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Fundamental Investigations of the Biobleaching Interactions Between Xylanase, Ozone, and Dimethyldioxirane

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FUNDAMENTAL INVESTIGATIONS OF THE BIOBLEACHING INTERACTIONS BETWEEN XYLANASE, OZONE, AND DIMETHYLDIOXIRANE.

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ABSTRACT

The synergistic interactions between xylanase pretreatment of kraft pulps and subsequent chemical bleaching reactions were explored with dimethyldioxirane (DMD) and ozone. Laboratory studies indicated the biobleaching process was favorable for either hardwood or softwood kraft pulps. The pretreatment of kraft pulps with xylanase followed by (DMD)E(H_2O_2/H_2NCN) resulted in higher brightness values for the fully bleached pulp. Likewise, xylanase treatments of an oxygen delignified, extended delignified kraft pulp enhanced the bleachability as determined using an OXZ(EO)D bleaching sequence. Interestingly, although the xylanase stage in general reduced the viscosity of the pulps in comparison to control pulps, these differences in viscosity appeared to diminish during the bleaching process.

These studies illustrate the important role that biobleaching processes have on improving the bleaching capabilities of oxygen-based bleaching sequences.

INTRODUCTION

Over the last decade, worldwide concern has developed over the impact that industrial processes, including pulp and paper operations, have on the environment.[1] In response to these concerns, kraft pulping and bleaching operations have begun to modify their operations so as to improve their environmental performance.[2] Although a substantial portion of these research efforts are directed at improving chlorine dioxide-based bleaching operations, research efforts are also ongoing at developing improved oxygen-based bleaching agents. As recently summarized by Forber,[3] although many chemical agents have been examined as bleaching replacements for chlorine, only a selected few appear to possess attractive bleaching properties. Currently, the most promising oxygen-based bleaching agents are molecular oxygen,[4] ozone,[5] hydrogen peroxide,[6] and dimethyldioxirane (DMD).[7]

Fortuitously, developments in nonchlorine bleaching have been paralleled by advances in biobleaching technology.[8] Preliminary research studies by Viikari et al. in 1986 demonstrated that the pretreatment of kraft pulps with xylanase (X) was effective at reducing the charge of chlorine needed to achieve target brightness.[9] From these initial studies, significant resources have been directed toward transferring this technology from the laboratory to the paper mill.[10] Numerous laboratory[11] and mill studies[12] have made it apparent that pretreatment of kraft pulps with xylanase significantly enhances the bleachability of these pulps for chlorine-based bleaching sequences such as (DC)EDED or DEDED.[13]

The development of oxygen-based bleaching agents for kraft pulps opens an alternative avenue of research for biobleaching technology. Based upon the synergism observed between xylanase and chlorine/chlorine dioxide bleaching procedures we had anticipated that biobleaching technologies could improve the bleaching efficiency, pulp properties, and chemical costs associated with oxygen-based bleaching technologies. Indeed, recent research studies in our laboratory have demonstrated that xylanase can substantially improve the bleaching performance of several oxygen-based bleaching agents, including ozone, DMD, and hydrogen peroxide. This paper reviews the results of these exploratory studies.

RESULTS AND DISCUSSION

Xylanase/DMD

Although the fundamental oxidative properties of DMD[14] have been extensively studied, its application as a bleaching agent has been only recently examined. Studies by C.-L. Lee[7b,15] and Ragauskas[7a] have shown that this reagent, generated from peroxymonosulfate and acetone, (see eqn. 1) has exceptional bleaching properties.

eqn. 1)

$$^{-}OO\text{-}SO_3^{-} + CH_3\overset{O}{\overset{\|}{C}}CH_3 \;\text{-->}\; SO_4^{=} + CH_3\overset{O-O}{\overset{\vee}{C}}CH_3$$

(DMD)

Representative delignification properties of DMD are summarized in Table 1. Although several technical challenges must be solved before this process is commercially implemented, recent pilot-plant studies by C.-L. Lee et al.[16] have demonstrated the feasibility of this bleaching system.

Table 1. DMD Bleaching Properties for Kraft Pulp.

Pulp	DMD Charge	Kappa #	TAPPI Brightness
Hardwood	5%		
Brownstock		11.5	29.7
Bleached/Extracted		2.6	44.2
Softwood	5%		
Brownstock		39.5	23.1
Bleached/Extracted		11.9	34.0

Preliminary biobleaching studies by Ragauskas et al.[17] highlighted the synergistic interactions which occur between DMD and xylanase. As shown in Figure 1, pretreatment of a hardwood kraft pulp with xylanase prior to bleaching with distilled DMD was shown to be exceptionally beneficial in terms of delignification and brightness development for the enzyme treated pulp. To ensure that the results of the enzymatic treatment were not due to subtle hydrolysis effects, all of the control pulps were processed in an analogous manner as the X-stage except that the protein was not added (W-stage).

Pretreatment of a softwood kraft pulp with xylanase was also shown to be beneficial for subsequent bleaching reactions of

DMD as shown in Figure 2.

Figure 1. Synergistic delignification properties for xylanase and DMD treatments of a hardwood kraft pulp.

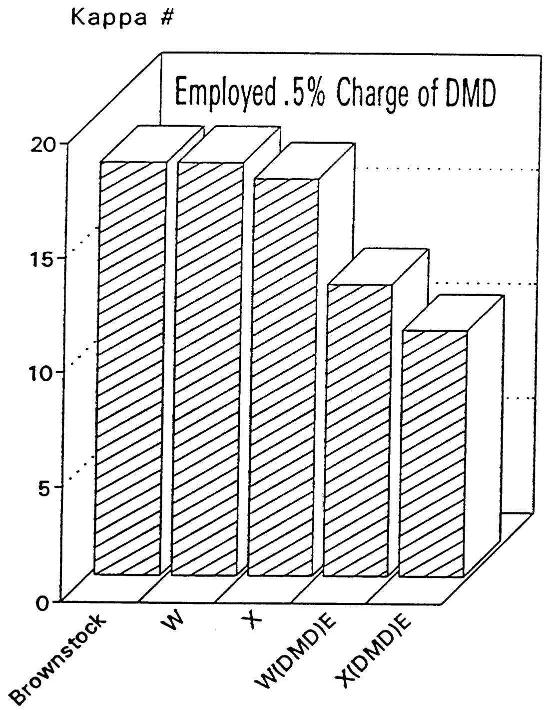
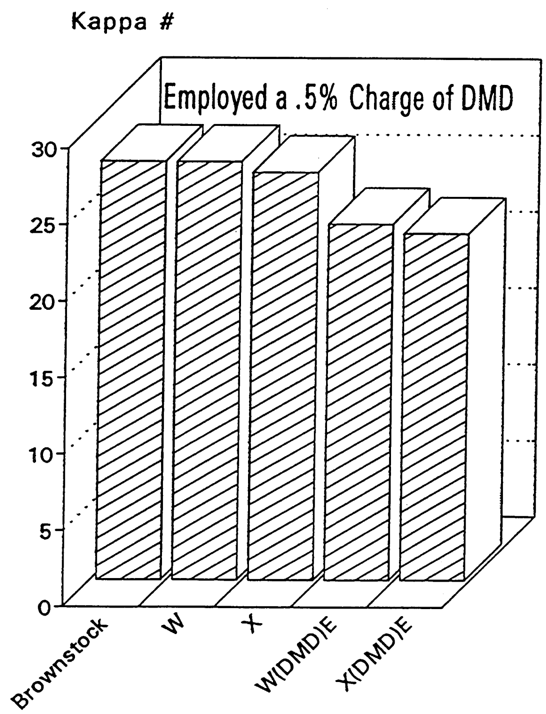
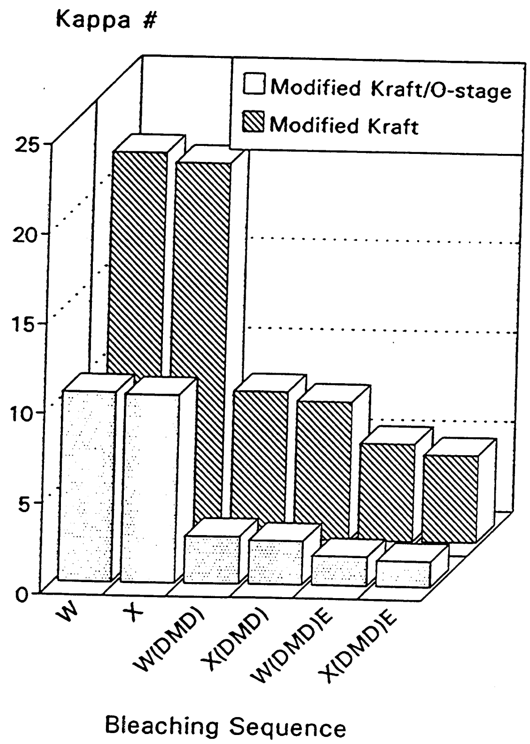


Figure 2. Synergistic delignification properties for xylanase and DMD treatments of a softwood kraft pulp.



Although these results were promising, practical considerations[18] require that DMD bleaching operations be accomplished employing *in-situ* generated DMD and that the bio-bleaching treatment be compatible with this latter approach. Furthermore, recent studies[19] have suggested that *in-situ* DMD and distilled DMD exhibit subtle differences in their bleaching properties. To determine if the previously observed biobleaching results are transferrable to *in-situ* DMD bleaching procedures, we prepared a series of xylanase-treated softwood and hardwood kraft pulps. The pulps employed for these bleaching experiments were acquired from commercial operations and consisted of a southern softwood modified kraft (kappa # 21.2), an oxygen delignified southern softwood modified kraft (kappa # 10.7) and a hardwood kraft pulp (kappa # 11.7). After the enzyme treatment the pulps were bleached with *in-situ* generated DMD employing a 15% charge of peroxymonosulfate. These pulps were then extracted with alkaline solution and further treated with peroxide bleaching agents in an attempt to generate 80+ brightness pulps. The results of the enzyme-pretreated kraft pulps were then compared against analogous series of bleaching experiments employing control pulps.

Figure 3. Xylanase/*in-situ* DMD delignification effects for softwood kraft pulps.



DMD stage employed a 15% charge of peroxymonosulfate

Figure 4. Xylanase/*in-situ* DMD brightening effects for softwood kraft pulps.

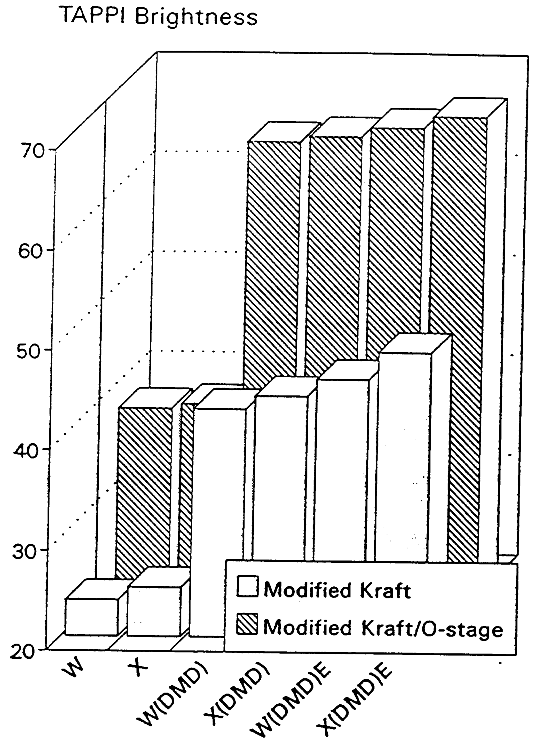
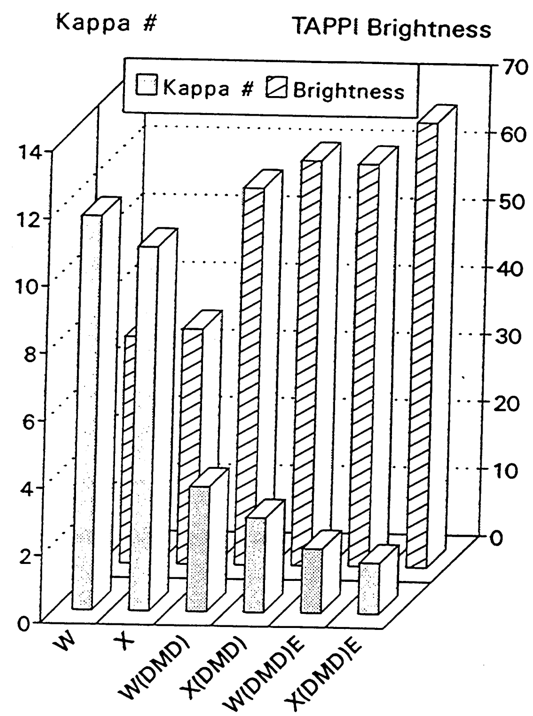


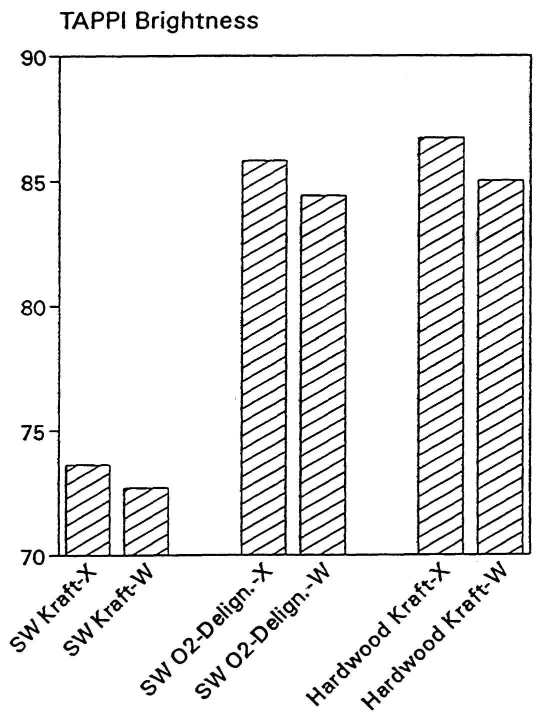
Figure 5. Xylanase/*in-situ* DMD bleaching effects for hardwood kraft pulps.



As summarized in Figures 3, 4, and 5, all three of the hardwood and softwood kraft pulps exhibited promising bioboosting effects when treated with *in-situ* DMD. Examination of the delignification results indicate that despite the relatively large charge of *in-situ* DMD employed in these studies the enzyme-treated pulps continued to exhibit modest enhancements in the extent of delignification. Of greater practical interest was the observation that the xylanase-treated pulps also yielded higher brightness values both after bleaching and caustic extraction.

To further explore the bleachability of these pulps, we treated the X(DMD)E and W(DMD)E pulps with a 3% charge of hydrogen peroxide/H_2NCN (Pn-stage). Nitrilamine has been shown to be an activator for hydrogen peroxide,[20] enhancing the brightening and delignification reactions of peroxide. Treatment of either the hardwood or oxygen-delignified kraft pulps yielded favorable responses as shown in Figure 6.

Figure 6. Brightness properties for X(DMD)E(Pn) and W(DMD)E(Pn).



Examination of the bleaching results for the hardwood kraft pulp and the oxygen-delignified softwood kraft pulp indicate that the enzymatic pretreatment procedure was beneficial for the production of 80+ brightness pulp. Although the higher kappa softwood kraft pulp also exhibited benefits from the xylanase pretreatment procedure the nitrilamine/peroxide stage did not yield an 80+ brightness values. These results were presumably due to the substantial amounts of lignin remaining prior to the Pn-stage. Indeed, if the same sequence is repeated and the charge peroxymonosulfate is doubled for the *in-situ* generation of DMD the lignin content of the pulp prior to last peroxide stage is comparable to that reported for the oxygen-delignified kraft pulp and responds equally well to the Pn-stage.

The overall changes in viscosity for the bleached pulps are summarized in Table 2. These results indicate that the X-stage does slightly reduce the viscosity of the incoming pulps for the two low kappa pulps examined, and these results appear to carry over into the fully bleached pulps.

Table 2. Selected Viscosity Values for Biobleached Pulps.

Viscosity/mPas Pulp	X/W	X(DMD)E(Pn)/W(DMD)E(Pn)
Hardwood	20.3/22.5	12.8/14.0
O_2 Delig. Softwood	19.5/22.1	12.7/14.1
Softwood	22.3/22.2	10.2/9.6

In summary, the application of xylanase prior to bleaching with *in-situ* DMD offers a unique method of improving the delignification and brightening properties of this promising bleaching agent. The observed bioboosting properties for the *in-situ* generated DMD stage are not transient and are beneficial during subsequent bleaching treatment.

Xylanase/Ozone

Among the many alternative bleaching agents for TCF bleaching, few have generated as much interest as ozone.[21] Research developments over the last few years have rapidly allowed for commercial application of this agent for a variety of pulps.[22] Although most research activities are directed toward developing a high brightness TCF kraft pulp, commercial operations have shown that ozone is also a viable agent for ECF bleaching sequences.[23] Research activities in this laboratory[24] along with Eriksson[25] and others[26] have shown that xylanase pretreatment procedures can effectively improve ozone-based TCF bleaching sequences. This report summarizes our recent studies directed toward improving ECF ozone-based bleaching sequences by pretreating kraft pulps with xylanase.

Following the general experimental approach highlighted in the previous section, a commercial southern softwood, extended delignified kraft pulp was oxygen delignified following standard laboratory procedures. The resulting pulp was split into two samples and treated with either xylanase or a control wash treatment. This pulp was then ozonated with a 0.6% charge of ozone and extracted with an (EO) stage. Analysis of the lignin content of these pulps for the control and enzyme-treated pulps indicated that xylanase pretreatment removed 7% of the lignin, and these pulps exhibited moderately improved delignification and brightening properties during the Z and (EO) stages, as summarized in Figure 7.

Figure 7. Xylanase/Ozone biobleaching effects on delignification and brightening properties.

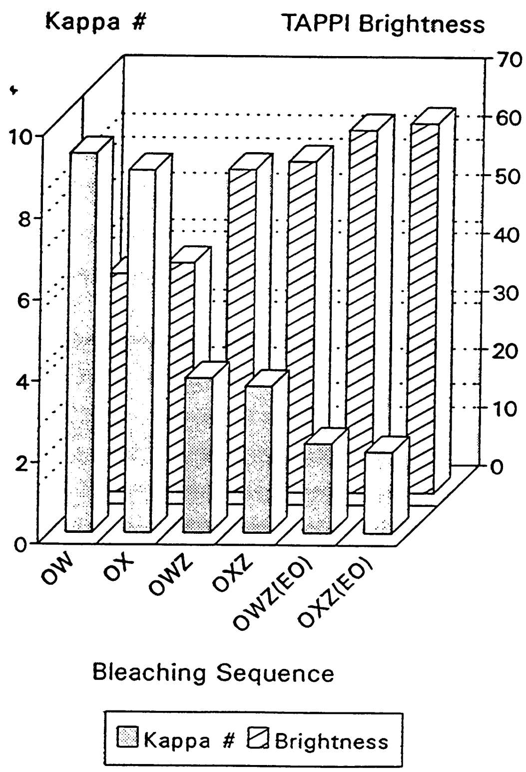
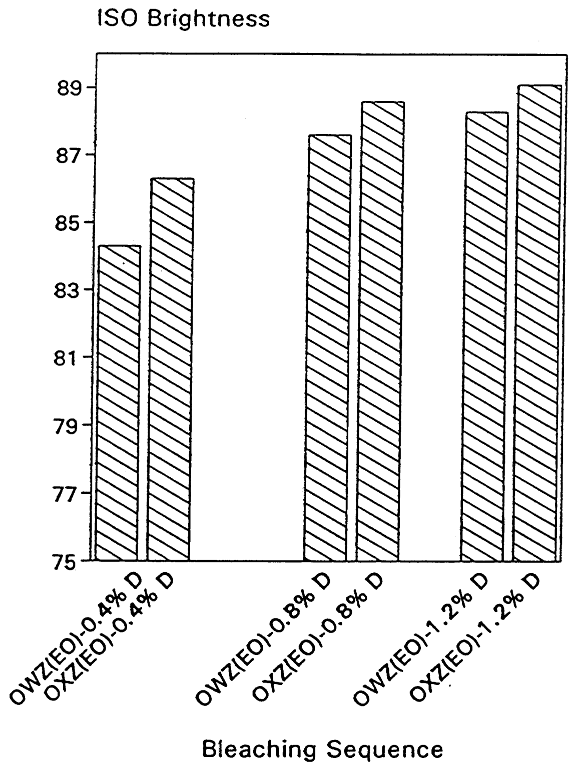


Figure 8 summarizes the response of these pulps to three different charges of chlorine dioxide. The brightness data clearly indicate that the xylanase-pretreated pulps yielded higher brightness pulps, although the results are most favorable for the low chlorine dioxide charge.

Figure 8. Brightness evaluations for OXZ(EO)D and OWZ(EO)D bleached pulps.



The viscosity properties for the control and enzyme-treated pulps bleached with OXZ(EO)D or OWZ(EO)D sequences are summarized in Table 3. Examination of these results indicate that the biobleaching effects are accompanied by a decrease in the viscosity of the pulp. Interestingly, the differences in viscosity apparently are reduced after each subsequent stage of bleaching with ozone, alkaline extraction, and chlorine dioxide.

Table 3. Viscosity Changes for OXZ(EO)D and OWZ(EO)D Bleached Pulps.

Pulp[a]	X	W	Z	(EO)	D[b]
X	18.9	-	12.4	10.6	10.8
W	-	-	13.2	11.5	10.5

[a]viscosity of the starting oxygen delignified softwood kraft pulp was 19.8 mPas; [b]viscosity values for 1.2% D charge.

In summary, pretreatment of kraft pulps provides a convenient method of improving the overall bleaching properties of ozone not only for TCF bleaching sequences but also for ECF scenarios.

SUMMARY

The studies reported in this paper suggest that xylanase pretreatments provide a unique method of improving the bleaching properties of DMD and ozone. Both hardwood and softwood kraft were shown to exhibit improved bleachability after the X-stage, yielding higher brightness pulps for a given chemical charge. Although occasionally the enzyme pretreatment procedure yielded lower viscosity pulps, these effects appear to diminish once the pulps are bleached to 80+ brightness values.

EXPERIMENTAL METHODS

Pulps and Materials

Bleaching experiments employed commercial, never-dried kraft pulps. Chemical supplies such as oxone™, $NaHCO_3$, acetone, NaOH, H_2SO_4, and H_2NCN were commercially purchased and used as received. The xylanase preparation was kindly provided by ICI, Canada.

DMD Bleaching Reactions and Caustic Extractions

The *in-situ* DMD bleaching reactions were preformed following the experimental procedure described by Ragauskas[7] employing a 1:1 ratio of acetone and water, and a 30% charge of oxone™. Caustic extractions (2% NaOH charge) were carried at 70° C, 10% consistency for 1 h. Physical characterization of the pulps in terms of brightness, lignin content, and viscosity was accomplished following standard testing methods.[27]

Note: All DMD reactions result in the generation of organic peroxides, and these experiments were carried out in accordance with the generally recommended laboratory procedures for handling peroxides.[28]

Xylanase (X) and Control Wash (W) Stages

The xylanase pretreatment stage followed standard literature methods employing pulp at 10% consistency, 2 IU of xylanase/gram of dry fiber, and treating the mixture for two hours at 70° C. Control pulps (W-stage) were treated in an analogous manner except that the enzyme was not added to the mixture.

H_2NCN, Ozone and Chlorine Dioxide Bleaching Procedures

Nitrilamine bleaching procedures were preformed following the general methods described by Sturm and Kuchler[20] employing a 3% charge of H_2O_2, 0.5% charge of nitrilamine, 2.5% charge of NaOH. The pulp mixture (10% consistency) was sealed in a polyethylene bag and placed in a isothermal, 70° C water bath for 2 h. The bleached pulp was removed, filtered and analyzed.

The ozonolysis procedure[24] employed for these studies used a modified roto-evaporator to treat the pulp (high consistency) with a 0.6% charge of ozone at pH 2.5. After bleaching the pulp samples were washed with water and analyzed.

The (EO) stage was preformed at 10% consistency, 1% caustic, and 60 psi for 1 1/2 h.

The final D-stage bleaching treatments, free of chlorine were employed for the ECF bleaching experiments. The bleaching solution was prepared by calculating the amount of free chlorine in the solution and adding stoichiometrically equivalent amounts of sodium chlorite. All chlorine dioxide bleaching experiments were preformed in Mason jars, at 6% consistency, 70° C, 3 h and pH 3.5.

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