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Effects of Surface Sizing Agents on BOD of Recycled Papers

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by

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Table of Contents

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Abstract

Surface sizing agents can be major contributors to a mill's BOD loading. A 2% solids application of polyvinyl alcohol will give little or no BOD as compared to a high BOD resulting from a 8% solids application of anionic and cationic starch. The use of polyvinyl alcohol will give equivalent or better strength properties along with better sizing and high wax picks with only about one-half to three-quarters of a pound pick up per 3300 ft^2. High sizing values were achieved with the starches but at higher pick up levels. Polyvinyl alcohol could be best used in combination with starch at the size press.

Introduction

In the paper industry today, starches have found wide use and acceptance. In their many years of use, starches have caused significant problems in the area of environmental control. Starches have been shown to have contributed much to the BOD loading of a mill's effuent. New developements in starch research have produced new starch derivatives such as: the cationics' which have helped to lessen the problem. Further research has developed starch substitutes like polyvinyl alcohol, (PVA).

Starches are used in all areas of pulp and papermaking especially the area of surface sizing. In this area the new starch derivatives and substitutes have made significant headway as the problem of environmental control is emphisized.

Surface Sizing

In the surface sizing process, a starch paste is applied to the sheet. This treatment is done to improve appearence and erasability, to inhibit ink penetrations, and to generally form a hard surface for writing and printing. Some extra added improvements which can be achieved are improved strength, reduced surface fiber picking, and preparation of the sheet for subsequent coating.(1)

The degree of penetration and pick up for any given starch may be varied to some extent by changing roll nip pressure, starch temperature, and puddle depth at the nip. The size press conditions may vary over a large range, most of which would fall within the broad limits of 50- 70 degrees Centagrade, 2 - 12% solids, and have a Brookfield viscosity of 10 - 50 cps. (No. 1 spindle,20 rpm) (5)

Anionic Starch

The anionic starches have been used by the papermaker as surface sizing agents for many years. Through the years a varity of anionic starches have been produced: the chlorinated, the oxidized, and the ethylated.

The anionic starch was so named because of the negative charge on the starch molecule found on both modified and native starches. Groups like: hydroxyls,chlorines,carboxyls and ethyls were added as a result of the modification steps to help distribute the negative charge over the entire starch molecule. Because of their strongly negatively charged nature, groups of this type have helped to increase the magnitude of the already negatively charge native starch.

The early starches were used at the size press to give the sheet an improved surface quality leading to better printability and increased printing speed. Some of the modified starches with the ethylated starches in particular were most effective because of their superior film forming qualities. (4) The problem, however, with these modified starch is that they are strongly negative—the same as cellulose. Problems come up with the efficiency of these starches along with environmental concerns, which will be discussed in a later section.

Cationic Starch

The use of cationic starch is fast becoming a widely used size press starch. It has been shown that less cationic starch is needed to maintain surface strength and quality. When cationic starch is applied to a sheet, it is immediately attached to the fibers on the sheet's surface. As more starch is applied, it seals the sheet's surface and hinders any further starch penetration into the sheet. Of coarse, some starch does flow to various depths of the sheet, but the majority remains on the surface.

There are many advantages to using cationic starch over conventional starches at the size press. One advantage is that it improves printing characteristics of the sheet. A combination of fiber bonding and surface orientation explains the improvements in printing properties. The fiber bonding provides a good strong surface while the uniform starch concentration on the surface makes for a uniform ink receptivity and good ink hold out.

Some of the improvements in printing characteristics noted: (8)

1.) Better print uniformity

2.) Better print definition

3.) Greater depth of color

4.) Less ink show through on reverse side of sheet

5.) Fewer pickouts on offset presses and less dusting

A second big advantage is the cationic starches ability to retain pigment to the fiber. This means that higher opacities can be obtained with less use of TiO_2 and filler clay because less of it is lost through the saveall systems to the sewer. This can represent a big money saver for the papermaker.

Polyvinyl Alcohol (PVA)

Polyvinyl alcohol is now being looked at as a starch substitute for use in the surface sizing of paper. At the present, it has been experimented with mostly as an additive to the starch but may one day replace starch as a surface sizing agent.

Some applications of PVA are in surface sizing of paperboard which imparts gloss and smoothness, solvent, oil and ink holdout; and printability. In pigmented paper coatings PVA will raise it's efficiency to permit lower binder levels, higher pigment volume concentration with increases in grightness and opacity.

Some cautions to be noted in preparing solutions of PVA for the size press treatment of paper are: (10)

1.) Add PVA to cool tap water with good agitation to form a lump-free slurry

2.) Check to confirm a lump-free slurry since these would subsequently form difficult - to - handle gels.

3.) If a paddle mixer is used the vessel should be equipped with baffle plates.

4.) PVA should be heated for not less than 200°F for not less than 30 minutes.

5.) When externally steam heating PVA the temperature rise should be gradual so not to get a heat build up which cause an insoluble insulating coating of PVA to form on the inner walls of the vessel.

The use of PVA in sized papers showed marked improvements in the papers physical properties. It was shown that tensile, elongation and work-to-rupture properties were all clearly increased in the sizing treatment as the portions of PVA were increased. Also fold endurence, wet tensile, and abrasion resistance properties were improved by increasing the quantity of PVA in the size solution. It was observed that stiffness was slightly increased while the hygroexpansivity was unaltered. (2)

Environmental Concerns

One of the biggest problems starch contributes to the environmental problem and the papermaker is that it adds to the turbidity problem in mill wastewater effluent. (9) With the emphasis on broke and secondary fiber usage, this problem has grown. The primary adverse effect of starch-bearing broke or secondary fiber results from the repulping of this material. In the repulping operation the starch is dissolved thus releasing pigment and fiber fines from the rest of the fiber. As this material is reintroduced to the system much of it is lost thru the machine wire and saveall system and discharged as mill

effluent. This trubidity contains fiber, filler, and chemical additives which the papermaker sees as higher production cost when lost to the receiving streams. Today, the aim is for reusable water which must be obtained economically by treatment of white water. If the white water turbidity can not be removed it must be ultimately discharged to the receiving stream. The starch-turbidity problem is increased three-fold: 1.) The fresh water use is increased, 2.) the volume of waste water to be treated is increased, and 3.) a more difficultly treated effluent is produced. (8)

Another problem not to be overlooked is the biological oxygen demand, (BOD) of the starch componet of the waste effluent. It has been shown that starch can exert from 0.5 to 0.75 pounds of BOD per pound of starch used. (6) It is then highly favorable to have the starch remain with the filler and fiber to be removed at the savealls to be reintroducted to the paper furnish and eliminated from mill waste water returning to the receiving stream.

The anionic starches have showed many of these problems stated above. Because of this reason the papermaker is in search of a new starch or chemical substitute for a sizing agent. The cationic starches have been found to partially solve the problem of stream pollution. It has been observed that cationic starches can greatly reduce effluent BOD. (3) The size press can be a major contributor to BOD of the mill effluent. Because of cationic starch's high electrochemical attachment to the fiber, it isn't removed during the repulping cycle where much of conventional starch is lost to the sewer.

The study of PVA as to its environmental contributions have shown that it yields a low BOD. (2) Also, the fact that it binds tightly to fiber and filler aids in keeping PVA losses to the sewer minimal.

Objective

It is the purpose of this paper to show that surface sizing agents especially starches can be major contributors to the BOD loading of a mills effluent. Also, some polymers like polyvinyl alcohol can be substituted for starch at the size press to give a significant reduction in BOD with equivalent or better sizing properties.

Experimental Procedure

The actual sizing operation was done on the verticle size press on the pilot machine at the department of Paper Science and Engineering. The three sizing agents tested were: anionic starch, cationic starch and polyvinyl alcohol (PVA). The sizing was applied to a 50 lbs. (25-38-500) offset sheet. Both starches were applied at 8% solids while the PVA was applied at 2% solids. The sheet was run at 200 fpm with sizing being done at 140° F.

Next, samples were taken from each sizing agent tested and held out for sizing and some physical testing. The remaining paper went for sample preparation for the BOD test.

The BOD test used was the 5-day test taken from the procedure set up in NCASI bulletins. The sample preparation for the BOD test was as follows:

1.) approx. 10g of sample taken
2.) Add 500ml of distilled water
3.) Put mixture into Waring blender
4.) Repulp on high speed for 5 minutes
5.) Filter pulp through a Buchner funnel
6.) Save filterate for the BOD test

The BOD's were run using the standard 300 ml bottles at varing dilution ratios.

The Hercules size test was run next using a 90% reflectance setting in hopes to magnify any difference in the three sizing agents used. The rest of the tests run were: tensile, Mullen, % Elongation, porosity, wax pick while pick up data was calculated.

Table I

Test	Base Stock	Penford Gum 280	Sta-Lok 60	Poly-Vinyl Alcohol (PVA)
Application (% solids)	-	8	8	2
Pick up (lbs/3300 ft^2)	-	1	1.5	0.5
BOD (ppm)*	46	66	68	38

* ppm - parts per million

Table II

Test		Base Stock	Penford Gum 280	Sta-Lok 60	Poly-Vinyl Alcohol (PVA)
Application (% solids)		-	8	8	2
Pick up (lbs/3300 ft^2)		-	1	1.5	0.5
Hercules Sizing* (sec.)	F	30.5	78.9	73.8	63.2
	W	147.2	186.6	183.9	234.0
Wax Pick**		11	20	20	20

* F & W - Felt & Wire sides of paper

** Number recorded was where pick was first seen

Table III

Test	Base Stock	Penford Gum 280	Sta-Lok 60	Poly-Vinyl Alcohol (PVA)
Basis Weight (25x38-500)	50	51	51.5	50.5
Caliper (inches)	.004	.004	.004	.004
Mullen (PSi)	25.2	27.1	28.8	24.3
Tensile* MD (Kg) CD	11.3 10.5	12.2 7.0	11.6 6.7	10.0 6.3
% Elongation* MD CD	2.0 1.8	1.8 3.9	1.9 4.7	1.8 2.9
Porosity (sec/100cc)	64.0	86.2	105.6	52.4

* MD - Machine Direction
CD - Cross-machine Direction

Conclusions

Biological Oxygen Demand test

The BOD test showed no significant difference between anionic and cationic starch, both yielded a high BOD compared to the unsized base stock. This is alittle different since cationic starch is reported to give reduction in BOD. In this case starch is starch and one should expect about three-quarters of a pound of BOD for every pound of starch used. The only benefit of using cationic starch is to improve retention in hopes that the starch will remain on the surface of the sheet during the repulping cycle. The PVA showed no contribution to BOD. There are two reasons for this: 1.) that the majority of the PVA remained on the surface of the sheet even during repulping, 2.) the little PVA cleaved off and dissolved into the water during repulping has no BOD associated with it.

Sizing

The Hercules size test yielded significant results for all three sizing agents. A noted difference between felt and wire side was seen. The interesting result here is that PVA only had a half-a-pound pick per 3300 ft^2 while the anionic and cationic starches had one pound and one and a half pound pick ups re-

spectively yet PVA yielded equivalent or better sizing. The wax picks increased from the base stock to the surface sized stock but all three sizing agents yielded the same value.

Physical Properties

The strength test, Mullen and tensile showed no real significant gains after surface sizing but remained constant as compared to the unsized base stock. Increases were seen in the cross-machine direction of percent elongation where high reading of 2.9% to 4.7% were recorded for both starches and PVA as compared to the 1.8% of the base stock.

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