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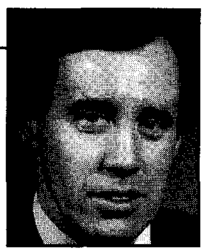
COMPARISON OF THE PERFORMANCES OF WATER- AND OIL-BASED DEFOAMERS

Test defoamers using the process liquid of the mill concerned

BY S-D. CLAS AND L.H. ALLEN

S-D. Clas, Paprican, Pointe Claire, QC. (Now with Merck Frosst Canada.)



L.H. Allen, Paprican, Pointe Claire, QC.

RECENT YEARS have seen a rekindling of interest in the use of water-based brownstock defoamers in the unbleached area of kraft pulp mills. This has been motivated partly by the unfortunate tendency of oil-based defoamers to deposit [1], especially if used at higher than average feed rates (average = 0.9 kg/t [2]). Another factor has been the wish to avoid the possibility of introducing chlorinated dioxin precursors with defoamer oils [3,4], although most defoamer manufacturers are now using oils free of these contaminants.

For many defoamer manufacturers, this has meant re-introducing to the market old formulations, usually involving silicone oils, that were used in unbleached stock before the advent of the more cost-effective oil-based defoamers [5]. Other manufacturers claim to have made substantial improvements in the technology of water-based defoamers [e.g., 6,7]. The question remains, however, whether water-based defoamers are actually as cost-effective as oil-based ones in combatting foam. Certainly, avoiding the petroleum oils of conventional brownstock defoamers by resorting to a water-based technology is a sound approach to circumventing the dioxin precursor problem.

Nevertheless, our laboratory experiments have indicated that some water-based, silicone defoamers deposit even more readily than oil-based ones [8].

The objective of the work presented in this report is to determine with a laboratory defoamer testing apparatus how effective water-based defoamers are at combatting foam, relative to oil-based defoamers. The apparatus used consisted of a reservoir for the foaming solution (e.g., diluted kraft black liquor) and a recirculation line through which it was pumped and re-introduced into the reservoir via a nozzle pointed into the liquid surface so as to entrain air, Fig. 1. Several other techniques exist to test for foaming and the efficiencies of defoamers. These include the Ross-Miles foam tester [9], which does not work well for oil-based defoamers and a method which uses a sparging unit in the foamant [10]. The method that we used is employed widely by defoamer manufacturers and suppliers.

Four different kinds of brownstock defoamer are presently manufactured [5,11-14]: oil-based, water extended, water-based (containing > 50% water), and water-based (no oil). To be cost-effective, they must be efficient both at destroying foam (defoaming) and at preventing foam formation (antifoaming). The defoamer tester employed in this work enabled both of these aspects to be evaluated for each defoamer. Seven defoamers, encompassing the three most commonly used kinds of defoamer were examined.

EXPERIMENTAL

Materials: Kraft black liquor was obtained from the pilot plant digester from cooks of lodgepole pine, Table I. Prior to use it was filtered through a 200-mesh screen.

Defoamers, both oil-based and water-based, were kindly supplied by several manufacturers. Further information on the seven defoamers tested is provided in Table II.

Many defoamer suppliers use synthetic black liquor for preliminary in-lab trials and quality control before going to the mills. A typical formulation for synthetic black liquor includes 3.5% lignosulphonate, 3.5% detergent and 3.5 % sodium carbonate in water. A 2% solution of this in water was used in the aerator to provide a stable and reproducible foam.

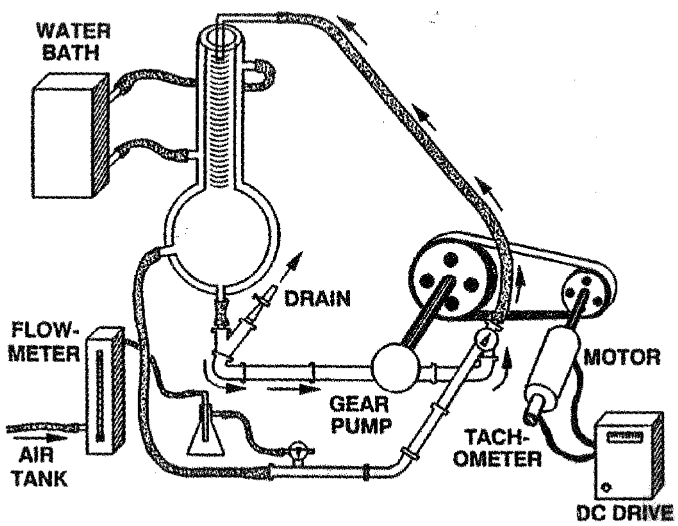
Defoamer testing apparatus: The defoamer tester, Fig. 1, was built using a design kindly given by B. Lajambe of Buckman Laboratories. It consisted of a glass cylinder (graduated in mm) attached to a

TABLE I. CHARACTERIZATION OF LODGEPOLE PINE KRAFT BLACK LIQUORS.

Length of cook (min)	189
Temperature of cook (°C)	171
H Factor	1.84×10^3
pH	13.1
Kappa Number of pulp	31.7
% Solids	14
Concentration of lignin (g/L)	54.2

TABLE II. DEFOAMERS TESTED.

Defoamer	Description
A	Water-based, containing silica particles.
B	Water-based, no hydrocarbon oil.
C	Water-based, containing silicone oil.
D	Water-based, containing silicone oil.
E	Oil-based, hydrophobic silica plus amide wax particles.
F	Oil-based.
G	Oil-based.



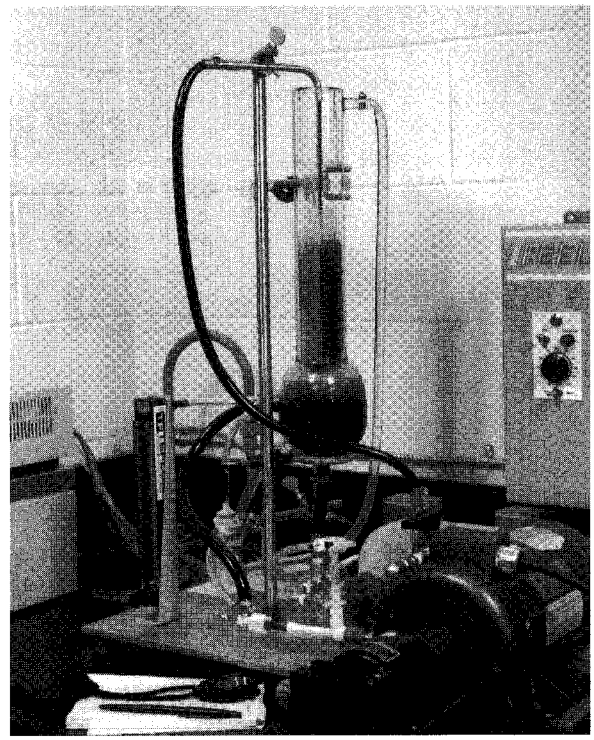


FIG. 1. DIAGRAM AND PHOTOGRAPH OF THE LABORATORY DEFOAMER TESTER. IN THE INVESTIGATION, THE PROVISIONS FOR INJECTING AIR FROM A TANK WERE NOT USED.

reservoir. The design was modified slightly to provide a column of steady foam with which to make reproducible measurements at constant temperature.

The idea for the shape of the glass reservoir was obtained from conversations with R.E. Patterson of PQ Corporation and from one of his publications [15]. A gear pump was used to provide constant circulation of the black liquor. Stainless steel tubing was used for connections to the pump. Elsewhere, Tygon tubing was used. A Baldor (Baldor Electric Co., Ft. Smith, Ark.) dc motor (187 W) fitted with a Beel control box (Series 600, Beel Electronics, Montreal) was found to provide reproducible output.

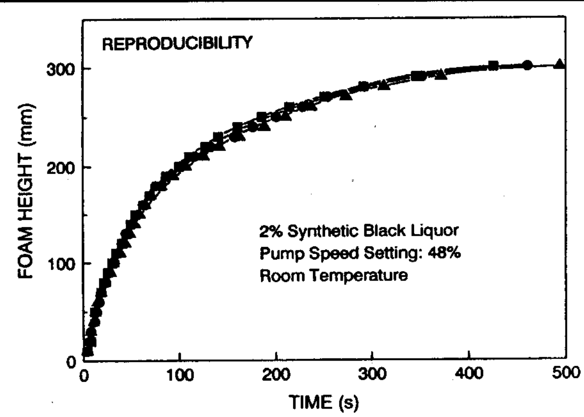


FIG. 2. TEST FOR REPRODUCIBILITY OF FOAM HEIGHT DURING THREE RUNS WITH A 2% AQUEOUS SOLUTION OF A SYNTHETIC BLACK LIQUOR.

Method: Prior to all experiments, water was added to the apparatus using a hose attached to the top of the reservoir and the motor was allowed to run for at least 5 min. The water was drained from the reservoir and the side arm for 5 min. It was important to be consistent as there was always a certain small amount of water trapped in the aerator. The drain was closed after 5 min. To the apparatus in Fig. 1 was added the foamant (600 mL), for example, 10% kraft black liquor in deionized water previously heated to the desired temperature. For most experiments a temperature of 60°C was chosen as representative of the temperatures occurring in the washers. Higher temperatures do occur in the early stages of washing; however, this was the most easily attainable temperature with the tester.

The black liquor was added slowly down the sides of the reservoir to prevent foaming. The black liquor was equilibrated in the thermostatted column for 5 min. For a foamant to be effective it was necessary that the foam build up in a reasonable time which was measurable, generally of the order of at least 200 seconds to reach a foam height of 300 mm.

This was rapid but it gave easily measurable times when defoamers were added. Otherwise, large errors are introduced. For synthetic black liquor, a 2% blend was found to be useful, while 10% aqueous solutions of kraft black liquor from white spruce and lodgepole pine were found to provide reproducible results.

To conduct a run, the pump speed setting was adjusted (e.g., to 50%). The timer was started after the foam had built up to 100 mm, at which time the defoamer was added under the shower using a Hamilton 10 µL, Model 701 syringe without a needle (10 µL was used unless otherwise specified, corresponding to a 0.8 kg/t defoamer feed rate at 2% pulp consistency). This method allowed measurement of the defoaming action (the ability of the defoamer to destroy already established foam) and also measurement of the antifoaming efficiency of the defoamer (or foam prevention ability). Duplicate experiments were carried out in all cases.

At the end of each experiment, the apparatus was rinsed with copious amounts of water by circulation through the side-arm and the tubing to the shower. When defoamer was used, the apparatus was rinsed with water, then with 10% sulphuric acid, followed by more water. This was repeated until the aerator was clean.

Immediately after the construction of the defoamer testing apparatus, initial experiments were performed to calibrate the pump and to determine the effects of pump speed, pH, and temperature on the foam formation of 10% black liquor in deionized water, and on the defoaming and antifoaming efficiencies of defoamers. The results are reported in the Appendix*. The output of the pump, measured at the nozzle (7 mm i.d.), was a linear function of the pump speed setting from 20 to 100%. At the 50% setting, the flow rate of water was 50 mL/s (Appendix).

RESULTS & DISCUSSION

Reproducibility: The build-up of foam occurred in spurts rather than as a continuous process. The defoamer tester was checked for its reproducibility using both synthetic black liquor and kraft black liquors, diluted with deionized water, to 2 and 10%, respectively. Excellent reproducibility was obtained using synthetic black liquor, Fig. 2.

However, if the time to reach an arbitrarily chosen foam height, such as 250 mm, was used, as is often the case in industry, then a 10% difference in foam heights was obtained. This may go as high as 20% when kraft black liquor is used, Fig. 3. Good reproducibility was obtained with defoamer. In all cases, duplicate experiments were carried out for each run.

Comparison of performances of water-based and oil-based defoamers: The defoaming and antifoaming efficiencies of the defoamers in 2% synthetic black liquor are shown in Fig. 4. The defoaming efficiency or foam knock-down is defined as the ability of the defoamer to destroy already formed foam, which occurs immediately on addition of defoamer. The foam then builds up again. The ability of the defoamer to retard this build-up is defined as the antifoaming efficiency.

In 2% synthetic black liquor, two of the water-based defoamers (C and D) demonstrated the best defoaming efficiencies. Defoamer A did not show any defoaming or antifoaming action at the chosen concentration of addition. Doubling the amount of defoamer A improved the defoaming efficiency; however, it did not prove to be as efficient as the other defoamers under these conditions. Oil-based defoamer E

* *All of the information contained in the Appendix is available from the Technical Section, CPPA, Databank on request, free of charge. Alternatively, this paper has been printed, complete with Appendix, in the preprints of the 79th Annual Meeting of the Technical Section of the CPPA.*

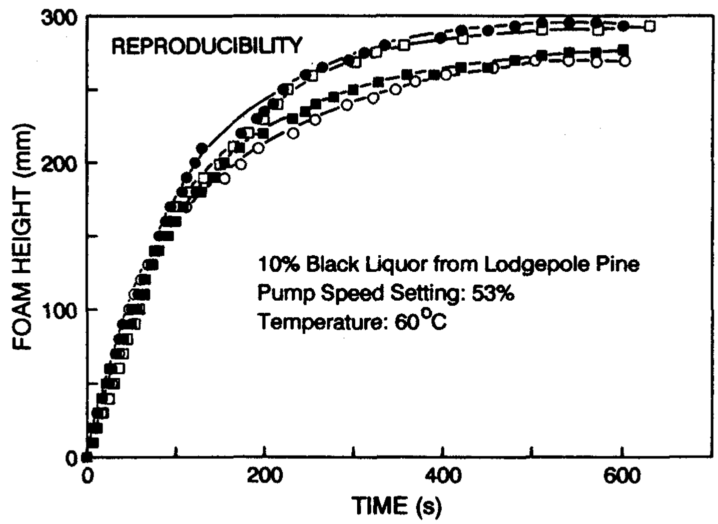


FIG. 3. TEST FOR REPRODUCIBILITY OF FOAM HEIGHT DURING FOUR RUNS WITH A 10% AQUEOUS SOLUTION OF A KRAFT BLACK LIQUOR.

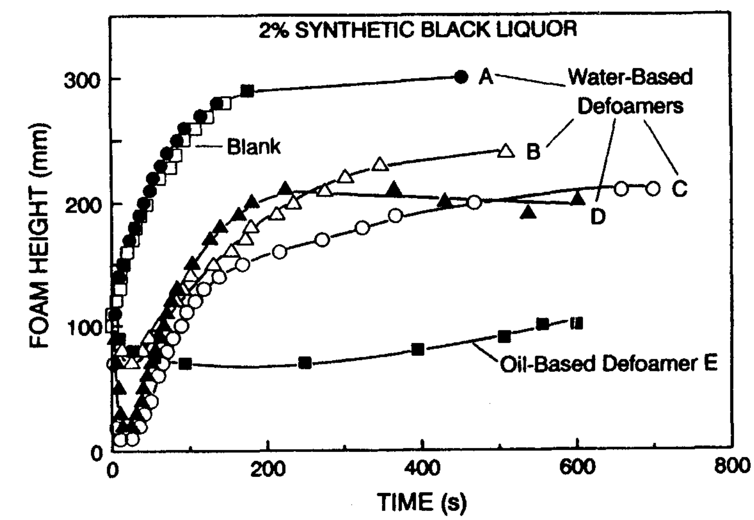


FIG. 4. FOAM HEIGHT AS A FUNCTION OF TIME FOR THE SYNTHETIC BLACK LIQUOR, ALONE (BLANK) AND WITH VARIOUS DEFOAMERS.

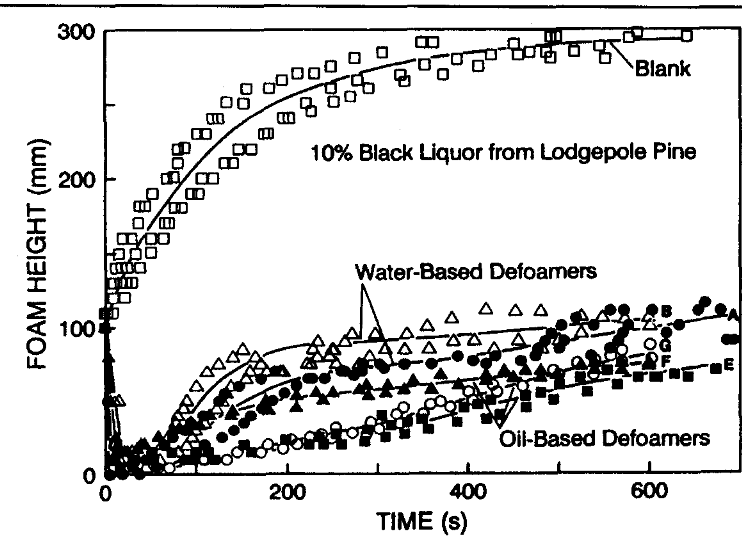


FIG. 5. FOAM HEIGHT AS A FUNCTION OF TIME FOR THE KRAFT BLACK LIQUOR, ALONE (BLANK) AND WITH VARIOUS DEFOAMERS.

proved to be the best defoamer at maintaining low foam heights but it did not have as good a knock-down ability as did water-based defoamers C and D.

The completely oil-free defoamer B had poor knock-down but had similar antifoaming efficiencies to defoamer D up to 300 s. Thus, in this set of experiments the best knock-down of the foam was obtained with silicone oil-containing water-based defoamers C and D.

Similar experiments using 10% lodgepole pine black liquor, Fig. 5, demonstrated that there was very little difference between the water-based defoamers tested, that is, defoamer A containing silica particles and defoamer B with no oil. The water-based defoamers studied demonstrated excellent foam knock-down in the first 50 s, Fig. 6, but they did not appear to be as effective antifoaming agents as oil-based defoamers E, F, and G. Two of the oil-based defoamers, E and G, were equally effective at destroying foam and at preventing foam formation at less than 400 s. Oil-based defoamer F was not as efficient at times less than 400 s.

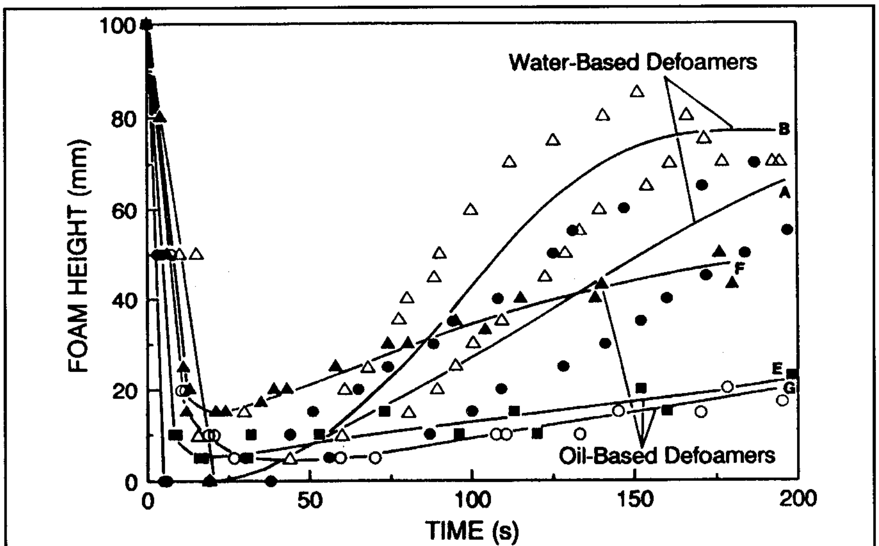


FIG. 6. ENLARGEMENT OF THE LOWER LEFT-HAND PORTION OF FIG. 5, WHICH SHOWS MORE CLEARLY THE DIFFERENCES IN THE INITIAL EFFICIENCIES OF THE VARIOUS DEFOAMERS.

CONCLUSIONS

The defoamer tester has proven to be useful to study the defoamer and antifoaming efficiencies of different defoamers, both water- and oil-based. The apparatus can be used both with synthetic kraft black liquor and kraft black liquor. It is reproducible and can be used at different temperatures, pH values, and shear rates. The relative efficiencies of water- and oil-based defoamers depended on the type of foamant. Thus, it is better to test defoamers using the process liquid of the mill concerned at the proposed point of defoamer addition to determine which defoamer is best for that particular mill. In general, oil-based defoamers were more effective at keeping the foam from forming; that is, their antifoaming efficiencies were better than those of water-based defoamers.

On the other hand, water-based defoamers had slightly better initial knock-down of foam under the conditions used.

The decision of whether or not to use a water-based defoamer must take into consideration the points of air entrainment, foam formation and defoamer addition. In instances where defoamer is added to stock with a lot of pre-formed foam, the superior knock-down properties of water-based defoamers may be advantageous. On the other hand, if the defoamer is added upstream of the point of foam formation and the situation requires a good hold-down of foam, oil-based defoamers would probably be superior. Observation of industry experience suggests that, in the majority of brownstock applications, the oil-based defoamers are more cost-effective.

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Résumé: L'efficacité respective de quatre antimousses commerciaux de pâte brune à base d'eau et de trois autres à base d'huile a été mesurée en laboratoire à l'aide d'un appareil d'essai d'antimousse. Les mesures ont été prises avec une lessive noire kraft et une lessive noire synthétique. Les antimousse à base d'huile d'hydrocarbure se sont généralement avérés plus efficaces pour empêcher la formation de mousse; c'est-à-dire que leur efficacité antimousse était plus grande que celle des antimousses à base d'eau. Cependant, les antimousses à base d'eau avaient un effect initial de réduction de la mousse légèrement meilleur dans les conditions utilisées.

Abstract: The efficiencies of four water-based and three oil-based commercial brownstock defoamers have been measured with a laboratory defoamer tester. Measurements were done with both a kraft black liquor and a synthetic black liquor. Hydrocarbon oil-based defoamers were generally more efficient at keeping foam from forming; that is, their antifoaming efficiencies were better than those of water-based defoamers. On the other hand, water-based defoamers had a slightly better initial knock-down of foam under the conditions used.

Reference: CLAS, S-D., ALLEN, L.H. Comparison of the performances of water- and oil-based defoamers. *Pulp Paper Can* 95(1): T14-17 (Jan. 1994). Paper presented at the 79th Annual Meeting, Technical Section, CPPA, at Montreal, QC, on January 26 to 29, 1993. Not to be reproduced without permission. Manuscript received December 8, 1992. Revised manuscript approved for publication by the Review Panel, September 15, 1993.

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