COMMERCIAL DEVELOPMENT OF ACQ IN THE UNITED STATES

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INTRODUCTION

The challenge to the wood preservation industry from ever-increasing environmental regulations has led to considerable research into the development of effective wood preservative systems and treatments which have enhanced environmental acceptability compared with those currently available. As a result of extensive research, a recent significant event in wood preserving technology is the commercialization of ammoniacal copper/ quaternary ammonium compound systems, known as ACQ in the United States.

The first such product commercialized in the U.S. is ACQ Type B, which is an aqueous ammoniacal formulation comprised of a 2:1 ratio of copper oxide to quat using didecyldimethyl ammonium chloride (DDAC) as the quaternary ammonium compound. The 2:1 ratio of copper oxide to DDAC has been shown to be optimal in laboratory and field tests. The ACQ preservative takes advantage of the biological effectiveness of copper coupled with a non-metallic co-biocide preservative, and an aqueous ammonia carrier that permits enhanced preservative penetration in a wide variety of softwood species.

TECHNOLOGICAL DEVELOPMENT

Research in the development of ammoniacal-based preservative systems for wood preservation has been on-going for many years. A range of ammoniacal systems have been developed. These have included cations such as copper or zinc, and anions such as arsenate, borate, phenol, and carboxylate (Hulme, 1979; Best and Coleman, 1981; Johnson, 1983; Preston et al., 1985). To date, only ammoniacal copper arsenate (ACA) and ammoniacal copper zinc arsenate (ACZA) have gained significant commercial recognition in North America. Both of these effective preservatives, however, are subject to the same environmental pressures as chromated copper arsenate (CCA).

Other research in preservative development centered on the use of alkylammonium compounds. Notable in among these studies were those in New Zealand (Butcher and Drysdale, 1977, 1978; Butcher et al., 1977; Butcher and Greaves, 1982; Preston and Chittenden, 1982; Preston, 1983) which led to the commercialization of quaternary ammonium compounds in that country in 1978. Later research carried out in North America (Nicholas and Preston, 1980; Preston et al., 1987) also demonstrated that unamended quaternary ammonium compounds could provide protection against decay in above ground applications. As a consequence, in 1988 an American Wood

Preservers' Association (AWPA) Standard was adopted for the use of didecyldimethylammonium chloride (DDAC) as a water-borne preservative with a view to the treatment of lumber for above-ground uses. A preservative standard covering the use of DDAC in P9 Type C solvent aimed at the treatment of millwork was also later adopted.

Although alkylammonium compounds were approved for use above ground, it was quickly recognized through New Zealand experience that these unamended formulations give inadequate control of decay fungi during service in ground contact exposures. This observation led to the studies on the modification of quats with copper salts (Butcher et al, 1979; Drysdale, 1983; Tsunoda and Nishimoto, 1987) and later to the development of ammoniacal copper quat systems (Findlay and Richardson, 1983 and 1990; Sundman, 1984; Wallace, 1986). As a consequence, ACQ products were first approved and used commercially in Scandinavia in 1988 and more recently approval and commercial use has taken place in Japan. Subsequently, many aspects of using ACQ as wood preservatives have been exhaustively investigated. Publications (Jin and Archer, 1991; Jin and Preston, 1991; Jin, Roberts and Preston, 1992; Jin, Archer and Preston; 1991 and 1992; Hosli and Mannion, 1991) and documents (ACQ Proposal to AWPA Preservatives Committees, 1991; ACQ Proposal to AWPA Treatment Committees, 1992) have included the studies covering laboratory and field performance, fixation and distribution, surface weathering characteristics, water repellency, fixation mechanisms, effects on wood and use properties.

The technical properties of the ACQ treated wood are briefly reviewed as follows:

1. BIOLOGICAL PERFORMANCE

Over the last decade, the effectiveness of ACQ treated wood has been thoroughly investigated and demonstrated through a variety of industry accepted accelerated testing methodologies, such as soil block tests, fungal cellar/soil bed tests, field above ground and in ground stake tests. The experiments have been performed by various laboratories and field samples have been exposed in disparate locations within and outside the U.S. under a range of climate and soil conditions. An extensive presentation and discussion on the performance of ACQ is outside the scope of this paper but is available from the documentation and publications listed in above section. Some of the soil block (Table 1), soil bed (Table 2) and field ground contact stake test (Figure 1 and 2) results in comparison with commercially used preservatives are included in this paper for the purpose of illustration.

The laboratory soil block test results (Table 1) show excellent control of both brown and white rot fungi at low retention levels, including against the copper tolerant fungus *Postia placenta*. ACQ formulations exhibit equivalent, and in some cases, better performance than CCA and ACZA in such tests.

The comparative efficacy of southern yellow pine treated with ACQ and other water-borne preservative systems in an unsterile soil bed exposure was monitored for a period of 50 months (Table 2). The data show that the performance of the ACQ is at least equivalent to that of CCA and better than ACA at equivalent loadings of total active ingredients.

Field stake tests on the comparative performance for five years' exposure at Hilo, HI and Harrisburg, NC test sites are shown in Figures 1 and 2. The performance of ACQ is comparable to that of CCA and slightly better than ACA at equivalent retention levels.

2. PRESERVATIVE PERMANENCE

Studies on the water leaching and soil depletion of wood preservative components from ACQ treated wood in comparison with other commercial systems have been discussed extensively (Jin, Archer and Preston, 1992). As far as the ACQ formulation concerned, the amount of copper as copper oxide leached in water and depleted in soil is in the range of 10-20% which is lower than that from ACA and ACZA formulations. In comparison, the loss of copper in CCA-C from the CCA treatment varies between 8 to 27% across the several retention levels. The loss of DDAC is minimal in water leaching (3%) and in the range of 20-40% in soil contact exposures. Chromium and arsenic losses from CCA are very retention dependent, as illustrated in an above ground field exposure where losses varied from 19 to 73% for arsenic and 14 to 24% for chromium with retentions from 4.0 tc 1.0 kg/m^3.

3. ANALYTICAL METHODS FOR QUALITY CONTROL

Analytical procedures have been established covering all required aspects of ACQ treating solution and ACQ treated wood.

DDAC determination in solution and wood

The concentration of DDAC in ACQ concentrates and working solution can be determined by titration using sodium tetraphenylborate as titrant and 2', 7'dichlorofluorescein as a color indicator.

The content of DDAC in ACQ treated wood can be determined using two methods. One of these is a high performance liquid chromatography (HPLC) method which uses a HPLC unit equipped with an ion exchang. column and a UV detector. UV absorbent benzyltrimethyl ammonium chloride is added to the HPLC mobile phase to allow indirect UV detection of DDAC type quats from samples generated from solvent extraction. This method is recommended for use when a HPLC unit is available. For on-site analysis in treating plants, a wet chemistry method is available for the analysis of DDAC in treated wood. In this method, DDAC is reacted with excess anionic surfactant, then the excess anionic surfactant is back-titrated with a standard cationic surfactant in a chloroform/water two phase system.

The above three analytical procedures were submitted to AWPA Preservative Committees and have been provisionally adopted for inclusion in the AWPA Standards.

Copper determination in working solutions and wood

The copper content in ACQ concentrates and working solutions as well as in treated wood can be determined by several available analytical methods. However, X-ray fluorescence spectroscopy is the most practical method for wood treatment operations.

The procedures for this method are described in AWPA Standard A9-90 "Standard Method for Analysis of Treated Wood and Treating Solution by X-ray Spectroscopy".

Other available methods include:

1) Atomic absorption spectroscopy (AWPA Standard: A11-83)
2) Inductively coupled plasma (ICP) emission spectroscopy This method has been provisionally adopted for inclusion in the AWPA Standards.

Sample preparation for the atomic absorption spectroscopy method described in AWPA Standard A11-83 section 8.1 or in A7 can be also used for sample preparation for the ICP method.

ACQ penetration determination

Since the depth of penetration of the quat component of ACQ is essentially equivalent to the copper, the penetration of ACQ in wood can be determined using the Chrome Azurol S stain for copper, as described in AWPA Standard A3, Part 2.

Split borings or freshly cut surfaces of treated wood are sprayed with the Chrome Azurol S solution, and the presence of ACQ (copper) is indicated by a deep blue color.

4. TREATED WOOD PROPERTIES

Appearance of ACQ treated wood

The color of ACQ treated wood will vary from a brown to a deep olive green depending upon the wood species, chemical retention and the rate of ammonia evaporation. Color and appearance characteristics can also be controlled by modifying the treatment cycle parameters and post-treatment handling procedures. Typically, treated southern yellow pine and Hem-fir will exhibit a olive green color, while Douglas-fir will appear with a darker olive to brown color. With exposure to sunlight, the color of ACQ treated wood will weather to a brown tone in a short time period.

In order to prevent the formation of a blue coloration and surface deposits after treatment, it is recommended that freshly treated wood be covered to protect from rain and to allow controlled ammonia dissipation for a minimum of 48 hours. Treated wood should not be shipped until wood surface is dry.

Strength properties

Strength testing data on 25 x 25 x 410 mm (6.4 kg/m^3 retention) and 50 x 100 x 1800 mm (9.4 kg/m^3 retention) clear southern yellow pine beams treated with ACQ and CCA as well as (Submission to AWPA Treatment Committees, 1992) show no adverse effect on the wood strength properties due to the chemical treatment.

Finishing and fasteners

Wood treated with ACQ may be painted or stained similarly to other preservative treated wood, such as with CCA, ACZA and ACA. Thorough drying of the treated wood is essential before applying a finish. The corrosivity of ACQ solutions to metals and the metals in contact with ACQ treated wood has been investigated. Based on the results, corrosion-resistant fasteners such as hot-dipped galvanized or stainless steel are recommended. Aluminum should not be used in contact with ACQ solutions or treated wood.

Hygroscopicity

A study (Jin, Roberts and Preston, 1992) was carried out to obtain data on the water repellent properties of ACQ compared with that of CCA, ACZA, ammoniacal copper carbonate (AC) treatments and untreated wood. The results showed that treatment of wood with ammoniacal copper imparts significant water repellent properties to wood. This was clearly demonstrated with the AC and ACZA treatments, while the CCA and ACQ treatments also provided limited and comparable water repellency. The results of other work on the weathering characteristics of wood surfaces (Jin, Archer and Preston, 1991) from above ground field weathering exposure tests showed that ACQ treatment can provide significant protection from weathering. In certain aspects the protection imparted by ACQ is superior to that from CCA treatment. The evidence suggests that the formation of cross-linked copper complexes with lignin as well as cellulose in ACQ treated wood is the likely mechanism for this protection from weathering.

Fire resistance

A test has been carried out to determine the after-glow characteristics of ACQ treated southern yellow pine posts. Although ACQ treatment does not contain chromium, which is known to promote after-glow, there was no significant difference between after-glow in the ACQ and CCA treated posts. This is probably due to the higher content of copper in ACQ formulation. In comparison, the ACZA treatment displayed lower after-glow characteristics. This is in agreement with the earlier suggestion by Clarke and Rak (1976) that copper salts seem to promote glowing combustion whereas zinc salts may not.

Pilot plant treatment trials

Southern yellow pine lumber (50 x 100 x 2400mm and 100 x 100 x 2400mm), incised and unincised Douglas-fir (50 x 150 x 2400mm) and Hem-fir (50 x 100 x 2400mm) lumbers were treated at CSI facilities in Harrisburg NC using a 600 x 2400mm cylinder. The Douglas-fir and

Hem-fir lumber were treated with a solution at 55°C and four hour pressure time. The individual charge conditions and results are listed in the ACQ Proposal to the AWPA Treatment Committees (1992). The results show that ACQ treatments meet the current penetration and retention standards for other water-borne preservative systems. Furthermore, the treatments demonstrated that ACQ is able to treat incised and unincised Douglas-fir and Hem-fir, and still meet the penetration and retention requirements. This adds a valued feature to this preservative system.

COMMERCIAL DEVELOPMENT

ACQ Patent Coverage

The ACQ wood preservative technology is available under two series of patents issued to Domtar of Canada and to Kenogard of Sweden. Details of the specific geographic and technology coverage are available from the patent literature.

Standardization of ACQ technology

ACQ technology was first addressed in the AWPA in 1986 in a paper by Wallace then in a submission in 1989 (Richardson) to publish for information only as an Appendix to the Sub-committee P-4 report. Subsequently, a proposal to include two ACQ formulations (ACQ Type A and ACQ Type B) in AWPA Standard P5 was made to the Preservatives Committee in 1991. These standards were accepted along with a recommendation to the Treatments Committees for minimum retentions for terrestrial uses at the same levels as for CCA, ACA and ACZA. In 1992 a further submission was made to the AWPA Treatments Committees for inclusion of ACQ Type B treatments in various commodities and these proposals have been accepted by both the specific sub-committees and the General Treatments committee.

ACQ Type B treatments have also been accepted under the International Conference of Building Officials (ICBO) building code approval scheme for use in the region covered by this code.

Product Registration

ACQ technology is registered for use in the U.S. by both federal and state regulatory agencies such as the Environmental Protection Agency (EPA). The product is currently supplied as a two component system permitting maximum flexibility in the formulation of working solutions.

An ever-increasing compendium of toxicological and ecotoxicological studies are being carried out to allow the further commercialization of ACQ and related technology in a range of markets.

Commercial treatments

ACQ treatments are carried out on both the West and East Coasts in commercial treatment plants.

Commodities treated include lumber, plywood, posts, and poles. Treatment characteristics have been found to be excellent in both regions. While the southern pine treatments are rapid and complete as for CCA treatments, the use of ACQ has been found to enhance treatment rates and penetrability into Douglas fir and Hem-fir lumber. The opportunity for the production of unincised decking material from these species treated with ACQ is currently being explored.

Quality Control

A comprehensive quality control program has been developed and is operating for use with ACQ treatments.

FUTURE DEVELOPMENTS

Potential for using additives with ACQ treatment

Research is currently underway for the commercialization of water repellents, colorants and other product enhancement products with ACQ treatments. Water repellent technology for ACQ treated pine species has been under performance testing for several years and data in this regard shows excellent performance. Commercialization of this technology in the U.S. is imminent, while developments currently underway promise to enhance the application of water repellent technology beyond that currently available for use with CCA treatments.

Treatment of ACQ with various wood species

The recent proposals to the AWPA Treatments Committees covered a limited number of wood species for lumber, timber and fence posts. Plywood was also included across a range of species. Current development work seeks to broaden the number of species covered under the lumber and timbers commodity standards.

Use of ACQ treatments for different commodities

As described in the preceding section, to date only a limited number commodity standards have been sought for covering the use of ACQ Type B treatment in the AWPA Standards. Developments for pole and pile standards are underway, as are extensive investigations into the use of this technology in the marine environment. Further standardization activity will be undertaken as appropriate to the developed information base for these different commodities.

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Table 1. **Preservative performance in soil block tests (AWPA Standard E-10)**

Chemical	Retention (kg/m^3)	*G.trabeum*	*P.placenta*	*C.versicolor*	*I.lacteus*
ACQ Type B	1	13.1	21.7	1.1	2.0
	2	2.3	9.2	0.6	0.1
	4	1.0	0.8	0.0	0.2
	6.4	1.0	0.1	0.8	0.3
CCA Type C	1	36.7	6.9	2.3	0.1
	2	12.5	1.7	1.4	0.1
	4	5.9	0.0	0.8	0.2
	6.4	3.7	0.3	0.1	0.2
ACZA	1	26.9	26.0	0.8	4.1
	2	6.8	18.9	0.0	1.2
	4	6.2	1.7	0.3	1.6
	6.4	3.1	0.2	0.3	1.5
Untreated	0	55.5	37.6	34.4	36.3

Using Southern Yellow Pine - 19 x 19 x 19 mm blocks

Table 2. Soil bed performance of preservative systems

Formulation	Retention kg/m^3	Performance % Mean Soundness			
		13 month	23 month	34 month	50 month
ACQ Type B	9.6	100.0	100.0	97.4	93.0
	6.4	97.0	92.0	79.4	62.0
	4.0	94.0	76.0	56.0	29.0
	2.0	72.0	67.0	4.0	0.0
CCA Type C	6.4	99.0	91.0	70.5	43.5
	4.0	92.0	76.0	38.0	6.5
	2.0	73.0	63.0	0.0	0.0
ACA	9.6	92.0	72.0	62.5	27.5
	6.4	77.0	70.0	37.2	20.5
	4.0	87.0	73.0	58.0	21.0
	2.0	77.0	64.0	15.0	0.0
Untreated	0.0	53.0	4.0	0.0	0.0

Data are based on 15 replicates with 12 x 25 x 200 mm stakelets.

Figure 1. Field Performance in Ground Contact in Hilo,HI. (3/4x3/4x18" stakes, 57 months).

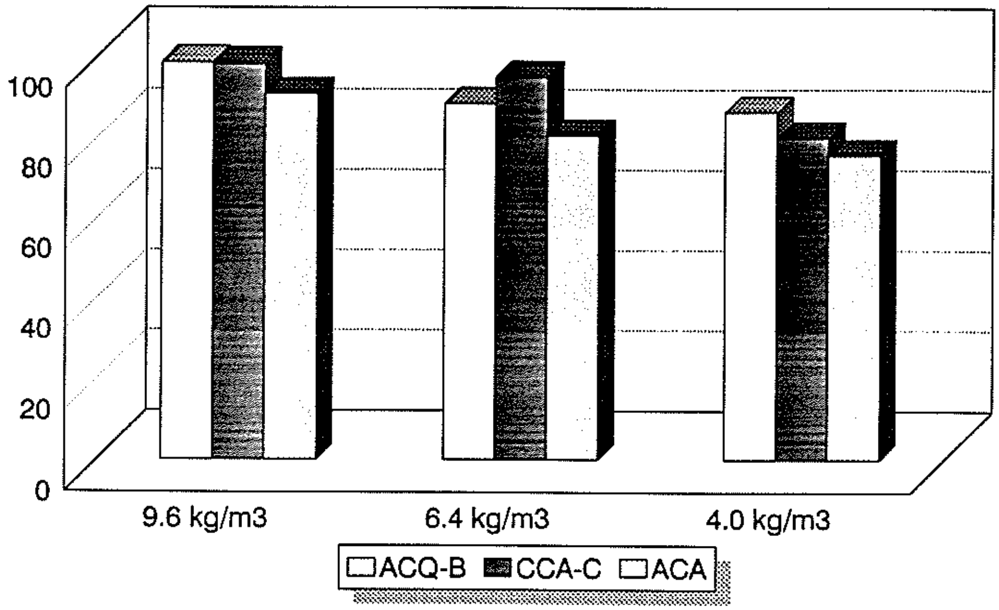

Figure 2. Field Performance in Ground Contact in Harrisburg, NC (3/4x3/4x18" stakes, 57 Months exposure)