Use of Chemicals and Additives in Stock Preparation–A Review

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ABSTRACT

The objective of presenting 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 requirements of improved paper quality and higher productivity at the same time, These require a new approach for efficients 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 along with relevant 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 for selection of these chemicals keeping in view the prevailing conditions of a given mill.

Introduction :

The basic objectives in stock preparation are to 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. 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 thus modify its properties. They are fillers, pigments, sizing chemicals and chemicals used for strength improvement etc. The control additives are used to affect the performance of stock at wet end operation without becoming a part of the paper such as retention/drainage aids, pitch control agents defoamers and biocides etc. The main factors affecting the wet end chemistry are dissolved and suspended material their electrokinetic and consequent surface charge properties and their dozing and consequent retention etc Indian paper industry has shifted gradually towards short-fibred fibrous raw materials like hardwoods, bagasse, and agri-residues etc. But the equipments and process infrastructure remained more or less the same in most of the cases. Hence, in order to manufacture a good quality paper with higher productivity, efforts are required to improve the overall efficiencies in different areas of papermaking. One potential source is effective use of

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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 of water, other liquids and their vapors is important for any structural or printing grade of papers. The paper is sized with chemicals having a hydrophobic portion which r sists water penetration and a hydrophilic portion that adheres to the fiber substrate. Rosin-alum is the oldest and still the most common internal sizing system used by Indian paper industry. Efforts are in progress to replace slowly with either Alkyl Ketene Dimer (AKD) or Alkenyl Succinic Anhydride. The difference lies in the fact that the former work in the acidic media whereas the latter in neutral or alkaline media (ASA) sizing agents. Other products which are also used in for the same application 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 precipitates on the paper fiber.

During sheet formation and drying, aluminium resinate covers the fiber to give relatively homogenous water resistance to the surface of the paper or board sheet. The control of sizing degree is achieved mainly by adjustment of the level of rosin added and the pH/ acidity of wet end system. The main problems related with 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 it can be used only as internal sizing.

Wax Emulsions :

Wax sizes are aqueous emulsion of very small particles of paraffin waxes held in suspension of emulsifying agents. There are different types of waxes namely paraffin and microcrystalline emulsions of which are precipitated with alum and are acid stable. These wax emulsions are used in combination with conventional rosin size. Normally, 50% of rosin size is substituted by 25% of wax emulsion. Any excessive addition does not yield results but 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 endurance and gloss of paper.
- Can be used in surface sizing too.

Disadvantages :

- Cannot be used as a sole sizing agent. It has to be used alongwtih a conventional sizing chemical.
- Dozing limited.
- Less stable and get denatured at very low and high temperature.
- Susceptible to evaporation.

Fortified and/or Dispersed Rosin :

The use of fortified rosin has been practiced in advanced countries for decades. It is becoming more and more common in Indian paper industry, both in small and large mills. The fortification is normally done by reaction with maleic/fumeric acids and subsequently dispersed. It can be used at a pH range of 4.5 to 5.5. Owing to the large particle size than rosin soap, it has a low degree of ionization and much smaller surface area. This results in less consumption of alum and better retention.

Advantages :

- Consumption of size and alum is lower.
- Lesser Corrosion.
- Easy handling because of a ready made chemical
- Reverse sizing is possible.
- Consumption of Gum rosin is reduced by around 40%. It is of high importance in a country like ours, where gum rosin is in short supply.

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, neutral and above, when compared to rosin fortified sizes, sizing by using cellulose reactive agents like Alkyl Ketene Dimer (AKD) and Alkenyl Succinic Anhydride (ASA). A co nparison of acid–alkaline sizing system is given in Table 1.

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 and liquid packaging etc.

Advantages of alkaline system over acid sizing

— Sheet strength improves

— Permanency of paper improves, especially for litracy documents litrative.

— Calcium carbonate can be used for Improving printing characteristics.

— Improved paper stability.

— Reduction in energy consumption.

— Higher ash content paper with retaining the strength.

TABLE—1

	Acid rosin sizing	Alkaline sizing (ASA/AKD)
Effective wet end pH range	3.5–6.0 (usually 4.5–5.5)	7 0–10.0 (usually 7–8 5)
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

— Reduced corrosion

— Increased system closure.

— More resistant paper to wide range of acids and alkalies.

— 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 biocided are ineffective at higher pH.

Alum and Poly Aluminium Chloride (PAC) :

Functions of alum in rosin sizing system is to precipitate the rosin, fix the dyes and also work as a retention aid. Papermakers alum is not true alum, i.e a double salt of aluminium sulphate but it is a single salt $Al_2(SO_4)_3 . 18 H_2O$. 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 condition and 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 paper.

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 why sizing at a pH 5.5 to 6 0 is not possible with alum. However, PAC size precipitate exhibits a healthy cationic charge upto a 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

— Readuction 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 of 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 residues 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 and 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 need. 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 starches — The cationization of starch imparts a high degree of dispersability to the product. It can be done by different methods and varies sereval fundamental ways depending upon parent starch variety, chemical nature of substituent, degree of substitution, molecular size, shape and distribution etc. Obviously the large number of variables preclude giving any otimum dosage.

Advantages :

— Strength improvement due to additionai fibre to fibre bond

— Increased retention of fines and fillers.

— Improved drainage.

— Use as a 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 phosphate is a most popular 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 starches are normally retained 100% on fibre. Antonic 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 to increase the filler retention and strength improvement.

Conventional chemicals like vegetable gums, synthetic resins and carboxyl methyl cellulose etc are also used for manufacture of different grades of paper. However, their use is comparatively 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 etc. are also used to give the specific property to 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 and 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 a synthetic product, its quality can be maintained uniformly unlike fillers available in nature.

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 its brightness to meet the present requirement.

Retention and Drainage aids

Retention aids are the chemicals which enhance the retention of fines, fillers and different chemicals 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 increases with valence. Most commonly used chemical is alum. This has the disadvantage of increasing the acidity of the paper detrimental to paper performance, Hence, it has a limited use 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. Amine 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 adsorbed 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 one million with a wide variety of charge density. The cationic polymers have the advantage of being readily adsorbed by the normally negative surfaces encountered in the wet end system.

It has been shown that the primary factor causing adsorption is the charge interaction and that the extent of adsorption on pulp fibres varies with pH.

Amphoteric Polyelectrolytes :

These are relatively new chemicals in the Paper additives field and are made by copolymerizing anionic and cationic monomers to give a dual character to the polymer.

Generally, the polyelectrolyte group of retention aids can be added to any system according to the requirement. The quantities are relatively small 0.02 to 0.09% but these are susceptible to high shear and therefore care should be taken to add these polymers at the point where shear is less.

Optical Whiteners :

They absorb the UV light and reflect visible light, when added to the stock. The whiteness improves 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 paper with a 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 used to combat the problem of slimes are quite effective for the purpose. However, due to some of their limitations including the environmental concern, it is becoming quite necessary to replace them by microbicides which are environmentally friendly.

A large number of such microbicides are available Hence, a proper assessment is required for its regular use to check the slime problem. However, before finally selecting the chemical, it 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 important chemicals extensively used for different grades of coloured and tinted paper and paperboard. Efforts are in progress to identify cost effective but suitable dyes which can give better appeal to paper. Role of fine chemicals/additives like defoamers, antifoamers, fluff reducers and descalants etc. has also become important to improve the overall performance of machine with a better paper quality.

Conclusion :

Various efforts are presently being made to identify, develop, and manufacture different types of chemicals and additives to be used effectively at stock preparation to improve overall efficiency of process with improved paper quality. Hence, it has become necessary for individual mills to review constantly the efforts in this regard, independently assess and select the products with maximum efficacy, suiting to prevailing system. It is concluded that selective use of these chemicals and additives would definetely improve overall productivity of the mill.

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