# New Chemical Additives for Pulp and Paper Industry

#### PANDYA V. H \*

Indian pulp and paper industry is at present operating under following constraints:

- (a) Shortage of fiber raw materials.
- (b) Increasing prices or shortage of common input chemicals eg. Caustic, Chlorine, Alum, Rosin etc.
- (c) Shortage of water.
- (d) Shortage and increasing cost of power and fuel.
- (e) Higher interest rates and shortage of capital funds.

It is possible to apply new speciality chemicals, now available in India, to overcome these constraints and thus improve profitability and productivity. This paper describes the areas where the speciality chemicals can be introduced and the benefits that can be expected.

# 1. PULPING:

Following list covers some of the major practical results expected from speciality chemicals and approximate improvements possible:

(a)	Pulp yield	:	1% to 2%
	Daily production		
(c)	Reduced chips consumption		
	per MT pulp	ş: <b>:</b>	4%
(d)	Reduced Alkali	:	4%
(e)	Reduced screen rejects	;	1% to 30% in terms of yield.
(f)	Uniform K number and quality	•	•
(ġ)	Improved pulp quality res- ulting in increased runnabili		
( <b>h</b> )	of machine. Dispersion of depositable	:	Variable, positive
	material (fewer shives)	:	Variable, positive
(ı)	Reduced bleaching chemicals		

: Variable, positive

- (k) Reduced white liquor, increased black liquor & reduced load.
  - : Variable, positive
- (1) Reduced time of cooking, saving energy.
- : Variable, positive
- (m) Higher brightness
- : Upto 7 points
- (n) Improved deinking, dispersion of ink, resins, wax, asphalt etc. while pulping waste paper.

Variáble, positive

To achieve most or all of the above results, the pulping additive (in addition to traditional alkali and calcium, sodium magnesium sulfite or other chemicals) is expected to have penetrating and dispersing properties-synergising the effect of heat, pressure and other It should have chemicals generally used in pulping. low affinity for the hydrophile surface of cellulose but preferentially get absorbed at resinified or lignified It should react with this surfaces of fiber material. lignin which bind the fibers into the wood structure, disperse the clogged chemicals. It should facilitate wetting and/or dissolution of resinous deposits which are known to line the walls or completely plug capillaries through which cooking liquors must move in achieving a uniform distribution throughout chips in a minimum amount of time.

The result is faster, more efficient, softening of the lignin binding the fibers together and more rapid opening of the elogged capillary pores. Consequently, there is a more efficient use of heat and cooking chemicals, which can enable reduction in cooking times, cooking temperature or amount of active cooking chemicals needed to achieve the quality of cellulose pulp desired.

Reduced cooking time.

<sup>\*</sup>Life Member Ippta, Technical Partner, Chemofarbe Industries, BOMBAY.

The most beneficial results from pulping aid/ additives are normally obtained when the plan for applying it includec some change in one or more of process variables. Which variable is to be changed will depend on what results are desired, but it will usually involve the amount of active cooking chemicals, or the cooking temperature, or the cooking time. For example, if it is desired to increase yield, the first step might be to reduce the amount of active chemicals supplied to the digester per unit quantity of wood while keeping temperature and time of cooking constant. If it is desired to increase the production of pulp per unit time, then the first step for taking advantage of the effects of the additive probably be to decrease the cooking time without changing the cooking time without changing the cooking temperature or quantity of cooking chemicals. If the objective is to reduce cellulose degradation, then the cooking temperature might be the variable reduced.

To obtain the maximum benefits from pulping aid it is necessary to uniformly distribute the product to all the wood chips. In continuous chemical or semichemical digesters, the product should be added continuously to the fresh cooking liquor as it is being fed to the digester. With batch digesters it is also p eferable to add the additive to the cooking liquor as it is being charged to the digester in order to get it evenly distributed throughout the chip charge. This can be done with a metering pump set to operate at the appropriate feed rate during the time the liquor pump is charging cooking liquor to the digester or an eductor can be fitted into the liquor line to draw in this chemical at the desired rate during liquor discharging. Dumping the chemical into the top of the digester is not recommended, because, in this case, most of the product will be absorbed by the chips near the top of the digester.

Increased pulp yield is obtained from one or more of the following:

- (a) Reduction in degradation of hemicellulose.
- (b) Protection of cellulose.
- (c) Reduction of rejects.

Lastly the additive cost must be less than the economic benefits resulting from its use.

#### STRAW PULPING:

It is possible to reduce alkali by about 2% to 4% saving money per MT of screened pulp. Time of pulping can be reduced by 20 to 30 minutes maintaining excellent pulp quality and yield. It is also possible to replace caustic so a with hydrated lime, Yield increase of 2% in soda pulping and 4% in lime pulping is possible.

#### WASTE PAPER PULPING:

The use of secondary fiber is a topic of interest to nearly everyone these days. As more and more secondary fiber from various sources has been included in paper machine furnishes, an increasing number of operating problems have also been encountered. These problems are tremendously varied and extend all the way from the repulper to the rewinder. Many of the problems relate to the design or the capacity of the equipment being used. However, a number of these problems can often be alleviated by the judicious use of chemicals. In particular, the application of what might be called the solvent—dispersant class of chemical additives can make a major contribution to overcoming many of the difficulties encountered in the use of certain grades of recycled fiber.

In the use of secondary fibers there can be problems with the defibering of certain papers to otain an adequately dispersed furnish. In many cases there in only a need for ordinary commodity type chemicals for the repulping operation. Some of the more commonly used commodity type chemicals for assisting in the defibering of waste paper include caustic soda, soda ash, sodium hypochlorite, alum hypochlorite, calcium acids1 These chemicals, when used with sufficient heat and the proper equipment, can usually perform adequately in the defibering of most grades of waste paper. However, particularly in the case of waste paper containing significant amounts of wetstrength papers, there can be problems in getting the papers quickly and sufficiently repulped. Speciality chemicals and solventdispersant additives can be used in these specical cases for assistance in the defibering operation.

In the use of secondary fibers there can also be numerous problems caused by the many contaminants that are brought in with the waste paper. These contaminants have often been identified as the cause of unmerous deposit problems throughout the papermaking system with the result of decreased production and possibly poor quality control. These deposit problems are often related to inadequate removal or dispersion of the contaminants coming into the papermaking operation with the waste paper. The proper use of certain solvent—dispersant additives can also help alleviate some of these problems.

#### WET STRENGTH:

One of the major problems in the use of recycled fiber is the rewetting and swelling of the cellulose fibers and the breaking up and redispersion of the fiber aggregates. Probably the most difficult paper or paperboard to defiber is that containing various types of wetstrength resins. It is here that we first start to encounter problems in which the use of proper speciality chemicals can assist productivity. Table 1 lists the classes of wetstrength resins in order of increasing difficulty of repulping, with the assumption that all the papers have the same degree of wet-strength.

TABLE 1: The degree of repulpability of wetstrength papers and board in order of increasing difficulty.

- 1. Urea formaldehyde
  Many brands.
- Melamine formaldehyde Many brands.
- Polyamine
   Monsanto RPC series (also Santo-Res series)
   Hercules Kymene 367
- Polyamide
   Hercules Kymene 557, 557H, 790 Borden PR420
   Houghton Resonett NXR-10

These are based on all the papers having the same degree of wetstrength. Wet-strength paper has extraordinary resistance to rupture or disintegration when saturated with water.

Fiber containing urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins may by reclaimed at temperatures around in the presence of sufficient acid or alum to reduce the pH to around 3.5 to 4.5. These low pH conditions induce acid hydrolysis of the amidetype groups in these resins, leading to depolymerization of the resin molecules and fragmentation of the resin attached to the fibers.

Fiber containing polyamide or polyamine wetstrength resins may be most efficiently reclaimed at an elevated pH of around 10 to 11. While polyamide-type resins resist acid hydrolysis, they are somewhat susceptible to alkaline hydrolysis, the rate of hydrolysis being dependent upon, among other things, the concentration of the base used. It has been found that chlorine or oxidizing salts such as hypochlorite can facilitate degradation of the polyamide-type resins, but their use is naturally limited to bleached wet-strength grades.

The use of relatively small amounts of an effective solventdispersant additive in the repulper can often facilitate the defibering of wet-strength papers. The function of such additives is to aid in the rewetting and dispersing of the fibers and resin fragments. With the assistance of an additive composed of the proper combination of solvents, dispersants, and wetting agents, the acidic or alkaline repulping medium can more quickly and more easily penetrate into the fiber aggregates being held together by the wet-strength resins. Thus, the water and chemicals can more quickly hydrolyze and depolymerize the resins. Then, as the resins are degraded, the fibers are freed for the hydration and swelling necessary to break the fiber-to-fiber bonds.

#### DEPOSIT CONTROL:

Many mills, particularly cylinder paperboard mills, have of course, used recycled or secondary fibers from the earliest days of their operation. However, due to a number of reasons, there is now an ever inceasing use of waste paper in machine furnishes, even among mills that never previously felt any need to consider such secondary fibers. Furthermore, many papermakers are having to utilize lower quality sources of these secondary fibers, often finding these include many extremely troublesome contaminants, hot-melt adhesives, asphalts, latexes, waxes, inks, eoating binders, pigments etc. The repulping of waste paper containing these and other substances is often difficult, but of utmost importance in that inadequate dispersion or removal of tnese contaminants will certainly lead to a number of problems on paper machines. In order to attack the deposit problem at the source, the first step is to initiate treatment at the repulper with chemicals that will aid in the repulping operation.

To begin with, it should be emphasized that many of the contaminants we are concerned with are essentially insoluble in water and very hedrophobic. One thing that has been developed to meet this challenge is the class of proprietary speciality chemicals that we have labeled solvent-dispersant additives. In many cases, these solvent-dispersant products are labeled, for convenience, 'repulping aids', but in fact they are the foundation for a general program of deposit control for machines using secondary fibers in the machine furnish.

While many of the contaminants in question cannot be completely dissolved, they can be chemically softened or dissolved or dissolved to such an extent that they are separated more easily from the rehydrating fiber bundles The repulping aids help penetration into the fibre/contaminant aggregates and as a result the fibers are more quickly loosened, rehydrated and dispersed in the water. However the really important function that the solvent-dispersent type additive can often perform is to effectively disperse and maintain in a suitable suspension the contaminants that are broken away from the fiber. Furthermore, a well-designed repulping aid and deposit control agent should contain sbstances that can from an extremely thin and monstickly protective film on exposed machine surfaces. This further retards deposit formation because the ordinarily sticky contaminants do not adhere as readily to the surfaces, Besides preventing deposit formation, such a mechanism can also help prevent sticking of the sheet and picking.

Although a solvent-dispersant additive at the repulper can constitute a sound deposit control program, it may also be necessary to make supplemental treatments with the solvent-dispersant or other dispersants when the contamination load is high or with certain especially troublesome contaminants. These additional applications are usually dictated by where deposits are forming, and may include continuous additions of the additive to wire showers, showers on press rolls and felt showers. There may also be a need for supplemental treatment to the stock before refining or at the machine chests.

#### 2. ADDITIVES FOR PAPER MAKING-POLYELECTROLYTES:

Retention, drainage, formation and strength are inter-related factors in the manufacture of paper. Same

or similar additives can be applied to achieve desired results/benefits.

Following are major performace expectations and possible achievements

- (a) Improved retention of fibers : 8 to 10%.
- (b) Improved retention of fillers : 10%.
- (c) Imporved retention of dyes &
  - pigments : Variable, positive
- (d) Improved dry strength : 15%
- (e) Improved flat crush (Concora): Variable, positive
- (f) Improved internal strength

(Scott Bond) : 10%

- (g) Improved tensile strength
  - (bagasse) : Variable, positive
- (h) Imporved burst (mullen) for

Kraft , : 7%

(i) Improved plybond for mul-

tiply board : 10%

- (j) Improved curl resistance : Variable, positive
- (k) Decreased moisture : 1% to 2%
- (1) Basis Weight (Bagasse based) . 5% to 8%

#### **GENERAL:**

- RETENTION is important from the point of saving valuable pulp and high cost fillers e. g. Titanium Dioxide for better sheet properties and to meet pollution regulations. Chemical additives available are:
- (a) Inorganic chemicals, such as alum, calcium chloride and sodium silicates.
- (b) Natural organic polymers, such as gums and starches, proteins, rosin acids and salts thereof.
- (c) Modified natural organic polymers, such as cationic and anionic starches.
- (d) Synthetic organic polymers, such as the polyacrylamides, acrylamide copolymers, polyethylenimines and new types of polyquaternary ammonium compounds.
- (e) Combination inorganic and organic retention and drainage aids, which may also serve as deaerators.

#### Dominant mechanisms of actions are:

by (a) neutralising negative charges on fibers, fillers, pigment etc (b) forming polymer bridges – a portion of polymer attaching to one portion attaching to another particle.

(c) Coagulation and flocculation - coflocculation.

#### DRAINAGE:

There are several drainage driving forces and drainage resistance forces. Careful study of such forces and using suitable chemical and/or eqipment can supplement the driving forces or overcome the resistance forces. Idea is to remove as much of water as possible by drainage to reduce load on press section and drying, Chemical deaerators are used for this purpose.

#### FORMATION:

There is complete inter-relationship between drainage and formation. The size and surface charcter-stics of fibers, kind and amount of filler and pigmants, pH ionic environment and amount of air in stock all have a bearing on formation as well as drainage. Mechanical devices—their nature and performance also have an influence on formation. However, use of chemical approach gives more benefits without necessity of significant capital investment.

#### STRENGTH:

Traditional or universal additives are gums andstarches (Even cationic starches). There already are several synthetic wetend adhesives or bonding agents to enhance both wet and dry stengths.

Use of cationic polyelectrolyte, after careful examination and scientific understanding of the system, can achieve most of the above expectations by synergising the effects of starch, gum and alum. In some cases, it is possible to considerably reduce quantity of these additives while maintaining qualitative and quantitative results obtained by very small dosage of polyelectrolyte. Many trials on cationic polymer electrolytes appear to fail and considering high cost per kg., customers loose faith in such additives. It is therefore, useful to list how to derive maximum effectiveness from use of such polyelectrolytes. Some important factors that influence effectiveness of polyelectrolytes (polymers) are given below:

(a) The adsorption of cationic (positively charged) polymers by anionic (negatively charged) paper-making solidsis extremely rapid.

Laboratory tests have shown that adsorption can be virtually complete at contact times of 0.1 second

or less. This emphasizes the importance of feeding procedures that ensure uniform distribution of the polymer, rather than letting it all be absorbed by a small part of the fibers and fillers. This is one reason for pre-dilution of the polymer to the maximum feasible amount and careful selection of a point of addition that will provide good mixing with all of the stock.

(b) Alum, cationic starch, and other cationic additive compete with the polymer for the negatively charged adsorption sites on the surfaces of papermaking solids.

Thus the presence of these materials in the furnish, especially in high concentrations can reduce the effectiveness of the polymer. This also means that the polymer should generally be more effective in systems in which little or none of these additives are used. It is possible to minimize the effects of alum for example, by adding the polymer at a point ahead of most of the alum addition. In any case, if alum use is required (e.g. to set rosin size) its concentration should be kept to minimum necessary. Since polymer is a highly effective dry strength additive, it can usually replace cationic starch as an internal additive.

(c) High concentrations of hemicelluloses (from the pulp). starch (e. g. from coated broke) and other materials that function as protective colloids can interfere with the action of cationic polymers as retention/drainage aids and as flocculants

This generally means that in such systems more of the cationic polymer will be required to achieve the desired retention, drainage, or flocculation effects.

(d) The action of Polymer as a dry-strength additive, retention/drainage aid, or flocculant does not require complete neutralization of the charge on the surfaces of the papermaking solids.

This is generally true of most synthetic polymers used in such applications, and it means that measurement and control of the so-called 'zeta potential' is not a valid means of optimizing the effects of such polymers, at least in most commercial papermaking systems. In fact, research test-

ing shows that the optimum effects can occur in various systems anywhere from a strongly negative to a strongly positive zeta potential. Zeta potential becomes even less of a factor in papermaking systems where the electric conductance of the white water is high, an increasingly common case as mills 'close up the system' to conserve water and reduce effluent volume.

(e) Drainage aids can help improve water removal at the fourdriner or cylinder mold and/or in the press section but the polymer providing the driest sheet off the couch may not always give the best results in the press section.

Improving water removal on the fourdrinier, for example, can enable operation at a lower headbox consistency and consequently improve sheet formation. On the other hand, if the sheet is drier coming out of the presses, than stem consumption (and thus energy costs) per ton of paper will be reduced. Therefore, the effectiveness of a polymer las a drainage aid should be judged on the basis of what the specific goals are.

# 3. SCALE INHIBITORS: EVAPORATORS:

These are subject to heavy scaling due to deposition of inorganic and organic compounds while 'Thin' liquor is concentrated to high solids content. Such deposits reduce energy efficiency of the evaporators. Speciality chemicals – such as scale inhibitors provide following benefits:

- (a) Substantial energysaving as no scale formation occurs.
- (b) Possibility to run at higher TS contents in the liquor to better burning in the boiler to less fuel oil consumption.
- (c) Less costs for cleaning whether it is NTA, nitric acid or mechanical cleaning.
- (d) Evaporators with forced circulation: less energy costs for pumps.
- (e) Longer running intervals and with higher capacity/efficiency.

New chemicals available are phosphonates, polyacrylic acid, polyacrylates, poacrylamides and polymetha-

crylates. They can used alone or in combination formulations where they provide complementary or synergistic effects in scale and deposit control.

Results possible are:

- a) Longer periods between cleaning-say 2 to 3 months instead of every month because of cleaner evaporator surfaces.
- (b) Reduced down time while cleaning because of soft and easily removable scale during boil-out.
- (c) Reduced consumption of boil-out chemicals.
- (d) Possibility of considerable increase in dry solids content in black liquor (10-15%) with lesser consumption of energy of evaporation.

#### 4. BLACK LIQUOR BURNING:

Following practical problems require chemical additive to improve burning of black liquor. Expected results are given below:

- (a) Easier pumping of black liquor, including elimination of fuel cavitation, Even low pressure pumps can be used to feed large volumes of Black Liquor, Viscosity reduction upto 25%.
- (b) Reduction in plugging of screens and nozzles.
- (c) Less variation in mixing tank levels.
- (d) More uniform droplet size improving combustion efficiency.
- (e) More rapid liquor drying and combustion of organics. Increase in solids content upto 67% BLS.
- (f) More uniform wall deposition in B & W units.
- (g) Less accumulation of slag or ash on superheater tubes and bank tubes, improving thermal efficiency.
- (h) Reduced carryover of particulate matter in flue gases provides pollution control.
- (i) Increased liquor throughput per unit time.
- (j) Longer operating cycles between washups from 2-3 months cycles to upto 6 months or more.
- (k) Reduced downtime for cleaning and costs thereof, improving plant availability and productivity.
- (1) Less hand lancing during operation.
- (m) Less mechanical cleaning during shutdowns and cost savings thereof.

The additive acts by changing rheological properties of highly concentrated black liquors. It is a 'fluidizer' reducing surface tension. Decrease in viscosity results in thinner film, better heat transfer and improved spray (reduced droplet diameter), It also reduces the burning temperature of solids.

The new chemical solves several difficult problems associated with bagasse black liquor such as high viscosity, slow combustion, high deposits in the boiler (requiring upto 2 days to remove) and inhibition in flow of flue gases.

Use of Magnesium Oxide as black liquor burning aid is widely practiced. However, it is a solid that could potentially be carried over and add to deposits on tubes. Feed/dosage of powder is also difficult to control. The new additives are liquids—easily dosed and dispersed in black liquor mixing tank.

# 5. MICROBICIDES/SLIMICIDES:

Performance expectations:

- (a) They should have broad spectrum activity. In pulp and paper mills, variety of microorganisms can be present. The microbicide is selected that is consist dered particularly effective against the dominant microorganisms or microorganisms which happen to exist at a specific time and at a specific time and at a particular place or places in the system.
- (b) All mirobicides should be compatible with each other as well as with furnish components and other additives used on the particular machine or grade.
- (c) They should be complementary in their action to the effects of other deposit control agents employed in the system.
- (d) They should be effective under pH and temperature range generally employed in the manufacture of pulp and paper.

The organisms involved in pulp and paper mils slime are primarily different specis of spore - forming bacterial (particulary capsulated forms, which secrete a gelatinous material that surrounds the cells as stiky capsule or sheath) filamentous fiungi of the mold type type and yeastlike organisms. If narrow spectrum biocides are used, some of the specsfic organism population will be reduced but population of other more predominant types may flare-up, caused by more

resistant organisms. Broad spectrum chemicals maintain the 'biological equillibrium' —reducing population of all types in a more or less same proportion at the same time preserving natural competition. There is less chance that one type will grow out of control because sts cometition has been eliminated. It is porsinle to quantitatively monitor rate of microbiological slime and deposit accretion by installing 'slime measuring units and using 'slime indicator'. Microbicldes are most most effective in slime control when their use is coordinated with total deposit control by keeping the system clean.

### 6. ANTI-FOAM & FOAM INHIBITOR

Antifoams destory foam which is already formed whereas judicious application of feam inhibitors prevents foam formation at source. Foam cen be a serious problem in pulp mills, paper mills and in effluent treatment systems. If foam is not controlled, production and quality are affected.

#### (a) PAPER MACHINES:

Addition of defomers in headbox or vats on cylinder machines can control foam. They are also required in coating or size press formulations. The new chemicals are emulsifiable formulations which are water based.

### (b) PULP WASHING:

Foam problems exist in this area due to the vaccum removal of liquors containing high levels of organic matter. In kraft pulping much of organics have been saponified to soluable soaps. It is not surprising that a high foam potential exists. Anti foam chemicals can control foam in such situations.

#### (c) EFFLUENT:

When waste treatment system undergoes an 'upset' or if the plant is operated at maximum capacity, foam in the effluent discharge unit frequently occurs. There is an increasing need for effective defoamers for this application. The foam must be 'knocked down' in the effluent as it is discharged to river or lake.

# 7. FELT WASHING COMPOUND:

Wet felts used on paper and paper board machines accumulate deposits coming from pulp raw materials such as waste paper, corrugated card board cuttings,

jute bag cuttings, straw etc. Simple soap or detergent solutions, caustic soda or Kerosene will not remove such deposits. It is therefore necessary to employ periodically or continuously specially formulated emulsifiable felt cleaning compound. It is combination penetrant, dispersant, and solvent, and its use in a continuous wet felt conditioning program reduces the accumulation of deposits in felts and helps to maintain their porosity and water obsorbency. Thus, the product provides increased operating efficiency in the form of improved water removal, a more uniform sheet moisture profile, and increased telt life.

## 8. NEW CHEMICALS AND ENVIRONMENT:

It is very important that the chemicals used in pulp and paper plants must be biodegradable and are cleared by approved environmental laboratories from the toxicity angle. Considering very low dosages and further dilutions/consumptions in process, is safe to presume that the chemicals will have no toxicity, However, considering awareness in our country, care must be taken to ensure that environment is not polluted by these new chemicals.