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Application Of Cationic Starch In Wet End Operation For Sustainability Of Small Paper Mills In India

ABSRACT

The economic growth of any industry depends on its technological competence, sustainability quality as per customer satisfaction at competitive cost. The Indian paper industry accounts for about 2% of world's production, and is presently producing around 12 million tons per annum paper and board, considering growth and demand in recent years at an average of 8% per annum Indian paper industry should plan for at least 25 million tones of production by 2025 for which the Indian paper industry should prepare itself to overcome various constraint in its growth. Industries taking due timely care can only survive and grow in this severe competitive age. With this view, application of cationic starch and dry strength resin at wet end for filler retention had been analyzed at lab scale and also plant trial was taken at a small scale recycled paper mill. The results were compared in terms of cost reduction on final paper production without compromising the quality and production rate.

INTRODUCTION

Over 20 years ago, it was thought that the paperless office (or close to it) would be a reality by 2011. Ironically, since then print volume has actually increased (**1**) as people now print emails, web pages, etc. Additionally, paper used for packaging, tissue products and newsprint demonstrate how prevalent paper usage is in daily activity. Due to unavailability of wood, agro based raw material pulp and paper making industries all over the world have moved into recycling. Recycling is process starting the collection of material, sorting and storing finally supplied to pulp mill. The collection method has been done by outside party or directly mill itself. The fig: 1 shows the sorting and storing of recycled fiber, Fig: 2 show the waste from the sorting process.

LITERATURE SURVEY

Copious research results were published regarding the application of Polyelectrolytes, cationic starch,

Fig No: 1 sorting process

Fig No: 2 sorting process waste

dry-strength resin, for various pulps. Few researchers were published the application of dry strength resin to get 10 -20 % strength improvement. Increasing ash content in paper has forced to in-depth research in this area. But till date it was not dried for recycled paper industry for improving filler retention studies with the help of cationic starch and dry strength resin only without adding any fixative and filler.

SCOPE OF THE PRESENT STUDY

The present study was carried out to show the proper selection of wet end additives based on chemistry gives tremendous cost reduction benefit and it makes a very strong platform to sustain in the market forum.

WET END CHEMISTRY

The weak nature of recycled paper needs the better understanding of addition of wet end chemicals to the system. Due to presence of ink, the writing and printing paper shows high cationic demand on fiber surface after deinking or slushing. Cationic demand can be divided to two categories: cationic demand in the water phase and cationic demand of solid material. Cationic demand in the water phase has a negative side, because it reduces the adsorption and functionality of cationic polymers. Instead of that, cationic demand in the water phase has also very advantageous side since it enables adding a high amount of cationic compounds such as starch and wet-strength resins. All paper makers tested only the cationic demand of filtered water of head box pulp suspension which is meaningless. Normally in all writing and printing recycled paper industry preferred acid sizing because of alum's multitalented reactivity. Now all the recycled paper industry moves to manufacture the high bright paper with AKD/ASA sizing which has high market demand .It is very important for AKD /ASA sizing to maintain > 50 % FPAR to optimize the sizing cost.

Almost all writing paper has min 10 % filler content while printing paper has 15-20% filler content .Generally it was thought that increasing a first pass ash retention will affect the machine runnability. So many recycled paper industries do not want to adopt a proper retention aid system. Without retention aid programme running the recycled paper industry leads to increased high cost of production and increased load (TDS, TSS) to effluent system where zero liquid discharge plays an important role.

RETENTION CHEMISTRY

The basic types of interactions (**2, 3**) between wet end colloidal particles along with the fiber, fillers which can cause flocculation in the furnishes are,

1. Electrostatic (or coulombic)
2. Hydrogen bonding
3. Hydrophobic
4. Covalent bonding
5. Van der Waals' forces.

The various existing chemical systems for retention and dewatering are mainly intended to act through electrostatic interactions or hydrogen bonding. Other types of interactions that might occur are hydrophobic and stearic interactions. High FPR is important to achieve a high degree of efficiency of the functional chemicals added in the wet end. In addition, unretained additives can cause deposits and provide nutrition for bacteria. The adsorption of additives such as starch, size, and wet-strength resin on different components in the wet end is predominantly related to the available surface area of the components. Since fines and fillers have high surface areas as opposed to fibers, a high percentage of the chemicals added will adsorb on them. High first-pass retention is favorable as long as it does not give too extensive flocculation, which would jeopardize the formation.

A high level of FPR ensures that more fines and fillers attach themselves to the long fiber fraction, thus reducing their mass transfer toward the wires and the tendency toward two-sidedness.

FLOCCULATION CHEMISTRY

Particles of the same electrostatic charge repel each other but, once this charge is neutralized, the attractive forces dominate and the furnish components flocculate. By increasing the addition of the flocculants, beyond the point of charge neutralization, the components are redispersed. Retention aids following this mechanism are generally low molecular weight highly cationic compounds, which do not extend beyond the electrical double layer but decrease the net charge to zero (**4**).

Examples of these (**5**) are

- Polyvalent cations (e.g., polyaluminum species)
- Polyethyleneimine
- Poly-DADMAC
- Polyamines
- Polyamideamine epichlorohydrine.

A factor to consider in the choice of polyelectrolytes of these types is the earlier mentioned penetration of the polymer into the pores of the fibers.

CHARGE CHEMISTRY

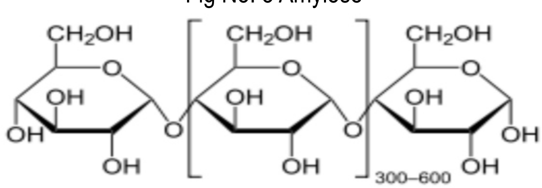
A thorough knowledge of the cationic demand is important to be able to understand and to control wet end chemistry. Except GCC, all filler and fibers have negative charge as: TiO_2 (Anatase) > china clay > TiO_2 (Rutile) > PCC>Talc >Barytes. Indigenous pulps had 2-3 times more negative charges than imported pulps. Bagasse pulp has highest negative charges followed by rice straw, wheat straw, bamboo, Jute. Increase in negative charge on fiber directly affects the filler retention. It is equally important to distinguish between the cationic demand in the water phase and the cationic demand derived from the solid material (fibers and fillers). A high cationic demand on solid material is often advantageous since it provides an opportunity to add a high amount of cationic functional compounds, such as starch and wet-strength resins. However, the cationic demand that originates from the water phase constitutes a negative factor, since it reduces the adsorption and effectiveness of cationic polymers.

ATCs reduce the cationic demand of disturbing substances, thus reducing their negative interaction with polymers. Practical experience confirms this hypothesis in that **organic ATCs** should primarily be selected when the objective is to reduce the cationic demand on the fiber surface (blocking polymer), while **inorganic ATC (PAC or alum)** should be used when the main objective is to reduce the cationic demand of the disturbing substances present in the white water . It should also be noted that an organic ATC has a strong negative effect on OBA efficiency (quenching), while a PAC is highly compatible.

CATIONIC STARCH CHEMISTRY

Starch or amylum is a carbohydrate consisting of a large number of glucose units joined by glycosidic bond , combination of two structure, amylase linear polymer, amylopection branched polymer as given fig 3, 4.

Fig No: 3 Amylose



FigNo: 4 Amylopection

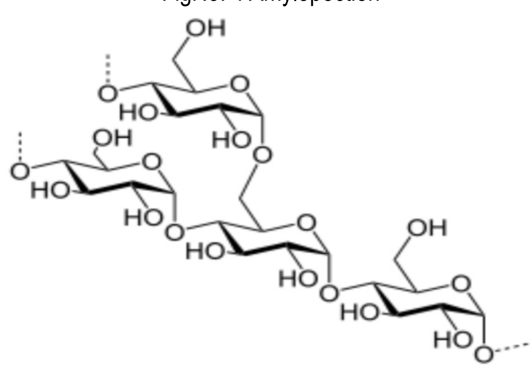


Fig No: 5 Cationic starch structure

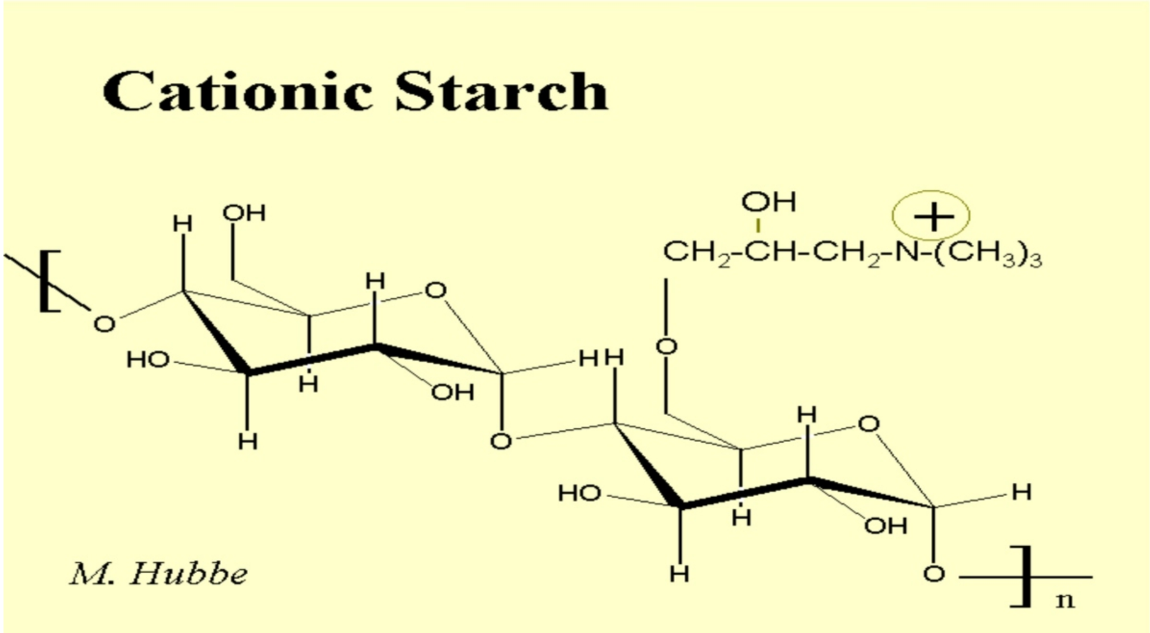


Fig: 5 gives the chemical structure of cationic starch .

PREPARATION AND PROPERTIES OF CATIONIC STARCH

Quaternary ammonium cationic starch prepared by treatment with 2,3 -epoxypropyltrimethylammonium chloride or the more stable chlorohydrin form is the major commercial cationic starch type. Quaternary ammonium cationizing reagents where one of the methyl groups is replaced with a hydrophobic group (e.g. dodecyl, cocoalkyl or octadecyldecyl) have been examined.

Tertiary amino starches made by etherification with diethylaminoethylchloride are also available. Protonation of the tertiary amine under acidic p^H conditions produces the cationic charge, which diminishes as p^H increases. The nature of the alkyl groups influences the pKa of the tertiary amino group.

Use of potassium rather than sodium hydroxide to catalyze reactions with the epoxide is claimed to provide higher nitrogen contents. Many mills in India are concentrating the percentage nitrogen content rather than degree of substitution which define the cationization effect(**6**) of starch.. Degree of substitution of starch only the specific parameter to be considered for the estimination of effectiveness of starch in the wet end. All other parameters are indicative only.

MATERIALS AND METHODS

Recycled paper sample were collected from mill and slushed. The following methods were used for lab testing. TAPPI , T 240 om -93: Consistency measurement, **TAPPI**, T 400 sp 95: Sampling and accepting a single lot of paper, paperboard Container board, or related product, **TAPPI, T 205 SP-95: Forming hand sheet for physical testing of pulp,** TAPPI, T 410 om-93: Mass per unit area (grammage), TAPPI, T 414 om-88: Internal tearing resistance of paper -Elmendorf-type method, TAPPI, T 494 om-88: Tensile strength, TAPPI, T 403 om-92: Bursting strength, IS:187, Standard atmospheres. Ash content TAPPI T 413, T 211 om-02.

PRACTICAL CONSIDERATIONS IN THIS TRIAL

In this trial freeness and zero span analysis were not taken into account. Direct observation of machine runnability , couch break , press break ,water on wire table, % ash content of paper were accounted for practical consideration . Freeness test meant for originally ground wood pulp, zero span tests estimates the single fiber strength .Ironically recycled fiber paper making process starts from weak fiber to strong paper.

Table No: 1 Running Hours and production before trial

Date	Running Hours Before the trial Hr: min	Days finished production Before the trial T
01.08.14	23.00	39.0
02.08.14	23.10	43.7
03.08.14	23.05	43.8
04.08.14	23.05	42.1
05.08.14	23.10	43.2

Table No: 2 Running Hours and production during trial

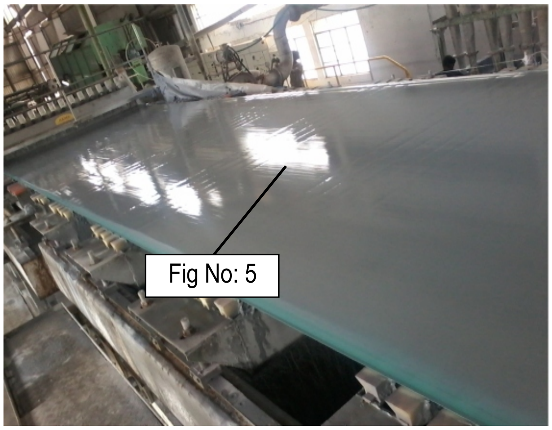
Date	Running Hours during the trial Hr: min	Days finished production during the trial T
09.08.14	23.30	40.0
10.08.14	23.40	45.0
11.08.14	23.45	45.0
12.08.14	23.35	44.8
13.08.14	23.40	45.0

PLANT TRIAL

Plant trial was conducted in a recycled paper mill for 5 days after finalizing the cationic starch, dry strength resin from the laboratory result to get 3-4 % ash increase in final paper. From the laboratory trial it was found that the optimum dosage of cationic starch (with the DS of 0.03-0.032) was 2 kg/ton and dry strength resin 1 kg/ton . With this consumption pattern plant trial was conducted and the machine running hours, productions were tabulated before and during the trial in Table: 1, 2.

Strength properties and paper breaks without / with cationic starch and dry strength resin were tabulated in Table: 3, 4.

Fig No: 6 Water on wire before trial



Water line get back during the trial

Table No: 3 Strength properties and paper breaks before trial

Date	Quality	Gsm	Avg Speed mpm	Avg Breaking length, m MD/CD	Avg Tear factor MD/Cd	Avg Burst Factor	Avg % Ash	Couch Break	Press Break
01.08.14	Cream Wove	52	335	4300 / 2400	43 / 30	18	10.0	10	14
02.08.14	Cream Wove	54	331	4200 / 2200	42 / 30	19	9.8	14	16
03.08.14	Cream Wove	54	338	4300 / 2200	42 / 32	17	11.5	13	14
04.08.14	Cream Wove	54	339	4100 / 2400	45 / 30	18	11.2	16	16
05.08.14	Cream Wove	52	340	4200 / 2400	40 / 32	18	10.9	12	15
Average			337	4220 / 2300	42 / 31	18	10.7	13	15

Fig No: 6 a,Water on wire before trial

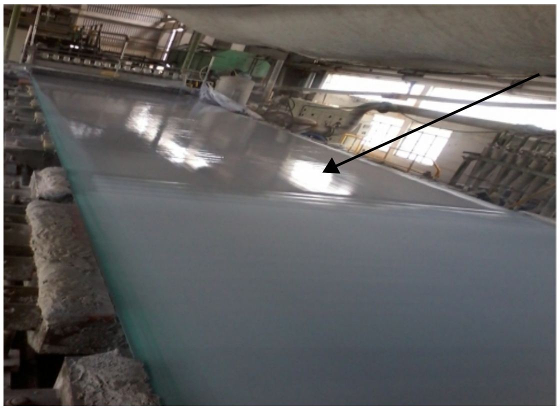


Fig No: 6 b,Water on wire before trial

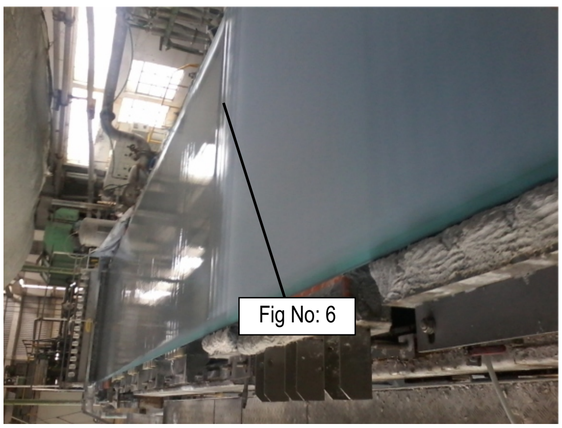


Fig No: 7 Steady couch draw during the trial

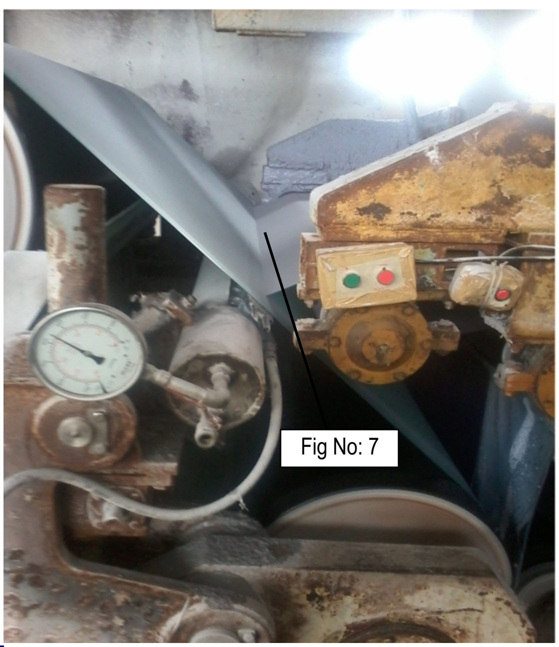
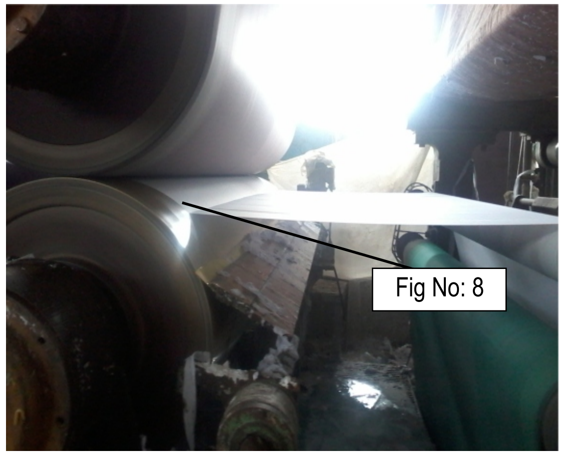


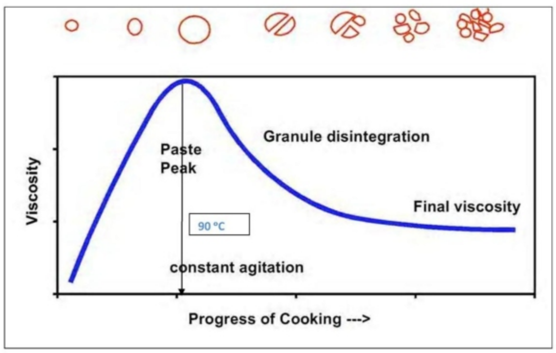
Fig No: 8 Steady state 2nd press draw to dryer during the trial-



RESULTS AND DISCUSSION

From the above trial it was found that the efficient use of cationic starch in wet end operation without any ATC machine runnability was good and increased ash percentage in paper was achieved. Breaks at couch and press were reduced. Trial was succeeded by giving concentration for preparation of starch. In many mills starch cooked at 50 – 70 % of its volume at 70 - 80 °C for 10- 15 min. Once cooking was over immediately cold water was mixed and transferred to storage tank. In this trial carefully starch cooked at 90 °C at 20 min with the level of 90 % and mixed with the water as followed by a mill. Retrogradation of starch and starch lumps is not due to cationic character of starch and nitrogen content, it is mainly due to improper starch cooking and inadequate temperature maintaining .The following graph gives the importance of cooking temperature and swelling relationship

Fig No: 9 Cooking of starch



The presence of anionic trashes in the system increase the chemical consumption and decrease the paper strength .The effective fixative selection plays a vital role in paper making. Highly cationic starch and dry strength resin without using ATC had a great impact on ash retention and machine runnability due to versatile nature of cationic starch.

REACTION MECHANISM OF CATIONIC STARCH AND DRY STRENGTH RESING

The cationic starch improves the bonding strength by increasing the relative bonded area of fibers or strength per unit of bonded area between fibers, fines and filler in a sheet of paper. In order to achieve this improved relative bonded area, the starch performance has to be maximized by retaining it on to the paper, restricting it to stay on fiber, fines and filler surface by improved cationicity and adding at proper addition point.

The usage of Cationic starch of high degree of substitution is recommended owing to high level of anionic trash and conductivity of the back water system due to high filler loading. Dry strength resin enhances the bonded area between the fines and fillers that makes paper very strength after drying. Fig No: 10, 11 clearly explain the reaction mechanism of cationic starch while Fig No: 12 deal with the reaction mechanism of dry strength resin.

Fig No: 10 Fiber and Filler particles in water

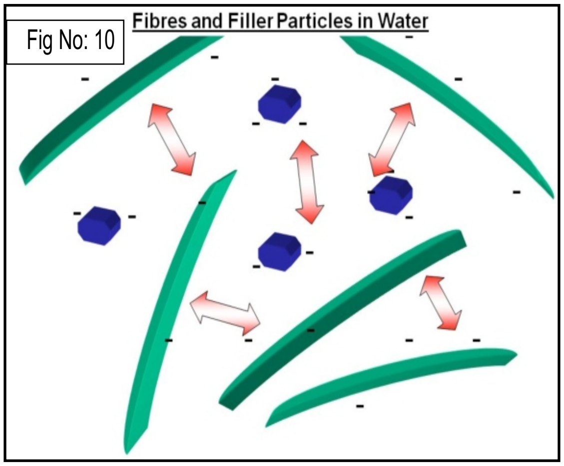
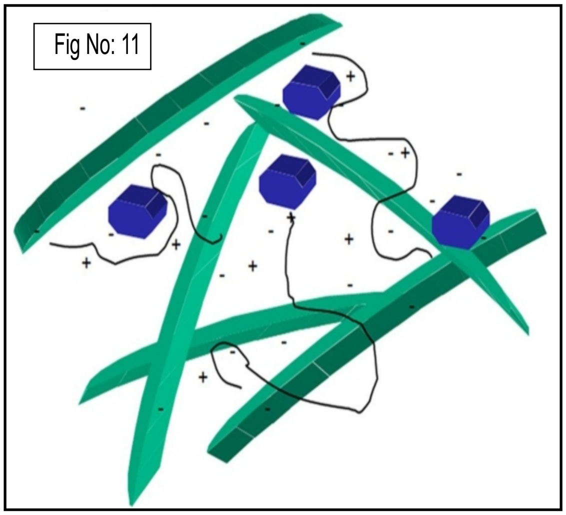


Fig No: 11 Flocks formed with cationic starch



Before the trial the running hours were found maximum 23hours 10 min and the production was maximum at 43.8 t/ day. During the trial both the running hours and average production has increased from 42.4 t/day to 43.8 .It equals to 1.4t/day with the increase of breaking length at about 500/500 MD/CD in meters, tear factor 5/7 MD/CD, 2 units of burst factor and 3.2% of paper ash. It has found while increasing the ash in the paper, there is no dusting in paper and also verified with in winder area. It has implanted at plant scale for long run to justify the results.

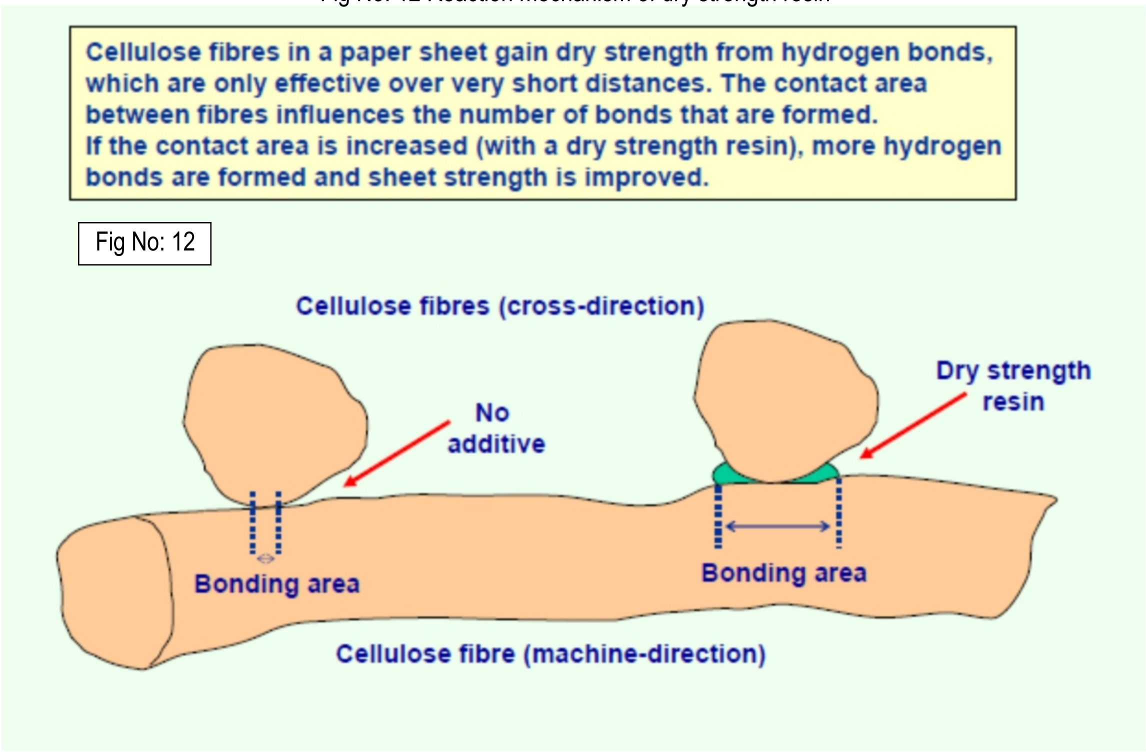
FEEDBACK FROM MANUFACTURE SIDE ABOUT THE TRIAL

The following feedback received from this trial

a) Tangible benefits

I. Improved FPR and FPAR lower fiber filler loss
II. Improved ash content by 3-3.2% without impairing strength
III. Improved machine runnability and lower downtime.

Fig No: 12 Reaction mechanism of dry strength resin



IV. Improved surface strength wax pick and lower dusting

V. Reduction in AKD consumption 9 kg/ ton from 12 kg/ ton For maintain same 22-24 g/m^2 cobb value

VI. Reduction in OBA

VII. Cleaner wet end system

VIII. Reduction in COD carry over by white water

IX. Elimination of dust control chemical

X. Increased ash content leads to cost saving of = 630/ ton

b) Other Intangible benefits

I. Stabilized wet end charge

II. Lower press breaks

III. No dusting increase even at increased ash

IV. Reduced fiber loss to ETP

Further application of this trial

This combination cationic starch and dry strength resin can be implemented at the following areas

1. High speed machine where the white water closed loop has been practiced.
2. Deinked pulp, Baggase pulp is used as furnish for making

CONCLUSION

By applying a selective / proper cationic starch and dry strength resin ash can be improved in final paper up to 3% leads to cost benefit 630.00 for recycled writing printing paper manufacturing paper industry . This is applicable for Integreated pulp and paper industries . With out application of wet end chemistry, paper can be made but the sustainability will be a question at present . Better understanding of wet end chemistry and implementation in plant scale save the recycled , Integrated pulp and paper industry againt market trend at present and future.

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