Recent Trends in the use of Chemicals and Additives in Stock Preparation

Rao S.S., Shirahatti P.V., Pai N.M. & Maheshwari Subhash

ABSTRACT: The objective of this paper is to provide an integrated overview of recent trends in the use of chemicals and additives in stock preparation based on the reported literature. Modern papermaking normally involves fast machines, closed white water system, increased use of recycled fiber while meeting the requirements of improved paper quality and higher productivity at the same time. These require a new approach for efficient and effective management of wet-end process.

A variety of chemical products used for various purposes such as retention and distribution of fines, sizing, microbiological and deposit control, proper coagulation etc. have to be used judiciously to get the desired result. This paper briefly discusses the merits and limitations alongwith other details regarding use of these chemicals. It has been concluded that the key to a successful wet-end operation is to adopt a systematic approach in selection of these chemicals keeping in view the process conditions of a given mill.

INTRODUCTION

The basic objectives in stock preparation are to mix fibrous and non-fibrous raw materials as per the requirement of the product to be manufactured. However, in recent years, major changes and developments have taken place in different areas of papermaking including raw material, process infrastructure and chemicals and additives. These developments have resulted in better quality products with increased productivity.

The chemicals and additives have an important role to play to control over all wet end operations. The main aspects that govern the runnability and quality papermaking depend on the complex wet end chemistry. The various chemicals used in paper stock can be classified in two groups:

* Functional Chemicals
* Control Chemicals

The functional chemicals are those which intend to become a component of final paper sheet and modify its properties. They are fillers, pigments, sizing chemicals, chemicals used for strength improvement etc. The control additives are used to affect the performance of stock at wet end operation without becoming part of the paper such as retention/ drainage aids, pitch control

The West Coast Paper Mills Ltd.
Bangurnagar, P.O. DANDELI-581 325
(KARNATAKA)

agent, defoamer, biocides etc. The main factors affecting the wet end chemistry are, dissolved and suspended material and their electrokinetic and surface charge properties, retention, addition dozes etc.

Indian paper industry has shifted gradually towards short-fibred raw materials like hardwoods, bagasse, and agri-residues. But the equipment and process infrastructure remained more or less the same in most of the cases. Hence, in order to manufacture the good quality paper with higher productivity, efforts are required to improve the overall efficiencies in different areas of papermaking. One potential area is effective use of different chemicals and additives at stock preparation stage. The present paper discusses these aspects in detail.

INTERNAL SIZING

The internal sizing of paper, which imparts resistance to water penetration, is an important to any structural or printing grades of paper. The paper is sized with molecules having a hydrophobic portion which resists water penetration and a hydrophilic portion that adheres to the fiber substrate. Rosin-alum is oldest established and still the most common internal sizing system used by Indian paper industry. Efforts are in progress to slowly replace it by either Alkyl Ketene Dimer (AKD) or Alkenyl Succinic Anhydride (ASA) sizing agent. Other products which are also used in same applications include polymeric sizing agents.

Rosin Sizing

In this system rosin size added to the stock reacts with alum or other precipitant such as Poly aluminium chloride (PAC) or sodium aluminate to form a complex hydrophobic compound, aluminium resinate, which precipitate on paper fiber.

During sheet formation and drying, aluminium resinate spreads over the fiber to give a relatively homogenous water resistance to the paper or board sheet. The control of sizing degree is achieved mainly by adjustments of the level of rosin added and the pH/ acidity of wet end system. The main problems related to rosin sizing are reduced strength and poor ageing properties. There is higher corrosion in the wet end system due to low pH. Very hard sizing is not possible by this system and at the same time it can be used only as an internal sizing agent.

Wax Emulsions

Wax sizes are aqueous emulsion of very small particle of paraffin waxes held in suspension of emulsifying agents. There are different types of waxes namely paraffin and microcrystalline wax emulsions which are both alum precipitation and acid stable. These wax emulsions are used in combination with conventional rosin size. Normal doze is about 0.5% on pulp and excessive addition causes spotting on sheet, accumulation on the presses, and a very slippery final sheet.

Advantages:

* Cheaper than other sizing agents.
* Effective at slightly higher pH (6-6.5) than rosin size.
* Improves folding and gloss of paper.
* Can be used in surface sizing.

Disadvantages:

* Cannot be used as sole sizing agent
* Limit of dozes
* Less stable and get denatured at very low temperature and slightly high temperature.
* Susceptible to evaporation.

Fortified Dispersed Rosin

The use of fortified rosin is becoming more and more common in Indian paper industry both in small and large ones. The fortification is normally done by reaction with maleic/ fumeric acids and subsequently dispersed. These types of rosins can be used in a wide pH range of 4.0 to 7.0. Owing to the large particle size than rosin soap, they have low degree of ionization and much smaller surface area. This results in less consumption of alum and better retention.

Advantages:

* Consumption of rosin and alum is lower
* Lesser corrosion if used at high pH

* Easy handling
* Reverse sizing is possible

Disadvantages:

* Sensitive to temperature
* More sensitive to hard water
* Contact with certain metals cause breaking and plating of rosin

Alkaline Sizing

Alkaline sizing is done at higher pH compared to rosin-alum sizing by using cellulose reactive agents like Alkyl Ketene Dimer (AKD) and Alkenyl Succinic Anhydride (ASA). A comparison of acid-alkaline sizing system is given in Table-1.

Table-1.

	Acid rosin sizing	Alkaline sizing (ASA/ AKD)
Effective wet end pH range	3.5 - 6.0	7.0 - 10.0
Compatible with alum	Yes	--
May be used as both wet end and surface size	No	Varies
Resistance to penetrants of varying pH	Not resistant to alkaline penetrants	Resistant over a range of acid and alkaline penetrants
Size storage life	Months, years	Hours, days, weeks.
Time to full sizing development	Seconds, minutes	Hours, days
Effect on paper coefficient of friction	No effect or increases COF	Decreases COF
Sizing response Vs. size concentration	Progressive increase in performance	Steep profile response from minimum critical concentration.
Typical size doses wt. % based on fiber	0.25 - 1.5	0.1 - 0.4
Dependance on drying environment for sizing performance	High	High
Robustness of entire sizing system	Robust	More sensitive

A substantial difference in performance between two systems may be found in comparing their capability to resist the penetrants. The strongly held co-valent bonds of alkaline system provide a fuller range of sizing protection, especially against the alkaline penetrants, e.g. aqueous coating colours, liquid packaging. As such the acid system could be considered more forgiving while the alkaline system shows a greater tendency towards an all or nothing behaviour.

Advantages of alkaline system over acid sizing:

* Sheet strength improves
* Calcium carbonate can be used
* Improved paper stability
* Reduction in energy consumption
* Higher ash content paper with retaining the strength
* Reduced corrosion
* Increased system closure
* More resistant paper to wide range of acids and alkalis
* Can be used in surface sizing.

Disadvantages:

* Wear out of wet end system will increase due to higher filler loading
* Very sensitive and critical
* Selection of suitable retention aid and dose are difficult to achieve
* Deposit formation is higher
* Standard biocides are ineffective at higher pH

ALUM AND POLY ALUMINIUM CHLORIDE (PAC)

Functions of alum in rosin sizing system is to precipitate the rosin and also as a retention aid. Papermakers alum is not true alum, i.e. double salts of aluminium sulphate but it is a single salt $Al_2(SO_4)_3 . 18H_2O$. Three types of alum are generally used in papermaking i.e. ferric alum, non-ferric alum and liquid alum. The amount of alum needed to set rosin size depends on a number of factors such as type and the amount of size, characteristics of stock, pH, water conditions and the other additives in the system. Insufficient alum can

cause poor sizing economics as a result of over-use of size. Use of non-ferric alum has distinct advantage of higher pulp brightness and lower iron content as required in some grades of papers.

In case of polychlorides of aluminium, hydroxylic groups give rise to polynuclear complexes by means of coordinating bonds with aluminium atoms. On hydrolysis, PAC gives rise to products of high molecular weight and a large number of positive electric charges able to interact with the cellulose fibres and size optimising the sizing phase and retention of fibres. The presence of preformed chains, part of them already hydrolysed, makes floc formations easier. The ability of PAC to operate over a wide pH range (3.00 to 9.00) makes it applicable both in classical pH range of sizing (4.5 to 6.0) and neutral sizing (pH 6 to 7).

In case of alum, once pH reaches 5.0, the alum size precipitate begins to lose its positive charge. This explains sizing at pH 5.5 to 6.0 is not possible with alum. However, PAC size precipitate exhibits a healthy cationic charge upto pH value of 7.5. The PAC precipitated size has a much greater positive charge and better sizing at neutral pH. Hence, to overcome the difficulties associated with alum in both classical and neutral sizing pH range, PAC can be used effectively and efficiently.

Advantages:

* Improved productivity
* Less colour reversion of paper
* Lesser pitch deposit
* Sulphate ion free environment
* Reduction in slime and foam formation
* Reduction in scaling even with hard water
* Utilization of alkaline fillers in neutral sizing

Disadvantages:

* Special storage and handling system
* Higher concentration chloride ions in the system (to be evaluated by mills individually for corrosion aspects).
* Lower shelf life

ADDITIVES FOR STRENGTH IMPROVEMENT

With the growing scarcity of long fibred raw materials such as bamboo etc., most of the mills have started using short fibrous raw materials such as hardwoods, bagasse and agricultural residue etc. This has adversely affected the runnability of the machine and the quality of the papers. In order to overcome these shortcomings, The use of strength improving additives such as gums, starches, synthetic resins, carboxymethyl cellulose (CMC) etc. has become necessary. Out of these, the use of starches has been getting preference over other chemicals due to versatality.

Starches

Many types of native starches are available such as corn, potato, rice, sago, sorghum, sweet potato, tapioca and wheat starch which are either used as such or after modifying physically, chemically, or in combination depending on the usage. Wholly unmodified starches are not generally well retained in papermaking because they are weakly anionic like cellulose. Therefore, ionic derivatives of starches are extensively used where strength, retention and drainage are of prime importance. Modified starches can be graded in the following manner:

Cationic starch: The cationization of starch imparts a high degree of dispersability of the products. The cationization of starch can be done by different methods and vary in many fundamental ways including parent starch variety, chemical nature of substituent, degree of substitution, molecular size, shape and distribution. Obviously this large number of variables precludes giving any optimum dosage.

Advantages:

* Strength improvement due to additional fibre to fibre bond
* Increased retention of fines and fillers
* Improved drainage
* Used as retention aid and emulsion stabilizer in alkaline sizing
* Reduction in BOD of the effluent because of higher retention

Disadvantages:

* Variation with optimal dosage causes reverse effect
* Drop in brightness of paper

Anionic starches: Anionic starches include starch phosphates, starches with carboxyl and sulphonic acid groups, starch xanthates and oxidised starches with both carboxyl and carbonyl groups. For wet end addition, starch phosphates is most important anionic starch. Their addition to the papermaking system requires a minimum of 1% alum in the beater stock in the pH range of 4.3 to 6.0. These straches are normally retained 100% on fibre. Anionic starches are to be added before refining to provide sufficient time for formation of desired complex with aluminium sulphate. These are comparatively cheaper than cationic starch but not effective for alkaline system.

Amphoteric starches: Because of widely varying conditions under which starches may require to perform, hetero-derivatives of starches that have more than one substituent have been made to meet these contingencies. These starches contains both cationic and anionic substituents, the ratio of which can be varied according to the need. These starches are effective in the pH range of 4 to 10 and effective to increase the filler retention and strength improvement.

Conventional chemicals like vegetable gums, synthetic resins, carboxyl methyl cellulose are also used for manufacture of different grades of papers. However, their uses are comparatively quite limited due to their unifunctional properties.

FILLERS

The principal fillers used in Indian industry is talc. However, other fillers like clay, titanium dioxide, aluminium trihydrate and calcium carbonate are also used to give the specific property of the paper.

Talc: Lot of efforts have been made to improve the quality of talcum in terms of particle size distribution and brightness. Due to these improvements, this filler with very high brightness is now available to substitute the costlier fillers like titanium dioxide, high brightness clay etc. in certain grades of papers without adversely affecting the paper properties.

Aluminium tri-hydrate (ATH): The introduction of ATH in Indian paper industry is of recent origin both as a filler and coating pigment. Since it is more or less synthetic product its quality can be maintained uniformly unlike naturally available fillers. The conventional fillers like titanium dioxide and clay are used for special grades of paper. However, efforts are in progress to improve the quality of clay, particularly the brightness to meet the present requirement.

RETENTION AND DRAINAGE AIDS

Retention aids are the chemicals which enhances the retention of fines, fillers and different chemicals which are added to the stock.

Inorganic aids: The addition of these chemicals reduces the repulsion between the surfaces by shrinking the double layer. The order of effectiveness increase with valence. Most commonly used chemical is alum. This has the disadvantage that it increases the acidity of the paper which can be detrimental to paper performance. Hence, it has limited uses for this purpose.

Organic polyelectrolytes: Polyelectrolytes are classified into four classes; nonionic, cationic, anionic and amphoteric. The main synthetic polyelectrolyte used is the polyacrylamide based polymer. - NH_2 group imparts water solubility and participates in hydrogen bonding. The effective retention increases with increasing molecular weight.

Anionic polyelectrolytes: These products are anionic in nature due to the dissociation of hydroxyl groups present in carboxylic group which is introduced in the polymer. The charge density depends on the number of functional groups and pH of the solution. In the paper stock, the anionic polymers are adsorber on cationic surfaces which are formed by the pretreatment with alum or low molecular weight cationic resins.

Cationic polyelectrolytes: Cationic charges are generated by introducing sulphonium, phosphomium, or ammonium groups to the polymer backbone. The ammonium ion is most commonly used for producing paper additives. Molecular weight of these often exceeds 1 million with a wide veriety of charge densities. The cationic polymers have the advantage of being readily adsorbed by the normally negative surfaces encountered in the wet end system.

It was shown that the primary factor causing adsorp-

tion is charge interaction and that the extent of adsorption in pulp fibres varies with pH.

Amphoteric polyelectrolytes: These are relatively new materials in the paper additives field. This polymer is made by copolymerizing anionic and cationic monomers to give a dual character to the polymer. Generally, these retention aids (polyelectrolytes) can be added to any system according to the requirement. The quantities are relatively small 0.02 to 0.09% but these are susceptible for high shear and therefore care should be taken to add these polymers at the point where shear is less.

OPTICAL WHITENERS

These are the chemicals which absorb the UV light and reflects visible light when these chemicals are added to the stock. The whiteness will improve along with slight improvement in brightness. Now-a-days different stilbene derivatives and other class of compounds have been developed which are stable in wide range of pH. In India, several mills are using these compounds for manufacture of high brightness papers and also to have better appeal. The use of these chemicals in liquid form is becoming more and more common.

MICROBICIDES

Most of the mills are putting their efforts to close the white water system to maximum possible extent for achieving improved overall efficiencies and to reduce the water consumption. But it leads to increased generation of microbiological slime deposits which ultimately adversely affect the runnability of the machine and quality of the paper. The conventional slimicides have been used to combat the problems of slimes and they are quite effective for the purpose. However, due to some of the limitations of the products including the environmental concern, it is becoming quite necessary to replace these chemicals by microbicides which are environmentally friendly.

A large number of such microbicides are available and require proper assessment for its regular use to check the slime problem. However, before finally selecting the chemical, ti is quite necessary to systematically evaluate the efficacy of the product to be used in terms of slime control, machine runnability and product quality.

OTHER CHEMICALS

Apart from above, dyes are also very important chemical and extensively used for different grades of coloured and tinted paper and paperboard. Efforts are in progress to identify the suitable days which can give better appeal to paper with cost effectiveness. Role of fine chemicals/ additives like defoamers, antifoamers, fluff reducers, descalants etc. has also become necessary to improve the overall performance of machine and at the same time to get better paper quality.

CONCLUSION

Various efforts are presently being made to identify, develop, and manufacture different types of chemicals and additives which are effective to be used at stock preparation to improve overall efficiency of process with improved paper quality. Due to this, it has also become necessary for individual mill to constantly review the overall efforts in this regard and independently assess and select the efficacy of various products available, suiting to their systems. It is concluded that selective use of these chemicals and additives would definitely improve overall productivity of the mill.

ACKNOWLEDGEMENT

The authors wish to thank the Management of The West Coast Paper Mills Ltd., Dandeli, for permitting them to publish this paper. Thanks are due to Shri GD Maheshwari, Vice President (Tech.) and Shri J.S. Sanwal, Dy. General Manager (Opn.) for their technical guidance.

REFERENCES:

1. Casey, J.P., Pulp and Paper Chemistry & Chemical Technology Volume III.
2. Sriram Subramanyam and Biermann, C.J., Tappi 75 (3): 223 (1992)
3. Kullick, R.J., Tappi 60 (10) : 74 (1977).
4. Crouse, B.W. & Wimer, D.G., Tappi 74 (7) : 152 (1991).

5. Wortley, B., Pulp and Paper (11) : 131 (1990).
6. Percival Asia Pacific Pulp & Paper (11) : 51 (1992)
7. Marton, J., Tappi 74 (8) : 187 (1991).
8. Scott, W.E., Tappi 69 (11) : 30 (1986).
9. Gill, R.I.S., Paper Technology 32 (8) : 34 (1991).
10. Lortz., R.H., Pulp and Paper Canada 88 (10) : 85 (1987).
11. Webb, L.J., Paper Technology & Ind., 28 (3) : 478 (1987).
12. Corry, P.A., Paper Technology 33 (9) : 33 (1992).
13. Roberts, J.C., Paper Technology 34 (3) : 27 (1993).
14. Unpublished work- R.C. Report, West Coast Paper Mills Ltd. Dandeli.
15. Gess, J.M., Tappi 60 (1) : 118 (1977).
16. Gess, J.M., Tappi 72 (7) : 77 (1989).
17. Cordier, D.R. & Bixler, H.J., Tappi 70 (11) : 99 (1987).
18. Goldstein, S.D., Appita Journal, 40 (3) : 213 (1987).