin soap under acidic condition, ASA emulsion and dispersed rosin under neutral conditions. It was observed that better sizing is obtained on sizing with 0.6 % ASA emulsion than 0.8 % dispersed rosin at neutral pH and 0.8 % fortified rosin soap at acidic pH. The extent of sizing development in case of agricultural residue pulps is lower than hardwood pulps at the same dosage level of sizing chemical. Addition of talc helps in improving the sizing for both pulp blends. ASA emulsion gave paper of better bonding characteristics than rosin sizes. The print quality as assessed by print density was however observed to be best for dispersed rosin sized paper. The optical properties reversion is more for acidic sized sheets than ASA and dispersed rosin sized at neutral pH.

INTRODUCTION

Indian paper industry has gone through a phase of chemical evolution in last two decades. Different new formulations of process and product additives have been introduced in the market and the sizing chemicals are one of them (1-11). From the conventional acid system with rosin paste and fortified rosin soap to neutral rosin dispersions, the industry is slowly changing to neutral/alkaline system with synthetic sizing materials like ASA (Alkenyl succinic anhydride) & AKD (Alkyl ketene dimer). The driving forces for the change are process advantage, product improvement and environmental considerations. The main advantages of neutral/ alkaline system over acid system are-

- Improved sheet strength.
- Improved paper stability on aging.
- Increased machine runnability, hence increased productivity
- Reduction in energy consumption.
- Increased use of $CaCO^3$ filled recycled fibres.
- Reduction in corrosion.
- Increased system closure.

Besides these advantages, there are few problems inherited with the neutral/ alkaline papermaking like low frictional coefficient of AKD sized paper, unstable sizing or difficulty in controlling sizing level, instability of size emulsion and their handling problems and formations of deposits in the papermaking system. In such scenario, sizing at nearly neutral pH with dispersed rosin emulsion offers good alternative with improved paper strength properties and machine runnability. The primary difference between rosin and reactive sizes AKD, ASA is that in rosin sizing it is rosin and aluminum species that are ionically bonded to each other and these precipitates render the fibers hydrophobic.

In the case of reactive sizes, a covalent bond is formed between the hydrophobic molecule and cellulose of the pulp fibers. A further difference is with the chemical structure of hydrophobic part. In case of rosin it is in the form of fused ring arrangement of aromatic ring whereas with reactive sizes it is typically a long hydrocarbon chain of aliphatic origin. The development of alkenyl succinic anhydride as sizing agent came later than the alkyl ketene dimer and took place in 1974 (5). Like AKD's they are also able to undergo reaction with cellulose and water. The ASA's are considerably more reactive than AKD's and can promote sizing without heat treatment (6). Unlike the AKD's which are derived from fatty acids, the ASA's are petrochemical based. ASA is an unsaturated fatty acid anhydride and is the most reactive amongst sizing agents. It must be emulsified on site and must be used shortly after

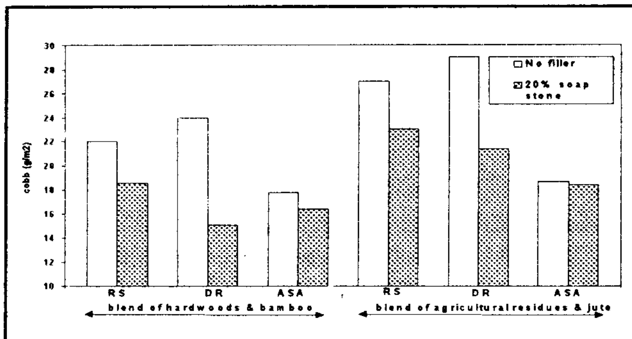

Fig. 1 Sizing response of different sizing chemicals on blends of mixed hardwoods & bamboo, agricultural residues & Jute pulp
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhdride at pH > 7

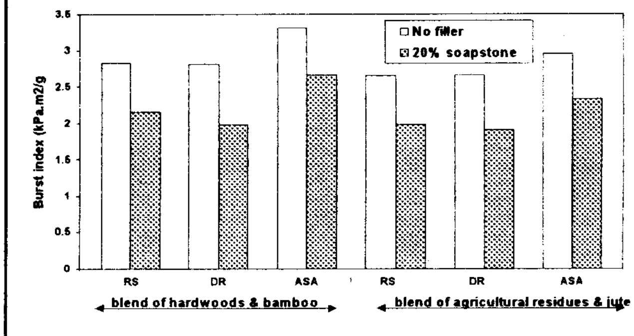

Fig. 3 Effect of sizing with different chemicals on bursting strength
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhdride at pH > 7

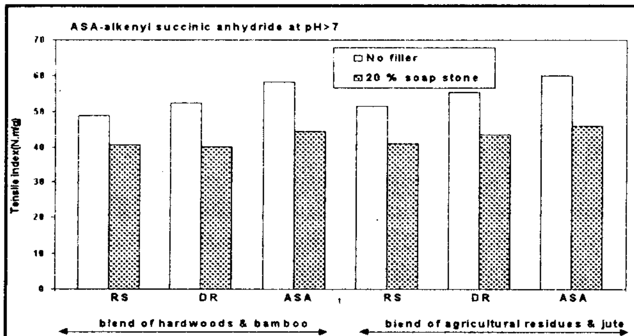

Fig. 2 Effect of sizing with different chemicals on tensile strength
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhdride at pH > 7

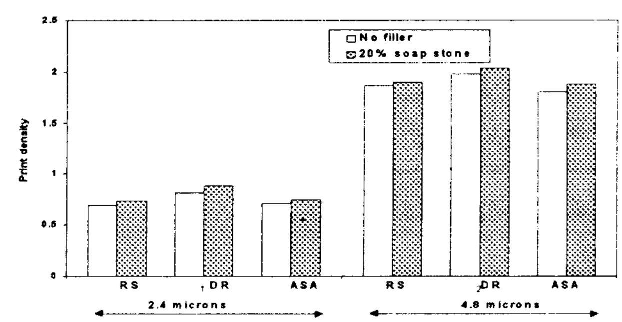

Fig. 4 Effect of sizing with different chemicals on Print density of blend of bardwood & bamboo pulp
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhdride at pH > 7

make up. In addition, first pass retention must be maximized usually with a cationic polymer or cationic starch addition, to prevent recirculation of the size in the wet end. All these steps will minimize hydrolysis, which can result in poor sizing (7-9). The hydrolyzate can also cause press picking problems because of its tackiness, but its effect can be minimized by employing sufficient aluminum ion at pH greater than 7 (10). An advantage of ASA sizing is that, due to its reactivity, 80-100% of the ultimate effect is achieved while on the machine. This effect allows for good hold-out of size press solution. The historical development of neutral papermaking and development of three main neutral systems have been well reviewed (2,3).

In India there is wide variation in raw material furnishes ranging from mixed hardwoods, bamboo, agro-residues to imported waste paper of Indian and foreign origin. The proper selection of size chemicals and sizing system becomes very difficult for such cases. Most of the mills in India are still following conventional rosin/alum sizing under acidic conditions and only a few have transformed to neutral/alkaline system. Lots of problems are being faced by such mills and, some of these mills have again gone to acidic sizing system after few trials of neutral sizing. The effect of sizing at different pH levels is not well established for indigenous pulps. In the present investigations some of the key differences between rosin based sized and ASA emulsion sized paper with regard to strength, aging and printing characteristics for indigenous raw materials like blend of mixed hardwoods & bamboo pulp (common furnish of Indian large mills) and blend of mixed agricultural residue & jute pulp (common furnish of Indian medium sized mills) have been studied in detail.

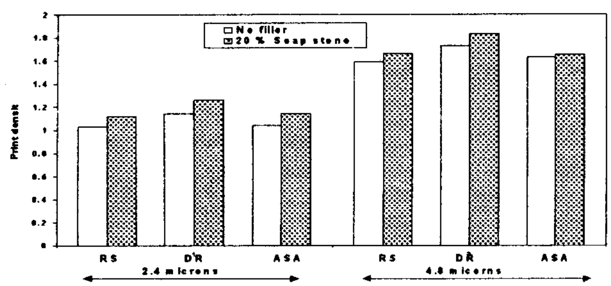

Fig. 5 Effect of sizing with different chemicals on Print density of blend of agricultural residues & Jute pulp
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhdride at pH > 7

RESULTS AND DISCUSSION

Sizing response of different sizing chemicals

Sizing with fortified rosin soap size, dispersed rosin size and ASA emulsion were carried out for blends of bleached mixed hardwoods & bamboo and bleached mixed agricultural residues & jute pulp collected from the paper mills. The sizing with fortified rosin soap was done at acidic pH where as for dispersed rosin and ASA it was at neutral pH. The sizing response of these are shown in Fig 1. There is a marked difference in the sizing response of three different sizes. ASA emulsion develops very good sizing for both pulp blends, followed by dispersed rosin size and fortified rosin soap. At the same dosage of chemicals, the sizing is comparatively lower in agricultural residues than hardwood pulp probably due to the presence of more fines in agricultural residue pulps and higher negative charge (12).

Effect of soap stone filler loading on different sizing chemicals

Fig. 1 shows the effect of filler on sizing with different sizing chemicals. It was found that with the addition of talc as filler the sizing got improved. This is probably due to the low surface energy and hydrophobic nature of soap stone filler. Since sizing phenomenon depends upon the free surface energy of the surface, the soap stone filler adsorbed on the surface of the fiber in the presence of cationic alum lowers the surface energy of the fiber which in turn increases the sizing efficiency of the fiber as shown by the lower cobb values. The decrease in cobb value is more in the case of fortified rosin soap and dispersed rosin size than ASA emulsion size. This is due to the fact that ASA is a chemically reactive size which reacts with cellulose and the presence of filler does not help much with the sizing process, while in case of fortified rosin soap/ dispersed rosin size, both size and filler get adsorbed on the fibre surface physically with the help of alum or any other aluminum containing chemical used in sizing.

These observations can further be explained on the basis of sizing mechanism of rosin soap, dispersed rosin and ASA emulsion. Soap size reacts with alum as soon as it is added to paper stock. Both Electro-static bonding and co-ordinate bonding participate in the reaction, which obviously results in a strong bonded complex. Since alum is able to form ionic and coordinate bonds with the rosin only at acidic pH, sizing with soap size has to be developed in the low pH region. On the other hand, dispersed rosin size consists of rosin acid droplets, which have considerable surface areas. Therefore, its retention is a consequence of colloidal and surface chemistry. Dispersed rosin does not react readily with alum to form aluminum resinate. The alum acts as a bridge between the negatively charged fiber and the negatively charged rosin micelle. In a rosin alum system, rosin in either its free acid or soap form will react with alum to give the aluminum ester products which create hydrophobicity. In the case of soap rosin size under acidic conditions, most of the rosin reacts rapidly with alum in solution to give aluminum ester. In case of dispersed rosin size the reaction of rosin size acid and alum/PAC does not proceed in solution, but occurs on the fiber surfaces in the dryer section. The dispersed rosin size particles are relatively free to migrate during the drying process in the paper web. However as the paper temperature increases on its movement over the drying cylinder, the heat creates a sintering process where the rosin particles melt & distribute uniformly over the surface area of the fibers to form the aluminum resinate (13).

In case of ASA emulsion, the ASA undergoes the reaction of anhydrides. They react with cellulose to form a cellulose ester. This bonded ASA provides sizing at wide pH range when it reaches at the dryer part of the machine. ASA is highly reactive, and the sizing reactions occurs very rapidly but the hydrolysis of the ASA is not desirable since the hydrolyzate is not effective sizing agent and may deteriorate sizing. In excess quantity, it may even destabilize the ASA emulsion (6).

Effect of strength properties on sizing with different chemicals

While comparing the strength properties of two pulps sized with different sizing chemicals under different pH values, it was found that sheets made under alkaline pH conditions were stronger than sheet formed in acidic pH for both mixed hardwoods and mixed agricultural residues pulps. The

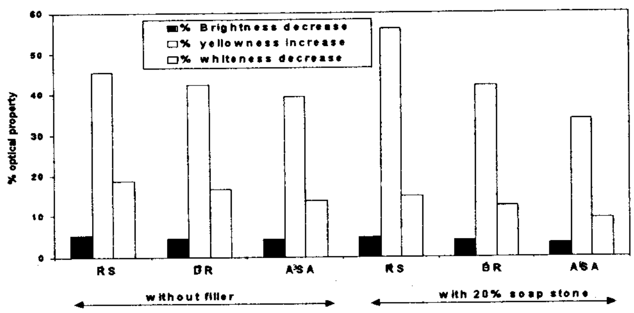

Fig. 6 Effect of sizing with different chemicals on Accelerated aging of blend of hardwood & bamboo pulp
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhdride at pH > 7

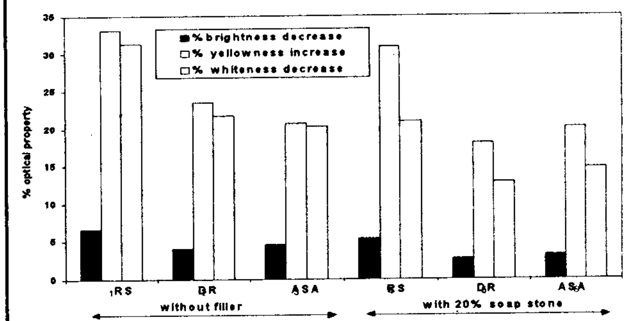

Fig. 7 Effect of sizing with different chemicals on Accelerated aging of blend of agricultral residues & Jute pulp
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhdride at pH > 7

tensile index and burst index were on higher side when the sheets were sized with ASA emulsion at neutral pH. The strength properties were comparable both in the case of fortified rosin soap and dispersed rosin. The strength is lower in case of sheets made in acidic pH with rosin soap. The reason for better strength in the case of neutral ASA sized sheets is due to the reason that at higher pH fiber swelling is more which in turn forms stronger bonds and thus making stronger sheet. Additionally the rosin-alum precipitates form bigger aggregates, which interfere in fiber to fiber bonding thus reducing the strength. When the pulps were loaded with 20 % soap stone as filler, the strength properties viz. tensile and burst for both pulps got reduced in comparison to the sheets without filler. At the same filler loading and ash retention, the reduction in strength properties is least in case of paper sized with ASA emulsion under neutral conditions than paper sized with rosin soap at acidic pH conditions Figs. 2 & 3.

Effect on print density on sizing with different chemicals

To study the effect of various sizing chemicals on printing, handsheets were evaluated for print density using IGT printability tester. Printing tests were carried out at two ink layers i.e., 2.4 microns and 4.8 microns . It was observed that for mixed hardwoods pulp, the print density at both ink layers is more in case of handsheets sized with dispersed rosin than ASA. The similar trend was observed for wheat straw pulp Figs. 4 & 5.

The print density of handsheets filled with soap stone, is on higher side as compared to handsheets without filler. Filler particles being smaller in size fill the void volume between the fibers thus providing more smooth surface which results in better printability.

Effect of aging on sizing with different chemicals

To study the effect on optical properties on accelerated aging of the handsheets sized with different sizing chemicals at different pH values, properties like brightness, yellowness, and whiteness of the sheets were measured after aging the handsheets at a relative humidity of 35 % and 400C temperature for 6 hours in Xenoweather fastness tester. There was decrease in brightness and whiteness of the handsheets and increase in yellowness for all the three cases. The percentage reduction in brightness and whiteness and percentage increase in yellowness was maximum in case of rosin soap sized handsheets under acidic conditions. Dispersed rosin at neutral pH has given lesser effect than acidic pH sizing but it is slightly more than ASA. The aging in acidic pH is due to the sulfate and aluminum ions which are free to react with available protons to produce weak acids. Acid hydrolysis is believed to be one chemical reaction resulting in loss of paper permanence (14).

In case of handsheets filled with 20 % soap stone filler, the trend remains the same. Acid rosin soap sized handsheets aged faster than neutral sized handsheets. The effect on the decrease in brightness and whiteness and increase in yellowness was on lower side for filled handsheets Fig. 6 &7.

EXPERIMENTAL

Pulps used in the studies were collected from the near by paper mills. These were bleached pulp blends of mixed hardwood & bamboo and mixed agricultural residues & jute. The sizing was done using

- Fortified rosin soap 0.8 % and 2% alum at pH 4 to 5

- Dispersed rosin 0.8% and 2% PAC at pH 6-7
- ASA emulsion 0.6 % at pH 7.0

Handsheets were made on Rapid Kothen former according to the ISO standard method T06/565N/706. The handsheets were conditioned at temperature 27 10C and relative humidity 65 ? 2% prior to testing.

The accelerated aging of handsheets were done using Xenoweather fastness tester for 6 hours.

The different tests were carried out according to the standards given below:-

Grammage-	ISO 536
Tensile strength-	ISO1924
Bursting strength-	ISO 2758
Brightness-	ISO 2470
Cobb-	ISO 535
Ash content	ISO 2144

Print density- Prints were made using IGT printability tester AIC2-5 at two ink layers i.e. 2.4 and 4.8 micron and print density was measured using Macbeth densitometer.

CONCLUSION

For the pulp blends of mixed hardwoods & bamboo, agricultural residues & jute without any filler, better sizing development is obtained on sizing with 0.6 % ASA emulsion than 0.8% dispersed rosin at neutral pH and 0.8% fortified rosin soap at acidic pH. The extent of sizing development is lower in case of blend of agricultural residues & jute pulp than hardwood & bamboo pulp. This is probably due to the presence of more fines and relatively higher negative charge in the furnish of agricultural residues.

Addition of soap stone as filler helps in improving the sizing to varying extent for both pulp blends in all the cases.

For both the pulp blends the handsheets sized with ASA emulsion under neutral pH gave better bonding properties like tensile strength and bursting strength as compared to handsheets sized under acidic rosin soap and dispersed rosin neutral conditions.

Print quality as assessed by print density at particular ink layer is relatively better for dispersed rosin sized sheets at neutral pH than ASA and fortified rosin sized sheets.

The optical properties reversion is more for acidic sized sheets than ASA and dispersed rosin sized at neutral pH. The best results were obtained for ASA sized sheets. Addition of soap stone as filler helps in reducing the extent of optical properties reversion.

The studies indicate that dispersed rosin with PAC may be the first option for trials of neutral papermaking, followed by reactive sizes.

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REFERENCES

1. Burke, Douglas, J. 'The alkaline revolution' special report
2. Hagemayor, R.W., 'History of neutral/alkaline papermaking' Neutral papermaking short course held at Atlanta, **Tappi press,** p 1 (1990).
3. Crouse, B, Wimer, D.G., 'Alkaline sizing an overview' Neutral papermaking shortcourse held at Atlanta, **Tappi press,** p 5 (1990)
4. Evans, D. B. Alkyl Ketene Dimer sizes, The sizing of paper, 2 nd edn., **Tappi press,** Atlanta, 1989.
5. Wurzburg, O. B., **US Patent** : 3.821, 069 (1974).
6. Roberts, J. C., Daud, W.R.W., 'Mechanistic aspects of alkenyl succinic anhydride sizing of paper' paper presented at 10th cellulose conference 'Cellulose and wood chemistry and technology' held 29th May-2nd at Syracuse, N.Y., U.S.A. (June 1988).
7. Farley, C.E. and Wasser, R.B., 'Sizing with ASA'. The sizing of paper, 2nd edn., **Tappi press**, Atlanta, (1989).
8. Proverb, R. J. and Dauplauwe, D. L., Papermakers conference proceedings, **Tappi press,** Atlanta, p 91 (1989).
9. Maher, J.E., Alkaline papermaking conference proceedings, **Tappi press,** Atlanta, p 89 (1985).
10. Scalfarotlo, R.E., **Pulp and Paper** 58 (4):126 (1985).
11. Abell, S., Alkaline papermaking conference proceeding. **Tappi press,** Atlanta, p 31 (1985).
12. Sood, Y.V., Report on fellowship training at **APPI,** Australia (1993)
13. Kapoor, S.K., Sood, Y.V., Tyagi, S., Manoth, M., Bharti., 'Effective sizing of waste paper containing calcium carbonate with roin and alum system', **IPPTA J.** vol. 13, No. 3:7 (Sept 2001)
14. Gurnagul, N., Howard, R.C., ZOU, X., Useaka, T and Page, D.H 'The mechanical permanence of paper', JPPS, Vol. 19, No4: JIGO (July 1993).