PERFORMANCE OF A NEW POLYETHYLENE GLYCOL (PEG) ADDITIVE FOR CCA TREATED RED PINE POLES

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ABSTRACT

CARBOWAX® PEG PLUS™, a new additive for CCA solutions, was more effective at reducing Pilodyn penetration hardness of red pine than PEG-1000. It also resisted leaching from water spray exposure more effectively and did not destabilize the treating solution as rapidly. The rate of kiln drying of pole sections was not significantly affected by addition of either PEG 1000 or PEG PLUS™ additive to the CCA treating solution. Gross solution absorption was not affected by the PEG additives. The CCA concentration gradient appeared to be steeper in red pine pole sections treated with CCA/PEG compared to CCA only treated pole sections.

1. Background

Chromated copper arsenate (CCA) treatment of poles was perceived to increase the hardness of the wood surface (Trumble and Messina 1985). The climbability properties of CCA treated poles can be improved by use of additives to the CCA treating solution. Polyethylene glycol (Trumble and Messina 1985), emulsified oil (Engdahl et al 1992) and wax micro-emulsions (Zahora and Rector 1990) have all proven effective in reducing pole surface hardness and enhancing climbability.

While the PEG 1000 additive provides softening that persists for several years and is the accepted treatment for pine poles by many utilities in Canada, the softening effect may be reduced eventually due to leaching of PEG. Furthermore, this additive accelerates the destabilization of CCA working solutions due to reaction between the CCA components and the PEG.

This paper presents the results of an evaluation of an alternative PEG formulation (CARBOWAX® PEG PLUSTM) developed to reduce or eliminate the above problems.

2. Materials and Methods

Preparation and the Treatment of the Red Pine Poles

Seven red pine (*Pinus resinosa Ait*) poles were evaluated. For each pole, two meter long pole sections were acquired from the butts, midsections and tops of newly air dried poles. Each pole section was cross cut into three 0.6 m long pieces to provide end-matched specimens for the different treatments to be evaluated. Two 25 mm thick discs were cut at the same time and their moisture contents determined by the oven drying method. These moisture content values were used to estimate the initial moisture content and oven dry mass of each shorter section. Both ends of the sections were sealed with two coats of an alkyd based paint to control end penetration and end drying. Each pole section was characterized for hardness by taking four measurements with a calibrated 6 Joule Pilodyn instrument.

For each red pine pole, and each location within a pole, end-matched sections were randomly assigned to one of the following treatments:

- Full cell treatment (0.5 h. initial vacuum at 24 in. Hg. (20 KPa); 1.0 h. pressure at 150 psi (1034 KPa); 0.5 h. final vacuum at 24 in. Hg. (20 KPa)) with 2.0% CCA-C.
 - Full cell treatment as above with 2.0% CCA-C/4.0% PEG 1000.
 - Full cell treatment as above with 2.0% CCA-C/4.0% PEG PLUS™.

All pole sections were treated in a 0.4 m diameter 1.2 m long experimental retort (2 sections at a time).

CARBOWAX PEG PLUSTM Softness Measurements

Following treatment, all pole sections were wrapped in plastic and stored at room temperature for 30 days to ensure that fixation of the CCA preservative was complete. Twelve sections (top, middle and bottom sections from four poles) were kiln dried in an experimental dry kiln under constant conditions (DB/WB = 60/43°C). Pole sections were weighed periodically and when the estimated moisture content of a section reached 30%, 25%, 20%, 15% and 10%, its hardness was re-evaluated. Also, as each moisture content was reached, a 10 mm diameter increment core was taken and the moisture content gradient determined at 25 mm increments using the oven drying method.

Phase 1 Accelerated Leaching Study - Set up and Softness Measurements

In order to compare the leaching effect of PEG on the softness of poles and the relative leaching stability of the PEG 1000 and the PEG PLUSTM treated poles, sections from the 3 remaining poles were assigned to an accelerated leaching cycle. This phase 1 accelerated leaching study was based on the total amount of rainfall for the last 12 years in southern Ontario. Pole sections were air dried in the laboratory to about 45% MC then placed upright in a polyethylene lined chamber and exposed to a uniform misting spray for six weeks. A total of approximately 17.8 m (700 inches) of fine spray was applied. After the

leaching period, the pole sections were air dried to estimated moisture contents of 35%, 25% and 20% and Pilodyn hardness determined at each moisture condition.

PEG Analysis

The PEG contents of selected leached and unleached pole sections were determined by high pressure liquid chromatographic (HPLC) analysis of the hot water extracts of treated wood. Ten mm diameter borings were taken from the pole sections before and after the test and cut at 25 mm intervals from the surface. The samples were ground in a Wiley mill to pass a 40 mesh screen and extracted with 50 ml hot distilled water for 60 minutes. The extract was analyzed by Waters 510 HPLC equipped with a Water 410 differential refractometer detector and Walters Ultra Hydrogel Permeation columns (500, 250 and 120) with known standards.

CCA PEG Stability Evaluation Procedure

One litre samples of each treating solution were stored at 21°C and the pH measured and the hexavalent chromium contents determined periodically by meter and by the diphenylcarbazide procedure (ASTM. 1987) respectively. Filtered samples were also analyzed for all CCA components by X-ray fluorescence spectroscopy (ASOMA Instruments Inc.) immediately after the sections were treated and 8 weeks later.

Phase 2 Simulated Leaching Study

In the Phase 2 simulated leaching study, a more elaborate set up was established to simulate the wet and dry cycles of the Ontario climatic conditions in Canada.

Samples Preparation

In this study, twelve 5 ft. long pole lengths, 6 of each commercially treated with CCA/4% PEG 1000 or CCA/4% PEG PLUSTM by LPB Poles were used. After removing the top 8 inches for each pole section to avoid the effect of end penetration, they were cut in midpoint. Then the two pole sections from each length were end-coated with two coats of alkyd paint. After the pole sections were labelled, they were randomly assigned to one of three groups of samples for leaching and drying exposure.

Simulated Leaching Set Up and Conditions

The design and the set up of the simulated leaching chamber is shown in Figure 1. It was essentially a large polyethylene container with spray nozzles (represented by sets of triangular arrows) fixed to the top of the container. The leaching cycle consisted of intermittent misting recirculated water spray (20 L of water recirculated at a rate of 20 L/min. This corresponds to a vertical rainfall rate of 150 mm/h as determined by water traps) and rest periods selected to approximately represent the ratio of rain and non rain days in Ontario. The use of a timer allowed 1 full hr. of misting and 3 full hrs. of resting (or non misting period). Each leaching cycle lasted 7 days with 8 pole sections (4 of CCA/PEG 1000 and 4 of CCA/PEG PLUSTM) distributed evenly around the leaching chamber. In order to ensure even misting on each pole section, the poles in the test chamber were rotated 180° on a turnable metal disc every 12 hours and moved 1 position clockwise every 24 hours.

After each leaching cycle, the pole sections were air dried at 21° C for 14 days in a dry kiln with only the kiln fans operating. In total, 4 cycles (each cycle represented 7 days in the leaching chamber) of leaching were conducted on each set of 8 pole sections to simulate approximately 15 years of wet and dry weathering condition in Ontario, Canada.

In summary, the measured water application rate was approximated at 150 mm (6") per hour, 900 mm (36") per day or 6300 mm (248") per cycle. Based on the 4 cycles used in the study, a total of 992" of rain had been used for the leaching purpose.

Sample Taking and HPLC Analysis

Before the onset of the leaching test, a marker pen was used to divide the circumference of each of the pole sections into six equal parts. The divisions were extended down the length of the pole to serve as reference lines for rotating the poles and for sample taking. Borings were taken to the full depth of treated sapwood at random locations on or near the reference lines using a 3/8 inch plug cutter before and after each leaching exposure. Only the first 25 mm (1 inch zone) of wood sample from each pole section was analyzed because this area was shown to be most sensitive to leaching as indicated by the phase 1 leaching study. All samples were oven-dried and ground in a Wiley mill for PEG extraction and HPLC analysis as mentioned above. Holes resulting from the sampling process between cycles were sealed with silicone caulking to prevent the water mist from entering the holes during subsequent leaching cycles.

Samples of the water were also taken at the end of each cycle for the HPLC analysis of PEG. However they were found to contain only trace amount of PEG 1000 or PEG PLUSTM at or below the detection limit of the analytical instrument.

3. Results and Discussion

CCA/PEG Retentions and CCA Gradients

The results of treatment, based on solution absorption are summarized in Table 1.

The presence of either PEG 1000 or PEG PLUSTM additive did not appear to affect gross CCA absorption. However, X-Ray fluorescence gradient analysis of the red pine pole sections suggest that incorporation of PEG in the treating solution resulted in a steeper CCA gradient in poles of this species (Figure 2).

Effect of Treatment and Moisture Content on Softness - Unleached Samples

For the unleached samples, both PEG 1000 and PEG PLUSTM additive treatments resulted in deeper Pilodyn penetrations in treated and partially dried red pine specimens at all moisture contents (Figure 3). Except at 45% MC, PEG PLUSTM treated specimens were significantly softer than PEG 1000 treated ones. For all treatments, the poles became harder as they dried out. However, even at 10% MC, the PEG PLUSTM treated pole sections were softer than the untreated wood at 17% MC.

Effect of Treatment and Moisture Content on Softness and PEG Concentration - Phase 1 Accelerated Leaching Study

In red pine, the PEG PLUSTM treatment maintained a greater surface softening effect following leaching than PEG 1000 (Figure 4).

Residual PEG analysis of the wood after leaching showed that the PEG PLUSTM applied as a component of the CCA solution was more persistent in the wood than PEG 1000 (Table 2). There seemed to be some migration of PEG deeper into the pole in two cases. This may have resulted from the continuous spray application that wetted up the interior of poles permitting diffusion of PEG towards the lower concentration interior as well as towards the exterior.

Because of the severity of the leaching test, the loss of PEG 1000 and PEG PLUSTM were both high at the first inch zone (46-48%). Overall, more PEG 1000 seemed to have penetrated into the wood. However, PEG PLUSTM appeared to be more leach resistant once it had got into the wood fiber. In all tested pole sections, none of them was totally depleted of PEG in spite of the severe leaching condition. This might explain the better dimensional stability observed in the field for the CCA/PEG treated poles when compared to the CCA only treated poles.

Effect of Wet and Dry Conditions on PEG Concentration - Phase 2 Simulated Leaching Study

In the phase 2 leaching study of pole sections cut from commercially treated red pine poles subjected to intermittent wetting and drying, the enhanced leach resistance of the PEG PLUSTM is confirmed by HPLC analysis of the wood samples. These % loss due to leaching are computed and listed in the last four columns of Table 3. As one can see most of the % loss results after four cycles of leaching for PEG 1000 are in the teens and twenties while the % loss results for PEG PLUSTM additive are between zero and ten. This shows that the PEG PLUSTM is leaching considerably less than PEG 1000.

A t-test was used to determine if these differences were considered statistically significant or were due to pure chance variation. All four calculated t-tests range from 8.6 to 9.6 for the four cycles of leaching. Since each exceeds the critical t-value for 15 or 16 degrees of freedom (df) of 2.13 or 2.12 respectively, this implies the average % loss for PEG PLUSTM is significantly lower than the average % loss for PEG 1000 under the simulated leaching test conditions for each of the four cycles.

Figure 5 shows a plot of the actual average % loss for PEG 1000 and PEG PLUSTM for the first four cycles. These curves are represented by the dashed lines and labelled "actual." The actual data show most of the leaching loss occurs during the first cycle. However, the rate of leaching decreases rapidly between the second through fourth cycles. Consequently, we assume the rate of leaching continues to level after the fourth cycle. A logarithmic model is fit to each of these curves and projected out to eight cycles to simulate 30 years of weathering conditions in Ontario. These curves are superimposed on Figure 5 and labelled

"predicted." From Figure 5 the maximum predicted % loss reached at the end of eight cycles for PEG 1000 is about 28% while for PEG PLUSTM is about 7%. In mathematical terms, there would be no more than 7% of PEG PLUSTM leaching out of the red pine poles after 30 years of service in Ontario assuming the rate of leaching is maintained as indicated by the phase 2 study.

Effect of PEG Formulation on Drying Rates of Pole Sections

We have observed in our laboratory that CCA/PEG 1000 treated pole sections air dry much slower than CCA only treated poles. We attribute this to a chemical seasoning effect whereby the hygroscopic PEG reduces the relative humidity gradient at the wood surface reducing the drying rate.

Under kiln drying conditions (DB/WB = 60/43°C) this effect was not observed (Figures 6-8). From the moisture content gradients shown in Figures 9 to 11, it is apparent that early in the drying process, the PEG treatments maintain the wood surface at a higher moisture content. This results in a lower moisture gradient in the pole which would ordinary slow drying. However, it is known that moisture diffuses more easily through wetter wood and at high temperatures, this effect may compensate for the moisture gradient effect.

Effect of PEG Formulation on Solution Stability

The hexavalent chromium content of the CCA-C solution did not change appreciably over the 8 weeks following treatment (Figure 12). There was a slight drop in hexavalent chromium content for the CCA-C + 4% PEG PLUS™ solution and significantly reduced levels in the CCA/PEG 1000 solutions with the 10% solution more reactive than the 4% solution.

The solution pH increases were in proportion to the chromium reduction; PEG 1000 solutions had highest pH's after 8 weeks (Table 4). Some precipitation was observed in the PEG 1000 solutions 8 weeks after treatment. The filtered solutions containing PEG 1000 had lower metal ion concentrations after 8 weeks. Both chromium and arsenic contents dropped significantly over this period as these components precipitated out. These results show that CCA/PEG PLUSTM has greater solution stability than CCA/PEG 1000, which has also been observed in plant trials.

4. Summary and Conclusions

CARBOWAX® PEG PLUS™, an improved additive for CCA solutions, was more effective at reducing Pilodyn penetration hardness of red pine than PEG 1000.

It also resisted leaching more effectively than PEG 1000 as shown in the accelerated leaching study. In the simulated leaching study, results suggested that PEG PLUSTM would encounter minimal loss in the field under the current climatic conditions in Ontario, Canada. Under no circumstance did either PEG leach out totally in the two studies and PEG PLUSTM additive did not destabilize the treating solution as rapidly as PEG 1000.

The rate of kiln drying of pole sections was not significantly affected by addition of either PEG 1000 or PEG PLUS™ additive to the treating solution.

Gross solution absorption was not affected by the PEG additives. The CCA concentration gradient appeared to be steeper in red pine pole sections treated with CCA/PEG compared to CCA only treated pole sections.

5. Acknowledgement

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6. Literature

ASTM. 1987 Standard test method for chromium in water. D1687-86. Annual book of ASTM standards. Vol. 11.01. Philadelphia, PA

Engdahl, E. K., R. F. Fox, T. O. Geiser and D. A. Webb, 1992. A climbing evaluation of pine poles treated with a CCA/oil emulsion system. Proc. AWPA. 88:57-70

Fox, R. 1987. Improved climbability of CCA-treated poles through modification of gaff design. Proc. AWPA. 83:191-213.

McIntyre, C. R. and R. F. Fox. 1990. Update on Wolman ETTM a new CCA/oil treating system. Proc. AWPA. 86:14pp.

Trumble, W. P. and E. E. Messina. 1985. CCA-PEG pole preservative research. PROC. AWPA. 81:203-213.

Trumble, W. and E. E. Messina. 1986. Performance results of wood treated with CCA-PEG. Int. Res. Group on Wood Preservation Doc. IRG/WP/3363.

Zahora, A. R. and C. M. Rector. 1990. Water repellent additives for pressure treatments. Proc. Can. Wood Preservation Association. 11:22-41

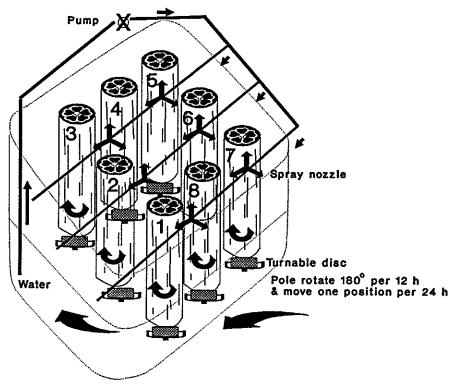


Figure 1. Schematic design and setup of simulated leaching chamber in the Phase II leaching study. (Exposure rate: 1 h spray of 150 mm rainfall followed by 3 h rest period).

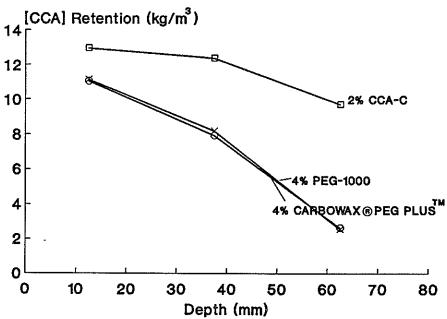
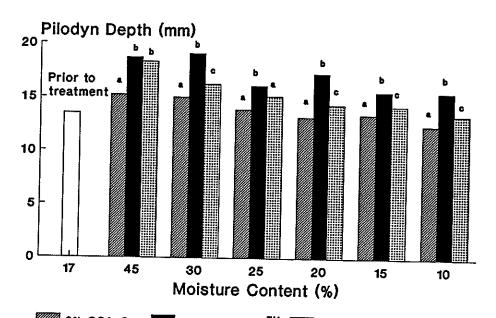
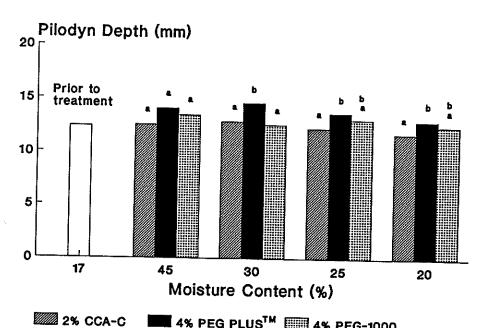


Figure 2. CCA gradient of red pine poles among CCA and CCA/PEG treatments.



2% CCA-C 4% PEG PLUSTM 4% PEG-1000

Figure 3. Effect of moisture content on pole hardness in unleached red pine poles.



2% CCA-C 4% PEG PLUSTM 4% PEG-1000

Figure 4. Effect of moisture content on pole hardness in red pine following Phase I accelerated leaching study.

Note: Within a MC group, treatments sharing the same letter are not statistically different at 0.05 level of significance.

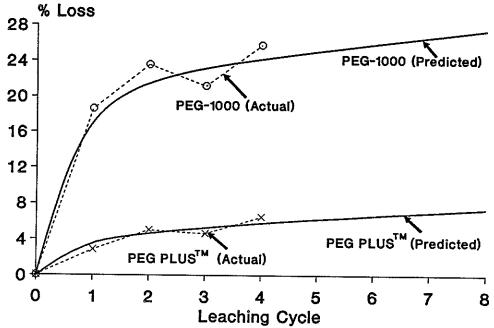


Figure 5. Predicted leaching loss of PEG from red pine poles following simulated rain exposure test.

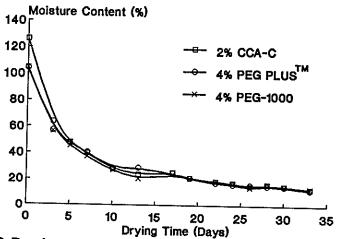


Figure 6.Drying rates for top sections of red pine poles.

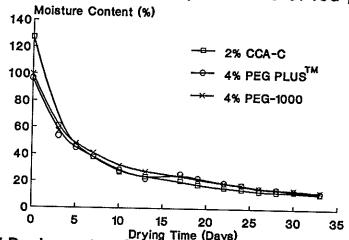


Figure 7.Drying rates for middle sections of red pine poles.

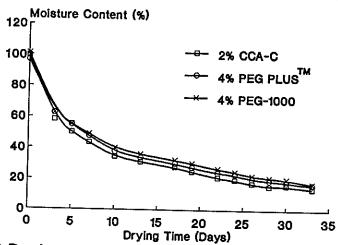


Figure 8.Drying rates for butt sections of red pine poles.

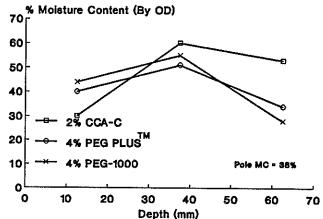


Figure 9. Moisture gradients in red pine pole sections during kiln drying at 140/110°F when whole pole MC is 38%.

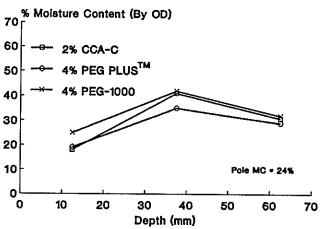


Figure 10. Moisture gradients in red pine pole sections during kiln drying at 140/110°F when whole pole MC is 24%.

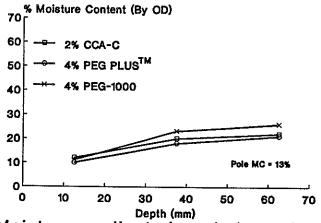


Figure 11. Moisture gradients in red pine pole sections during kiln drying at 140/110°F when whole pole MC is 13%.

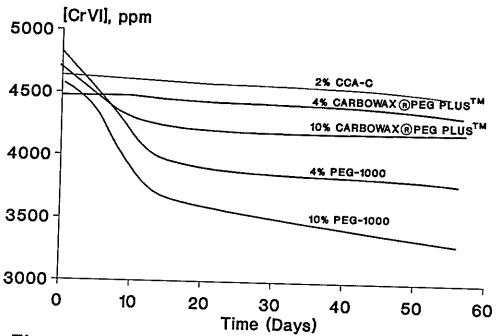


Figure 12. Effect of PEG formulations on solution stability during storage.

Table 1. CCA/PEG retentions for red pine pole sections following treatment.

Treatment	Group	Gross Retentions (ICCA			kg/m ³) PEG		
		Тор	Mid	Bot	Тор	Mid	Bot
2 % CCA-C	Leached Unleached	9.28 8.74	8.93 7.73	6.77 5.92			
2 % CCA-C + 4 % PEG-1000	Leached Unleached	11.05 8.16	7.81 7.64	9.60 8.00	22.1 16.3	15.6 15.2	19.2 16.0
2 % CCA-C + 4 % PEG PLUS TM	Leached Unleached	10.76 8.76	7.82 7.40	9.13 7.16	21.5 17.5	15.6 14.8	18.2 14.3

Note:

Each value from group assigned to accelerated leaching (Leached) is an average of three poles and from group assigned to kiln drying (Unleached) is an average of four poles.

Table 2. Comparison of PEG loading from treated red pine pole sections subjected to phase I accelerated leaching test (each value is an average of 9 samples).

Treatment	Analysis Zone (mm)	Initial PEG Loading (%)	PEG Loading Leached (%)	% Lost (Gained)	
4 % PEG-1000	0-25	2.39	1.30	46	
	26-50	0.91	0.51	44	
	51-75	0.11	0.14	(27)	
	whole zone	1.14	0.65	43	
4 % PEG PLUS TM	0-25	1.35	0.71	48	
	26-50	0.86	0.96	(12)	
	51-75	0.56	0.42	16	
	whole zone	0.92	0.70	24	

Table 3. Comparison of PEG leaching rates from commercially treated red pine poles subjected to Phase II simulated leaching test (outer 25mm zone) and their statistical significance).

PEG Pole #	Initial	% Leached**				
Formulation	[PEG], %	Cycle 1	Cycle 2	Cycle 3	Cycle 4	
PEG-1000						
1	4.33	16.4	18.7	18.6	19.7	
2	2.56	18.6	21.2	21.6	22.6	
3	1.42	20.0	24.3	24.3	27.8	
4	4.58	10.3	17.9	11.9	19.2	
5	2.50	26.6	34.0	28.2	38.1	
6	2.71	19.3	24.7	22.0	26.5	
Average	3.01	18.6	23.5	21.1	25.6	
Std. Dev.		5.2	5.6	5.4	6.7	
EG PLUS TM						
1	1.85	5.9	8.9	6.7	9.4	
2	3.61	2.3	3.0	3.3	4.2	
3	3.67	1.0	2.5	0.2	4.2	
4	3.36	3.5	4.4	4.4	5.3	
5	1.50	2.7	5.4	8.1	9.2	
6	0.61	1.7	5.8	2.7	6.5	
Average		2.8	5.0	4.2	6.5	
Std. Dev.	1.19	2.3	3.0	3.6	3.2	
EG-1000 VS. PEG	PLUSTM					
t-test		9.2	9.6	8.9	8.6	
df		15	16	16	15	
t (0.05)		2.13	2.12	2.12	2.13	
Significan	ce ?	Yes	Yes	Yes	Yes	

^{**-} Cumulated leaching loss following each cycle.

Each value is an average of two pole sections.

Table 4. Comparison of solution stability immediately after treatment and 8 weeks after treatment.

Treatment	Storage Time	р <u>Н</u>	<u>CrO</u> ₃	CuO %	<u>As</u> 2 <u>O</u> 5
2 % CCA-C	0	1.80	1.02	0.38	0.65
	8w	1.82	0.99	0.37	0.63
2 % CCA-C +	0	1.89	1.01	0.38	0.66
4 % PEG-1000	8w	2.09	0.92	0.38	0.66
2 % CCA-C +	0	1.82	1.01	0.38	0.65
4 % PEG PLUS TM	8w	1.86	1.01	0.38	0.67