ISSN: 0379-5462
IPPTA: Quarterly Journal of Indian Pulp and Paper Technical Association
Vol. 35, E3, 2023, p. 80-84

IMPROVING THE RECYCLED PULP YIELD BY RETAINING INHERENT STARCH OF WASTE PAPER

M. G. Panth
Technical Advisor (Freelancer),
Hyderabad – 500090, Telangana

Abstract:

Kraft Paper mostly liner kraft and fluting media producers use recycle waste of a various grades like NDLKC, DLK etc for raw material. Many of these Liner kraft grades are using now a days size press to reduce sizing costs, which is very much lower than internal sizing for cobb value. However most of they use starch in size press for various reasons. As we know utmost recycling is possible only seven times considering yield losses. On continuous recycle, fibre become short and less strength to further recycle. We are constrained to use any waste paper irrespective of its inherent strength due to fibre shortage. To boost the strength some additives are used in wet end to cross link fibre bonding and starch is sprayed over surface to cement loose fibres and improve burst factor for packaging needs. For the market demand and to push the product at better price huge amount of starch is used per ton of paper at size press ranging from 3-5% on paper. Additional carbohydrate comes as dextrin in corrugation gum form. Altogether it amounts nearly 5% of paper.

So whatever waste paper comes to kraft paper recycle mills, it invariably contain 5% starch with it, which is lost into circulation water posing various problems like Slime growth, BOD levels if discharged, VFAs and bad smell to paper due to anaerobic bacteria. Passivating this starch with paper is adding weight and value to the tune of Rs. 1000/ton. Waste becomes Wealth. Details are discussed in this paper. No odour, No Slime, less BOD.

Keywords: Pseudomonas bacteria, Endo-amylases, VFA.

Introduction

Due to scarcity of fibrous raw materials and restrictions over use of forest based raw materials except for selected mills, most of the paper mills in India rely on indigenous waste packaging paper/kraft paper as input for recycling and liner kraft and other paper grades. Imported waste paper like NDLKC and rich quality fibre are expensive to use even though they give good strength. Under these conditions, paper mill people hands are tied with limited resources for optimum use.

For the current scenario of paper making and market status, liner kraft and board varieties are less expensive for raw materials process simplicity. Cost cutting is the best way to stand in market competition and most of the paper makers of this kind of paper resort to repeated re-cycling of waste paper and as less as possible, chemical inputs to save a few bucks.

To upkeep the paper strength even with weak fibre, mill people switched over from conventional internal sizing of rosin based chemicals to less sizing cost surface sizing chemicals in size press application. Along with surface sizing/hydrophobic chemical formulation(s) application in size press, using starch is an indispensable and high quantity input. Most of the paper mills making liner kraft paper use as minimum as 40kg starch per ton of paper to as high as 100 kg per ton of starch for various BF(Burst Factor) grades of market demand.

Method of operation:

As we all know, Liner kraft mills use vertical or inclined size press with spray bars for starch spraying. For good dry strength and sheet compactness adequate quantity of starch with concentration ranging from 80-100 gpl is prepared depending on gsm, BF requirement and other operation parameters like machine speed etc. During this operation, well cooked starch solution is modified with either enzyme or with oxidative chemical to reduce the viscosity to handle solids content and spray time to induce sufficient loading. Cooked starch solution is allowed to cool, viscosity allowed to drop to desired G-4 Viscometer range, mixed with surface sizing chemical as per required dosage either supplied in powder form or liquid form and then pH is adjusted to 4.5-5.0 to induce best sizing value and reactivity.

According to this, starch uptake by paper ranges from a minimum of 40kg per ton to as high as 100 kg per ton depending on end result requirement. Additive like powder surface size with some cross-linkers consolidate inner polymerization and effectively seal pore space and make surface as well as paper body impeccable barrier for adequate water penetration only.

Starch Re-entry and Constraints in recycle process:

There is a famous say in Paper industry "Input is Culprit". These inputs can be either external by additives or internal by inherent ingredients in Raw materials like waste paper. Neither we can avoid nor can we escape from some inherent ingredients which are harmful to the process if not taken care properly.

One such example is Surface Size additive starch, which come along with recycle pulp. It is a valid point to note that starch and cellulose both are of carbohydrates with similar glucose fundamental building blocks. Hence chemical analysis may not differentiate between them but starch iodide test can give index. In addition thorough filtration of backwater/pulper water and testing for COD can give index of presence of starch. But in all practical accounts, we shall consider that from 40 kg per ton to 100 kg per ton surface coated starch come along with Liner kraft paper recycle. Other source of starch/dextrin entry is through corrugation boxes recycle in which adhesive gum is a major component of starch and dextrin along with supporting additives in brief.

At the outset, we shall not rule out the possibility that a minimum of 4-6% starch will be inherent in recycle kraft paper in pulper stage. As minimum as Rs.20 per kg of native starch, this starch incorporation back to paper making save a value of Rs.1000/ton, a huge amount if neglected.

Mechanism of Starch decomposition in circulation waters:

Starch used for surface sizing purpose is neither loosely bound nor strong enough to stick to. But some biological means make it easy process. During the pulper stage in Hydrapulper, some starch bound can dislodge and join to dilution water. However major happening is in continuous circulation of back water.

Starch is a major food material for bacteria as inherent chemical with pulp. Other organics also may serve as food but starch and Aluminium sulphate used in sizing become major source of food and energy for bacterial growth. Most prevailing bacteria in system water needs to separate starch from fibre surface. For this bacteria like 'Pseudomonas sp' secrete an enzyme called "Exo-Amylases" released from their cell walls to system water. Once these enzyme quantities reach a peak level, it starts acting on cellulose fibre top to dislodge bound starch and disintegrate the same to low molecular components as easy food for bacterial multiplication.

Many Paper mills in India use Liner kraft and OCC as furnish in their recycling process of paper making. But they overlook the presence of abundant volume of starch present with it. Nor they try to prevent degradation process of starch in it and allow to passivate to paper. This starch becomes nutrient for bacteria creating several problems in system.

At least mill people can try to stop enzyme activity by using enzyme reactivity blockers.

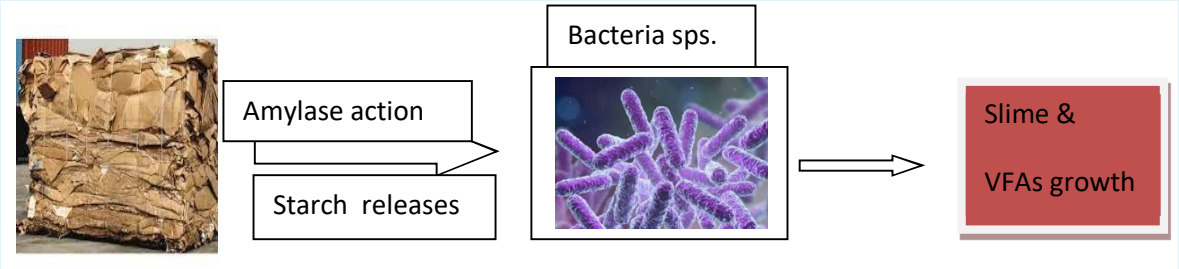

Fig. 1 Waste paper of Liner kraft, Corrugation box material, Exo-amylase enzymes produced by Bacillus and Pseudomnas bacteria cause starch detachment and decomposition, loss of starch, slime and pollution load [1]

Picture No.1 (Ref. 1)

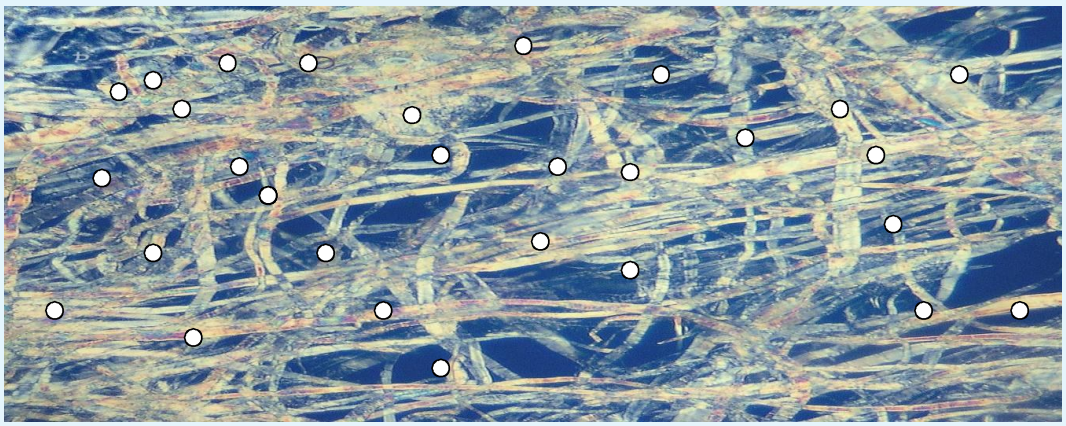

Fig. 2 Embedded starch granules in surface coated OCC paper pulp stock [2]

Tappi T -419 test method can help to determine amount of starch present on paper surface or in pulp as embedded as total starch.

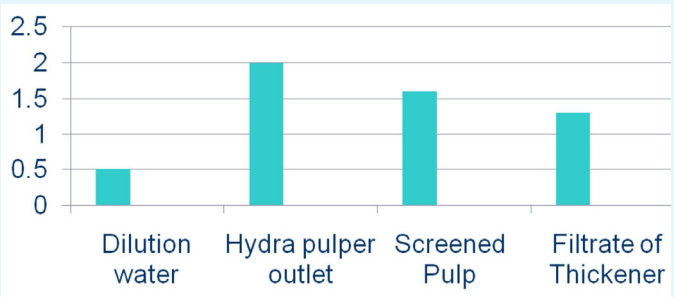

Fig. 3 Starch levels as g/L in dilution water, hydra pulper outlet pulp, screened pulp, and filtrate of thickener [2]

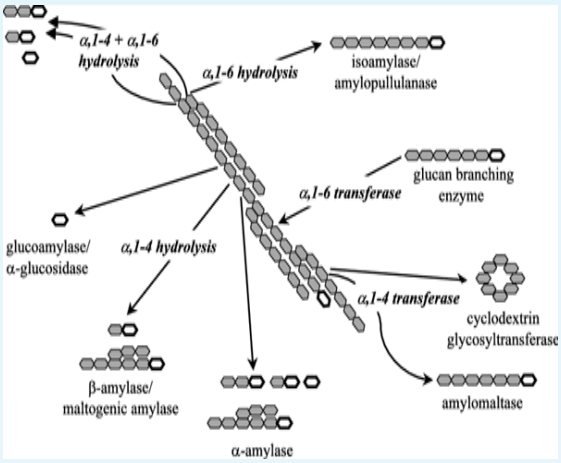

Fig. 4 Starch degradation mechanism in a kraft paper mill water loop by extra-cellular enzymes, mostly secreted are Alpha and Beta Amylases by Pseudomonas sp and Bacillus species - Enzyme activity on Starch granules [3]

Fig. 5 Amylase activity on dextrin molecules present in Corrugation gum and breakdown to smaller segments [4]

Most favourable conditions for this process are:

- Suitable pH conditions
- Sufficient population of bacteria feed on starch and decomposed starch
- Sufficient quantities of "Exo-Amylase" enzyme production in system water.
- Anaerobic conditions for quick decomposition of starch to VFAs (Volatile Fatty Acids) as pre-cursers of Methane generation
- In addition to starch degrading bacteria, synergic bacterial growth in anaerobic conditions are "Sulphur reducing bacteria" to generate H2S.
- At the outset Starch is lost and system becomes foul with bad smell.
- It is yield loss and causative factor for slime growth and unwanted problems.
- Slime gives paper breaks, downtime and production loss
- Bacterial growths do not stop with system water. It encapsulates in fibre matrix of paper making along with starch and succumb paper quality with Odour Problems.
- Odour Problems in packaging paper result in "tainting effect" to subsequent food packaging.

Remedies we have discussed in earlier papers of "Innovative Solutions for Odour Control" by me and some other papers by various people discuss chemical means to absorb and suppress odour. But these methods can suppress the problem but cannot eradicate the problem. We have to solve any problem in grass-root levels.

Paper industry using packaging liner kraft paper (Starch sized) having two options. Either allows them for bio-degradation, face the consequences of slime/odour problems, let the water go to Anaerobic treatment plant and earn energy. **But this is not a good practice and passivating starch with fibre by preventing degradation is best option to save money.**

Case Studies & Remedies:

In many cases, Paper mill people look into MNS and Branded products which are expensive in nature. It is a rare case that a freelancer is approached to give study report and solutions as permanent remedy. Two such mills are taken into consideration for solving the problem. It is beneficial to those companies because, other than consultancy charges, no chemical charge is involved. During the study, chemical sensitivity of type of bacteria producing "Exo-Amylase" enzyme, is identified and it is eradicated in various stages of pulping and paper making process. One paper mill is located in Hyderabad and another paper mill chosen far away from Hyderabad upon request of mill administration for commercial reasons.

Our Approach in Collaboration with mill personnel:

These two mills selected for problem solving had given free hand to study in detail, the reasons for the problems. As a freelancer, for obvious reasons, mill names were not disclosed herewith upon request from mill people. Privacy and secrecy are part of consultancy services. Our approach was to eliminate bacteria and neutralize Exo-amylase enzyme by chemical treatment. We also thought of using Enzyme activity inhibitors like Zinc Sulphate+Zinc chloride mixture in small doses. Zinc ion inhibits alpha amylase activity in system. We studied mills system for suitable approach.

Our observations in these two mills are:

- TDS Build-up of circulation water with increase in viscosity
- Odour problems in Paper, system and water being treated for re-circulation.
- Frequent paper breaks with slime spots
- Slime problems resulting in periodical downtime for system cleaning/boilout.
- Production loss for quality and quantity issues.

What is done to handle the problem?

1. After examining the system thoroughly with chemical tests like Iodine tests, COD tests of filtered water etc and VFA tests by feel and instruments, it is taken into consideration to go for systematic chemical dosages as discussed with mill people.

We have chosen three stage treatments as best remedy as follows:

- First stage treatment in Pulper stage to neutralize Alpha Amylases generated as extracellular enzymes from specific bacteria.
- This nullifying, killing Alpha Amylases in pulper during slushing process helps to prevent dislodging bound starch from fibre surface.
- For this we have selected desired dosage of chlorine dioxide to neutralize alpha amylases.
- We have incorporated two ingredient dosage system to generate chlorine dioxide in pulper stage at a required ppm level. Both these two ingredients are eco-friendly and non hazardous components.
- For this we have opted commercially available Potassium chlorate and Citric acid as inputs to generate chlorine dioxide in pulp system in-situ. Maintained 1ppm ClO2 for about 20 minute's treatment along with pulping in pulper.
- Second stage addition point is planned in the form of slow reacting chloramines in backwater plume.
- Chloramines remain in backwater system for substantial time and affective for longer duration to control the process.
- For this chloramines dosage, we have assessed total volume of back water in the circulation loop and time frame for circulation depending on holding capacity of system.
- For example, if head box consistency is 1% and draw is 3 ton per hour, water circulation with pulp per hour is 300 cubic meter per hour and for a total period of four hours to five hours hold up, it can be 1500 cubic meters.We planned in such a way that by adding/generating required chloramines in system, in four to five hours duration, system reaches saturation of 1 ppm residual chloramines.
- For generation of chloramines, we used Sodium hypochlorite, Ammonia and Caustic combination. We balanced mixing of chemicals in such a way as to have chloramines about 1.0-2.0 ppm in system for minimum 12 hours duration.
- This batch process continues throughout by gravity flow of chemicals in backwater plume.

- We monitored residual chloramines with test strips to control dosages.
- Third stage addition is Silver nano particle, Hydrogen peroxide recipe as mist spray in press section through spray bar.
- We used commercially available Hydrogen Peroxide and Silver nitrate, dissolved in water, pumped through high pressure pump passing air along and spraying on wet web as mist droplets.
- We advised mill people to spray the same on finished product also and allow the paper bags for air drying to avoid any further market complaints as bags are treated with Silver nano-particles and Hydrogen Peroxide recipe.
- Most of these ideas stemmed from Covid time experiences.

Some simple tips to produce required ppm level of active ingredients in-situ for treating pulp/stock and paper:

For First Stage operation.

- Sodium chlorite is commercially available at much cheaper rate than Potassium chlorite which is hazardous to handle and expensive.
- Commercial grade available in market is around 80% concentration product in powder form.
- According to this concentration of 80%, 4.35 gms of Sodium chlorite and 2.5 grams of Citric acid in system for one litre volume of pulper system do produce 1ppm level of chlorine dioxde.
- According to pulper stock volume, dosage shall be calculated and about 20 minutes residence time may be allowed for perfect reaction of killing starch decomposing bacteria as well as to neutralize Exo-amylases already produced in system.
- People sell commercial products in the form of Product 'A' and Product 'B' for this purpose with similar nature but different dose levels.

For Second Stage.

- Most of the kraft paper mills of 50-70 tpd capacity can have back water circulation of 6 hours repeat. Hence total water volume in system can be calculated from Paper machine to Fan pump and back.
- In back water plume/channel, by gravity flow adequate quantities of Sodium Hypochlorite, Caustic solution and Ammonia liquor can be dosed to generate 1-2 ppm Monochloramine level 6 hours circulation water.
- Chloramine is very effective and long lasting solution in backwater system to prevent any bacteria build-up, which was eliminated mostly in pulper stage through waste paper input.

Third Stage.

- It is quite optional and subject to available resources and for additional pre-caution.
- One option is available with spray bar in second press for this particular mill.
- Commercially available Hydrogen Peroxide, Silver Nitrate and Lemon oil combined recipe in required dilution is sprayed over partially wet web for long lasting effect of Peroxide and Silver ion as preventive biocides during future use of paper.
- The same can be used at rewinders also if feel necessary. Altogether, it will be fool-proof mechanism to prevent starch decomposition and Odour problems/Slime problems.

Results and Discussion:

After three days of system run with selected chemical dosages and continuity of machine running, we observed improvements and after 20 days of trial run, asked to proceed further for one or two months till they find no market complaints of paper with any Odour problems. The final observations or results are as mentioned below:

- Reduced slime growth or negligible with long machine runs without system boil-out for long intervals.
- Reduced viscosity of backwater and reduced/bare minimum COD values in circulation water filtrate.
- No Odour generation in finished paper for very long periods.
- No slime breaks for paper.
- Improved machine running. Well reduced COD values in circulation waters. (Filtrate water).
- Yield improvement noticed but couldn't be quantified as there is no way to calculate feed stock. Only procurements of truck weights can decide it long runs. But production is better and higher by 3-5%.
- Good market feedback compared to earlier complaints of Odour problems etc.

Conclusion:

I am thankful to the concerned mill people for the support rendered. Due to the reasons of privacy, mill people advised not to mention their names. First mill person asked not to take any similar trial for another three months for their commercial reasons in a mill nearby. Once the results shown positive, it is open now. Stage wise chemical treatment of process with inputs like chlorine dioxide, Chloramines, Hydrogen Peroxide and Silver Nitrate to produce Silver ion in system yield positive results of eradicating Exo-amylase producing bacteria as well as neutralising the "Exo-amylase" enzyme in circulating water.

Prevention is best cure. Solutions are simple chemicals with easy availability in market with very reasonable price. Neither hidden costs nor branded products used. Only with chemical knowledge with support of mill people and minor help as support to calculate dosage of chemical mixtures for appropriate quantity oxidative biocides for generation in-situ in ppm levels of active ingredients.

Cost savings are due to higher productivity and nil or very rare market complaints. But as the trial was not taken in a mill with size press application, starch consumption reduction couldn't be evaluated as it is MG machine. But we believe that there will be reduced starch input at size press as there is increase in production and decrease in COD levels in MG Machine case. If the same principle of operation is applied for a mill, where size press is operation for surface sizing, we could have noticed marked improvement in paper quality, productivity and starch consumption reduction in such mills. We are expecting to take a trial in mills with Size press operation for liner kraft manufacture to establish benefits and quantification of starch passivation. Otherwise starch will be lost in effluent or eternally circulate in system back water causing slime and odour problems.

Tangential benefits of this project are, Prevention and Passivation of starch with pulp, Prevention of growth of starch degrading bacteria, Prevention of Slime growth thereby and Prevention of Odour problems as by-product of all these.

Recommendations: Simple Oxidative biocides can suitably eradicate starch degrading bacteria from pulp systems and prevent release of starch to circulating water.

- Addition of suitable retention/encapsulating aids help further starch passivation.
- Use of Bentonite may be one such good idea.
- Zinc compounds like Zinc Sulphate and Zinc Chloride hinder enzyme activity in system.
- Some non-oxidizing biocides like DBNPA, MIT are compatible for the system.
- However Oxidative biocides like Chlorine, chlorine dioxide, hypochlorite, Hypochlorous acid, Hydrogen Peroxide, Silver ion, Peroxy compounds, bromides help a lot.
- We felt that our approach mentioned in paper is most economical way and save lot.
- One laboratory in France tests starch in paper mill water circuits like starch profile, Colloidal, dissolved and hydrolysed forms. It is needed in nearby mills.
- Lot of further study is needed about starch input in paper and starch recovery in re-pulping by above recovery methods and proper assessment methods for the same.

There is a say" Effluent quality tell us Paper quality Problems". (It is a Great Nanda Sir quote from JKPM in very old time).

If we take care of this aspect, we can say that "Waste is Wealth".

References:

1. Dimitrina Todorova, Ventsislav Blyahovski & Spas Ladzhov, "Prevention of starch making process for recycledpackaging paper" presented in 8th Conference on Information and Graphic Arts Technology. University of Chemical Technology and Metallurgy, Sofia, Bulgaria, June 2018.
2. CTP (Centre Techique du Papier), France, a Testing laboratory advertisement for testing facility of Paper mill circulation water system and starch evaluation in process waters. (Photos with courtesy)
3. Marc van der Maarel, "Properties and applications of starch-converting enzymes of the amylase family" - Journal of Biotechnology 94(2): 137-55, 2002. (Photo with courtesy)
4. A.Colomera, H.Kuilderd, Biotechnlological washing of Denim Jeans. A description in paper on how large dextrin molecurle breakdown by amylase enzyme with picture. In Denim 2015. Source: Science Direct - Journals & Books.