Preferred citation: G.G. Allan, R. Aravamuthan, C. Christien and M.K. Raghuraman. Chemical modification of pulp refining rates. In **Papermaking Raw Materials**, *Trans. of the VIIIth Fund. Res. Symp. Oxford, 1985*, (V. Punton, ed.), pp 879–894, FRC, Manchester, 2018. DOI: 10.15376/frc.1985.2.879.

CHEMICAL MODIFICATION OF PULP REFINING RATES

G. G. Allan, R. Aravamuthan, C. Christien and M. K. Reghuraman
College of Forest Resources and Department of Chemical Engineering
University of Washington, Seattle, Washington 98195, USA

ABSTRACT

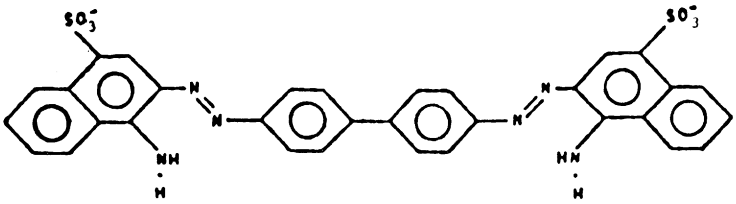
It has long been known that certain simple chemicals can either accelerate or retard the rate of refining of pulps. Based on surface adsorption and osmotic pressure considerations, a hypothesis is proposed to provide a rationale for the behavior of these chemicals. The validity of this theory is demonstrated by the prediction of the effectiveness of a colorless, photostable chemical as a new beating aid and the verification of its performance as an accelerator for the refining of both chemical and mechanical pulp as well as secondary fibers.

INTRODUCTION

More than a quarter of a century ago at a predecessor Cambridge conference, two Italians reported (1) that the rate of beating of wood pulps could be modified by the dissolution of chemicals in the suspending water. The effect of one compound, the dye Congo Red (I), was particularly noteworthy for it reduced markedly the energy required to develop a particular level of bonding capability in the pulp. However, because of the cost and bright red color, little commercial interest was ever manifested in this dye as a beater additive.

Nevertheless, the behavior of Congo Red is of considerable theoretical importance as a springboard to reach new performance levels in the chemical modification of beating and refining. From the chemical structure of I (Fig.1), and the dichroism exhibited when Congo Red is

adsorbed onto cellulose fibers (2), it can be inferred that the two amino groups and the two azo linkages are hydrogen-bonded onto the same cellulose chain.



I

Fig 1—The molecular structure of Congo Red.

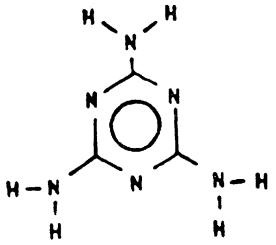
Clearly the adsorbed Congo Red is part of the cellulose phase and can be regarded as being dissolved therein. Consequently, the ionized sulfonate anions must also be a part of the cellulose phase. Furthermore, it can be postulated that the local concentration of dye on the cellulose surfaces must be quite large in contrast to the concentration of the dye in the surrounding water. This concentration difference then would lead to an osmotic flow of water from the aqueous into the dyed cellulose phase. The substantial osmotic pressure generated swells the fiber phase and acts in concert with the forces of mechanical beating to develop fiber fibrillation and delamination more speedily.

From this explanation for the behavior of Congo Red as a beating aid it follows that there must exist colorless equivalents. From the viewpoint of the pulp and paper industry, these new beating aids ought to be cost-effective, nontoxic and commercially available in quantity. This paper describes the discovery and testing of such a chemical.

RESULTS AND DISCUSSION

In ongoing studies of fiber surface modification (3), the concept of fiber-binder adhesion based on multi-centered hydrogen bonding was introduced (4). This concept was based

on the hypothesis that the polyaza nitrogen heterocycles, as a class, should have strong interactions with cellulosic surfaces. By a study of the adsorption of a variety of modelcompounds onto α-cellulose, the validity of this hypothesis was demonstrated. Of course, there are many members of this class, but among these one stands out from a practical, papermaking point-of-view. That compound is 2,4,6-triamino-s-triazine (II). This heterocycle, first synthesized in 1834 by Liebig (5), is now commercially manufactured in quantity from urea. It is a colorless crystalline solid, m.p. 350°C, with excellent photostability (Fig.2).



II

Fig 2—The molecular structure of 2, 4, 6-triamino-s-triazine.

The solubility of II in water (0.5,1,2 and 3% at 30, 45, 65 and 80°C respectively) where it functions as a monobase (pK_b 8.96) is adequate for convenient incorporation into papermaking processes. Equilibration with an α-cellulose pulp having a low carboxyl group content (0.02 meq/g) shows that the aza heterocycle is adsorbed and held, presumably by multi-centered hydrogen bonds. The variation of adsorption with concentration at three different pH values is depicted in Fig. 3. All of these characteristics make the s-triazine II a potential colorless equivalent of Congo Red.

The effectiveness of II as a beating aid was evaluated at various addition levels (0.5, 1 and 1.5% based on pulp) on several pulps in comparison with Congo Red, used as a 2m molar solution in water. The materials studied included commercial bleached and ubleached spruce kraft pulps, a commercial thermomechanical pulp consisting of 50% hemlock and 50% pine and secondary fibers from a Douglas-fir based kraft waste paper.

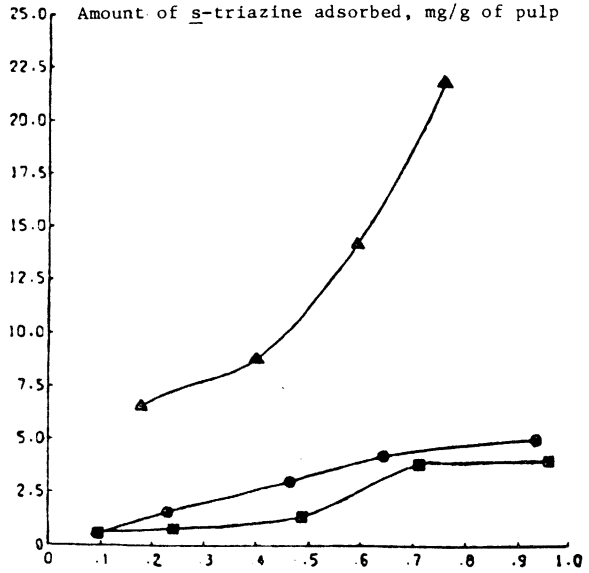


Fig 3—The adsorption isotherm of 2, 4, 6-triamino-s-triazine from aqueous solutions (pH 2.5, ▲ ;pH 7.6, ● ; pH 10.6, ■) onto α-cellulose.

All pulp refining was done in a PFI mill according to the procedures of TAPPI Standard T248 pm-74 while the water drainage characteristics of the beaten materials were measured as Canadian Standard Freeness (TAPPI Standard T227 os-58). Handsheets were prepared (TAPPI Standard 205 om-80) and tested for the physical and optical properties achieved (TAPPI T220 os-71). From the reflectance measurements, light-scattering coefficients were calculated by using the Kubelka-Munk Theory (6). Fiber fractionation (TAPPI Standard T233 os-75) was carried out in a Bauer-McNett classifier fitted with Tyler screens (28, 48, 100 and 200).

UNBLEACHED AND BLEACHED SPRUCE KRAFT PULPS

The effect of the addition of the two beater aids upon the development of freeness and other related physical properties for both the bleached and ubleached kraft pulps is

Table 1. The effect of Congo Red (I) and 2,4,6-triamino-s-triazine on the characteristics of unbleached (U) and bleached (B) spruce kraft pulps refined in a PFI mill.

Pulp refined	Chemical addition	Extent of refining, revs.	Freeness CSF mL	Tensile index Nm/g	Burst index kPa.m^2/g	Tear index mN.m^2/g	Folding endurance, double folds
U	None	7700	600	52	4.7	17.5	412
		10000	515	57	5.2	17.0	522
		12500	450	63	5.4	16.9	608
		15000	390	62	5.5	16.8	425
		19000	320	61	5.6	16.3	405
U	I	8000	545	54	5.0	19.0	397
		10000	500	58	5.2	18.6	410
		12700	440	62	5.4	18.4	486
		15000	385	63	5.5	17.9	542
		18000	320	62	5.7	17.9	590
U	II	7500	570	59	5.1	19.0	314
		10000	495	61	5.4	18.5	430
		12500	435	63	5.5	18.1	535
		15000	380	63	5.7	17.7	638
		18000	310	62	5.9	17.9	522
B	None	3000	630	60	5.4	21.0	470
		5000	550	61	5.9	19.7	525
		7500	430	64	6.2	19.3	665
		10000	355	66	6.4	18.7	740
		12000	330	57	6.7	18.4	610
B	I	3400	610	62	5.5	21.0	445
		5000	515	63	6.0	20.2	560
		8000	405	68	6.4	-	725
		10000	345	69	6.5	19.5	770
		12000	290	70	6.8	19.5	780
B	II	3500	615	63	5.4	21.6	485
		6500	455	65	6.1	19.9	690
		10000	325	69	6.6	19.4	980
		12000	290	71	6.8	19.1	810

shown by the data collected in Table 1 and visualized in part in Figs. 4-6. Over the entire range examined, the s-triazine accelerates beating comparably to Congo Red. Moreover, by a comparison of the properties of sheets made from the modified pulps it is apparent that the use of s-triazine leads to generally greater strength at all refining energy levels. Only for the tear index does the dye lead to slightly better values than does the polyaza nitrogen heterocycle. The folding endurance of the sheets, however, shows improvements due to the beater additives, only in the later stages on refining.

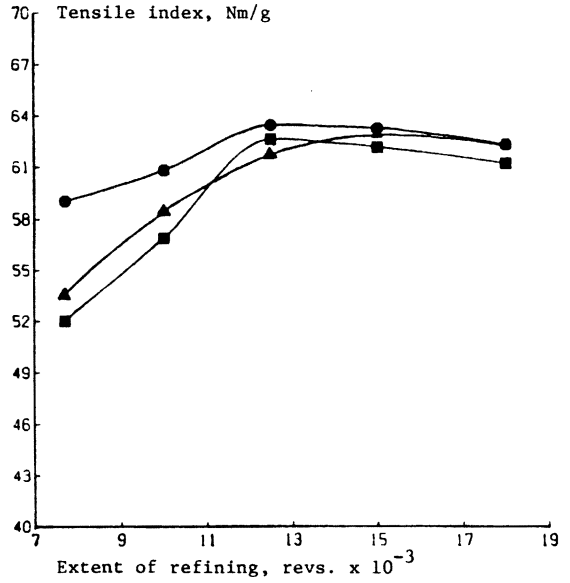


Fig 4—The effect of additives (none, ■ ; 1.4% Congo Red, ● ; 1,5% 2, 4, 6-triamino-s-triazine, ▲) on the rate of refining of an unbleached spruce kraft pulp in a PFI mill as manifested by the tensile strength of the derived paper.

For each of these pulps it is clear that both the beating aids have enhanced the strength of the resultant papers by about 10-15%. In an industrial operation this could be manifested as a saving in the refining energy needed to achieve particular paper performance levels.

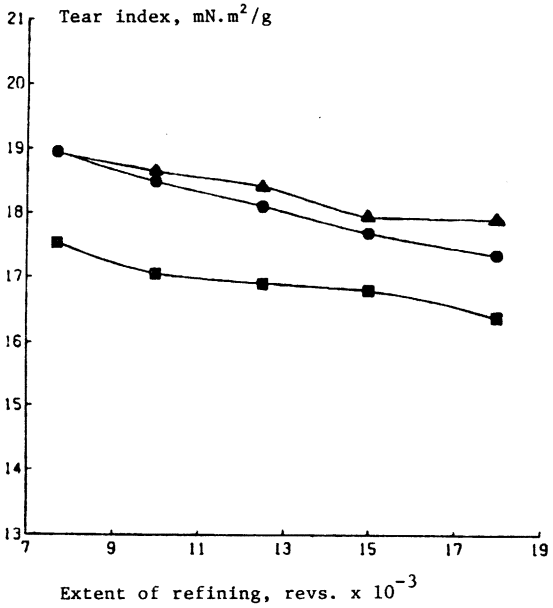


Fig 5—The effect of additives (non, ■ ; 1.4% Congo Red, ● ; 1.5% 2, 4, 6-triamino-s-triazine, ▲) on the rate of refining of an unbleached spruce kraft pulp in a PFI mill as manifested by the tear strength of the derived paper.

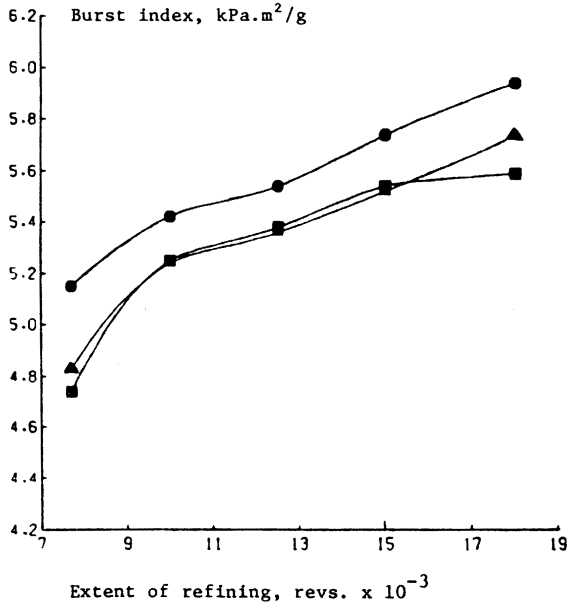


Fig 6—The effect of additives (none, ■ ; 1.4% Congo Red, ● ; 1.5% 2, 4, 6-triamino-s-triazine, ▲) on the rate of refining of an unbleached spruce kraft pulp in a PFI mill as manifested by the bursting strength of the derived paper.

PAPER RECYCLING

The question of conservation of energy in refining is of particular importance in the recycling of waste paper. The fibers in this already used raw material have previously been pulped, swollen, beaten, aggregated, collapsed, bonded and

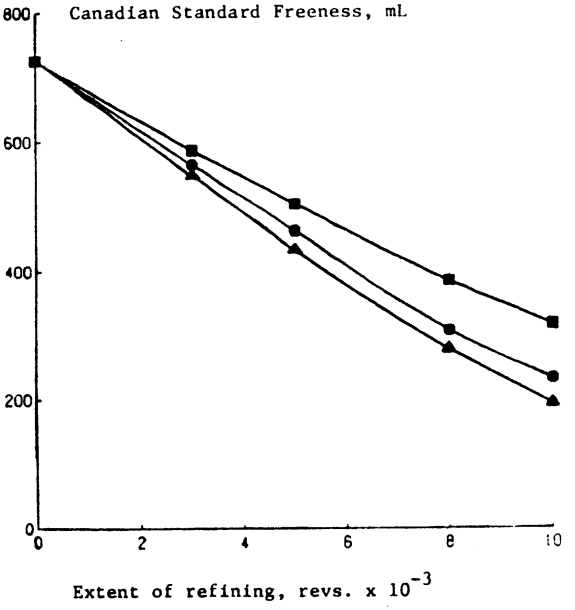


Fig 7—The effect of additives (none, ■ ; 1% Congo Red, ● ; 1% 2, 4, 6-triamino-s -triazine, ▲) on the rate of beating of a wastepaper (Douglas fir kraft) in a PFI mill as reflected by the Canadian Standard Freeness of the resultant pulp.

dried. To restore these secondary fibers to a useful papermaking condition requires a sizable energy input. The cost of this, of course, diminishes the economic attractiveness of the basic furnish. Clearly a chemical which would offset this effect would be important and accordingly some experiments with the s-triazine were undertaken. The source of waste paper was a Douglas-fir based, unbleached kraft paper which had not been in actual use. The sheet (25g) was torn up into small pieces (2'x 2'), suspended in water (1.5L), disintegrated, TAPPI Standard T205 om-81), and then refined in a PFI mill using the same conditions that were employed for the virgin pulps. The acceleration of the beating rate achieved by the addition of Congo Red (at the 1% level) was compared with that resulting from the incorporation of the s-triazine at the same level of addition. The results obtained are summarized in Fig. 7. These show that the aza heterocycle, although slightly less efficient than the dye, does diminish the amount of energy necessary to attain a given Canadian Standard Freeness. Thus, when 1% of the s-triazine is present in the refining liquid, to reach a CSF value of 350mL requires about 20% less energy than when the beating aid is omitted.

THERMOMECHANICAL PULP

Obviously, the economic attractivenss in any given situation is determined by the cost of energy at the location balanced against the cost of the s-triazine addition. This trade-off is likely to be most favourable to the papermaker when the pulp refining is energy intensive. Accordingly, an investigation into the effect of the s-triazine on the refining of thermomechanical pulp was undertaken. The actual laboratory experiments were designed to simulate the atmospheric refining (secondary) step of the thermomechanical pulping process. This was done by subjecting a hemlock-pine thermomechanical pulp which had undergone primary refining to treatment with different levels of the s-triazine (0, 0.5, 1 and 1.5%, based on pulp) in the PFI mill. The data collected in Fig. 8 show the effect on the pulp freeness values of various refining levels in comparison with those of a control run without additive.

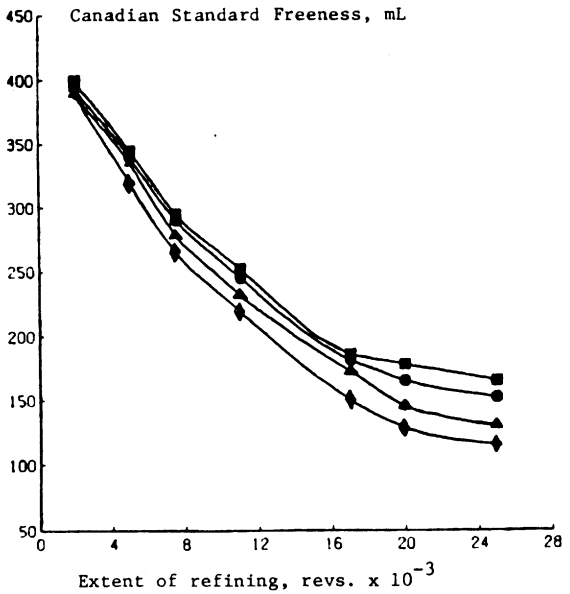


Fig 8—The effect of the level of addition of 2, 4, 6-triamino-s-triazine (0%, ■ ; 0.5%, ● ; 1%, ▲ ; 1.5%, ♦) on the rate of refining as reflected by the Canadian Standard Freeness of a hemlock-pine thermomechanical pulp.

At all refining levels the addition of the s-triazine is beneficial in reducing the energy requirements necessary to attain a particular Canadian Standard Freeness. However, the benefits of the s-triazine are considerably more significant at the 1 and 1.5% addition levels.

Nonetheless, as shown by the data in Fig. 9 and Table 2, the highest addition level (1.5%) is not dramatically more effective in augmenting the tensile index than the intermediate level (1%). This is consistent with the Freundlich adsorption isotherm (Equation 1) for the s-triazine on TMP fibers which indicates that the amount adsorbed (Y, mg/g of fibers) is not strongly dependent on the concentration of the s-triazine in the treating solution (C, g/L) of pH 6.5.

$$Y = 10.12\ C^{0.1422} \qquad (1)$$

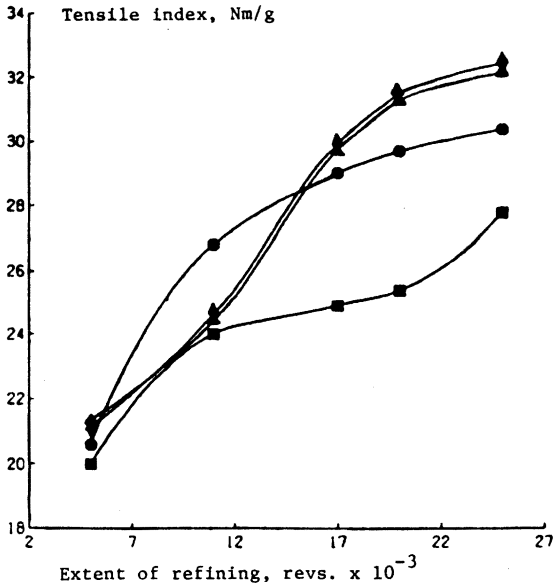


Fig 9—The effect of the level of addition of 2, 4, 6-triamino-s-triazine (0%, ■ ; 0.5%, ● ; 1%, ▲ ; 1,5%, ♦) on the rate of refining of a hemlock-pine thermomethanical pulp as manifested by the tensile strength of the derived paper.

Scanning electron photomicrography of modified and unmodified refined fibers indicate that the latter are more damaged. This is probably the reason why the strength properties of the former are superior. One reason for the reduced damage may be that, because of increased fiber flocculation and compressibility, a greater number of fibers bear the impact of the refiner at any instant.

In contrast to the effect on tensile strength, the 1.5% level of s-triazine addition does augment the tear resistance significantly more than the 1% level, as is clear from the data depicted in Fig. 10. This simultaneous increase of tear and tensile strength is quite unusual and at CSF values of 160mL the energy savings at the greater addition level (38%) are about 10% greater than those achieved with the 1% s-triazine modification (28%).

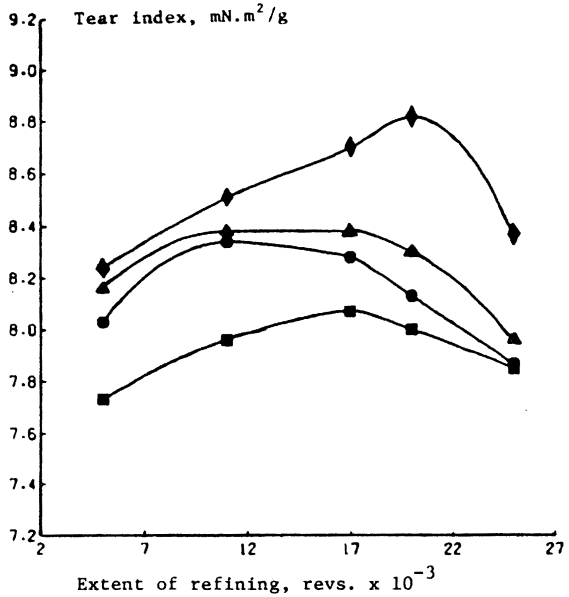


Fig 10—The effect of the level of addition of 2, 4, 6-triamino-s-triazine (0%, ■ ; 0.5%, ● ; 1%, ▲ ; 1,5%, ♦) on the rate of refining of a hemlock-pine thermomethanical pulp as manifested by the tear strength of the derived paper.

On the other hand, this degree of difference between the levels of s-triazine added was not observed with either the bursting strength, opacity or scattering coefficient data summarized in Table 2.

Similarly, all levels of addition were only slightly differentiated when the results of fiber size classification experiments at two degrees of refining were compared (Table 3). However, the slight increase in the amount of the ribbon-like + 48 fraction should contribute to the strength and optical characteristics even though it is created at the expense of the fines, which are an important component of bonding in TMP sheets.

From all of the foregoing data it can be concluded that the maxima in strength properties are developed faster when the s-triazine is used. In many cases, the maximum values obtained with chemical modification are not otherwise attainable.

Table 2. The effect on the properties of handsheets made from a hemlock-pine thermomechanical pulp refined in the presence of various amounts of 2,4,6-triamino-*s*-triazine in a PFI mill.

Property measured	*s*-triazine addition	Extent of refining, revs. 5000	11000	17000	20000	25000
Scattering coefficient cm^2/g	0.0	510.0	506.0	502.0	493.0	485.0
	0.5	497.0	501.0	489.0	494.0	498.0
	1.0	475.0	493.0	497.0	499.0	512.0
	1.5	488.0	496.0	504.0	517.0	527.0
Opacity	0.0	97.5	97.5	97.0	96.5	96.0
	0.5	97.0	97.0	96.5	96.5	96.0
	1.0	96.0	96.0	96.5	96.5	97.0
	1.5	96.0	96.5	96.5	96.5	97.0
Tensile index Nm/g	0.0	20.0	24.0	25.0	25.0	28.0
	0.5	21.0	27.0	29.0	30.0	30.0
	1.0	21.0	24.0	30.0	31.0	32.0
	1.5	21.0	25.0	30.0	31.0	32.0
Burst index $kPa.m^2/g$	0.0	1.6	1.8	2.0	1.9	1.8
	0.5	1.7	1.9	2.0	2.0	2.1
	1.0	1.7	1.8	2.0	2.1	2.2
	1.5	1.7	1.8	2.0	2.1	2.3
Tear index $mN.m^2/g$	0.0	7.7	8.0	8.1	8.0	7.8
	0.5	8.0	8.3	8.3	8.1	7.9
	1.0	8.3	8.4	8.4	8.3	8.0
	1.5	8.2	8.5	8.7	8.8	8.4

Table 3. The effect on the fiber size distribution in a hemlock-pine thermomechanical pulp refined in the presence of various amounts of 2,4,6-triamino-s-triazine in a PFI mill.

s-triazine addition level, %	Extent of refining, revs.	Fraction retained on Tyler screen, 28	48	100	200	Fines less than 200
0.0	0	0.30	0.20	0.15	0.04	0.32
0.0	17000	0.23	0.20	0.13	0.02	0.42
0.5	17000	0.25	0.24	0.10	0.04	0.36
1.0	17000	0.25	0.25	0.10	0.06	0.34
1.5	17000	0.26	0.26	0.08	0.05	0.35
0.0	25000	0.22	0.16	0.11	0.04	0.47
0.5	25000	0.20	0.20	0.10	0.05	0.46
1.0	25000	0.20	0.17	0.13	0.05	0.45
1.5	25000	0.22	0.20	0.10	0.04	0.45

CONCLUSIONS

The selection of experiments reported herein demonstrate that the acceleration of pulp refining rates, or waste paper recycling, by the use of low-cost colorless chemicals is technically feasible.

A series of ongoing mill trials is now showing that these laboratory findings are translatable to industrial facilities generally, and in particular to those where high yield pulps are produced by energy intensive processes.

ACKNOWLEDGEMENTS

This work was principally supported by MCI, Donaldsonville, LA 70346, U.S.A. and also in part by the Boxboard Research and Development Association, Kalamazoo, MI 49006.

Thanks are due to I.M. Allan, J.P. Carroll, G.D. Crosby, J.T. Geppert, D.F. Gibson, J.E. Laine, T. Mattila, A.N. Neogi, and T.H. Sloan, whose contributions as members of the University of Washington Fibre and Polymer Group helped lay the foundations of this article.

REFERENCES

1. G. Centola and D. Borruso, in "Fundamentals of Papermaking Fibers," Transcations of the Symposium held at Cambridge, England, September 1957, Technical Section of the British Paper and Board Maker's Association, F.M. Bolam, ed., London, U.K. 1958, p. 349.

2. R.W. Moncrieff, "Man-Made Fibers," John Wiley and Sons, Inc., New York, N.Y., 4th Edition, 1963, p. 189.

3. G.G. Allan and Y. Hirabayashi, Cell. Chem. Tech., 1984, 18, 83.

4. K. Akagane, G.G. Allan and E.M. Passot, Paperi Puu, 1974, 56, 5.

5. J. Liebig, Ann., 1834, 10, 17.

6. J.A. van den Akker, Tappi, 1949, 32 (11), 498.

Transcription of Discussion

Chemical Modification of Pulp Refining Rates

by G.G. Allan, R. Aravamuthan, C. Christien and M.K. Raghuraman

R.H. Reeves James River Corp., Neenah, U.S.A.

What relationship have you found between an increased number of revolutions in a PFI mill with refining in a production operation?

Prof G.G. Allan We have run a test at Bauer facility in the mid-west of the U.S.A. and obtained very similar results. Unfortunately, as I am sure you are well aware, running a test on TMP is a very difficult thing to do. We have also run two mill trials, one of which was very successful and one of which was not. We do not know why that occurred. We do have a problem in deciding in a mill situation where exactly to place the additive. Should it go into the chips before they go through the chip washer or should it be added to the eye of the refiner? We really do not know. We are finding it difficult to perform these experiments and obtain reliable data.

Reeves Have you tried to evaluate the homogeneity of the pulp you are refining in the laboratory compared with what is done in a mill?

Allan No, we have not.

Dr. H. Higgins CSIRO, Victoria, Australia

You mentioned the pioneering work of Centola & Borruso for which I have the greatest admiration also. However, I think it would be fair to the memory of another distinguished colleague, the late Dr. W.E. Cohen, to mention the early work of Cohen, Farrant and Watson on the effect of electrolytes.

Allan I wholeheartedly agree with you. We, however, have found their published work to be extremely inaccessible and have been working from the abstract only. I would be grateful if you could provide that paper for me.

Higgins The references are Appita Proc 3 : 72 (1949) and Appita Proc 4 : 176 (1950).

Dr. A.N. Scallan PPRIC, Pointe Claire, Canada

I would agree that osmotic pressure plays a big part in the swelling of pulp. However, I would disagree with your mechanism. If you adsorb material onto internal fibre surfaces, the material becomes part of the solid phase of the gel and will not contribute to osmotic pressure. What will contribute will be the ions dissociated from such a material. So, my question is do these dye-like molecules ionise?

Allan You want to connect the osmotic pressure to the counter ion associated with the triazine in this case?

Scallan Yes. You keep saying it is adsorbed. If it is adsorbed, it becomes part of the solid material and not part of the solution in the fibre. Osmotic pressure is a property of the solution.

Allan I think this is a semantic problem, Dr. Scallan. If you consider, say a super absorbent, you can have a material such as that without any ion attached to it.

Scallan Carboxymethyl cellulose is a superabsorbent in which carboxyl groups are attached to the cellulose. At neutral pH, it ionises and swells to a great extent. However, if you change to an acid pH, where it does not ionise, it will hardly swell at all. It is the counter ion that matters.

Allan You are talking about a polymeric stucture there. The osmotic effect of the swelling is going to be averaged over the whole polymer. For example, if you take carboxymethyl cellulose, and let us say you had one carboxyl group on it, would you calculate the concentration of carboxyl groups as one per mole or one per some fraction of the molecular chain?

Dr. P. Noe CTP, Grenoble, France

The use of freeness to measure the beating effect is a little confusing because Congo Red by itself has an influence on the drainage index. This can be demonstrated easily by adding Congo Red to a beaten pulp, when you will also observe a decrease in freeness. This means that the curves in Figures 7 and 8 do not give any indication of the rate of refining. The only index which measures the beating acceleration is the sheet density which does not appear in your results.

Allan I have no comment to make on that point.

Dr. I. Thorne DOW Chemical, Rheinmuenster, W. Germany

Could you speculate on what effects these chemicals would have on the dewatering of the sheet in the press section or driers?

Allan No, I know nothing about that.

Dr. D.W. Clayton PPRIC, Pointe Claire, Canada

Did you say you were doing some mill trials on chip refining?

Allan Yes, there is some work being done at a mill, one aspect of which is to add the chemical to the chip washer.

Clayton In your paper, you give the effect of pH on the adsorption isotherms, but you do not say which pH you used in the refining. What value of pH did you use and was it adjusted to a specific value?

Allan No, we just use the ambient pH whatever it ends up as.

Clayton Have you been able to detect a small increase in yield as a result of this adsorption?

Allan There is a Japanese Patent which came out very recently which claims that the addition of this same compound to pulping increases the yield by about 2%.