PROJECT SUMMARY SHEET

TITLE: Arsenic-Specific Stain for Identifying CCA-Treated Wood
COMPLETION DATE: October 31, 2005
PRINCIPAL INVESTIGATOR: Helena Solo-Gabriele, Associate Professor
AFFILIATION: U. Miami, Dept. of Civil, Arch., & Environ. Engineering
ASSOCIATE INVESTIGATOR: Timothy Townsend, Associate Professor
AFFILIATION: U. Florida, Dept. of Environ. Engrg. Sci., Solid & Haz Waste Prog.
STUDENTS: Upon initiation of the study, both Drs. Solo-Gabriele and Townsend will recruit students for this project. It is likely that students working on current and past CCA projects will be involved in the proposed project described herein. These students may include Michael Laas (Post Baccalaureate), Tomoyuki Shibata (Ph.D.), and Gary Jacobi (M.S.) from U.Miami and Brajesh Dubey (Ph.D.) from U.Florida.

OBJECTIVES: The objective of this proposal is to develop an arsenic-specific stain for identifying wood treated with arsenical preservatives, such as chromated copper arsenate (CCA). This stain will be useful for distinguishing CCA-treated wood from wood treated with other copper-based (non-arsenical) preservatives. The stain will be designed for use in the field which will decrease the need for laboratory analysis of wood samples.

METHODOLOGY: Due to the similarity between phosphate and arsenate ions, methods for analyzing phosphate in water will be modified to analyze for arsenate in wood. This work will focus on two stains that have been preliminarily evaluated: a stannous chloride stain and an ascorbic acid stain. Work will focus on developing these stains so they can be used to identify the presence of arsenic-treated wood. Specifically, work will focus on: a) decreasing the time for the stain to sorb into the wood and b) removing interferences observed in untreated wood. The stain will be tested in the field to evaluate its suitability for use on weathered and soiled wood.

RATIONALE: Distinguishing between arsenic treated wood versus wood treated with non-arsenicals is of importance due to the different disposal and recycling options available for each treated wood type. At the end of 2003, arsenic-treated wood (e.g. CCA) will no longer be manufactured for residential applications. The alternatives to CCA, which include ACQ and CBA, do not contain arsenic. These preservatives contain copper and an organic co-biocide. It is anticipated that these alternatives will be observed shortly within the disposal stream, at first as a small fraction but as time progresses wood products treated with copper (but not arsenic) will be found in a greater proportion (as ACQ- and CBA-treated structures are removed from service) and the need for sorting CCA-treated wood specifically will increase. The stain developed through this study will enable the wood recycling industry and regulatory agencies to more accurately spot-check loads of wood for disposal and recycling purposes.

ACCOMPLISHMENTS: Drs. Solo-Gabriele and Townsend have worked on CCA-treated wood projects for the Center for the past six years. They have presented their research results at many conferences and meetings, have produced 7 technical reports on the subject for the Center, and have published their work in peer-reviewed journals. They have collectively graduated 2 Ph.D. and 7 masters students on Center sponsored CCA projects and have 2 masters and 2 Ph.D. students currently working on the existing Center projects.

ARSENIC-SPECIFIC STAIN FOR IDENTIFYING CCA-TREATED WOOD

A Research Proposal Submitted to
The Florida Center for Solid and Hazardous Waste Management (FCSHWM)
March 22, 2004

Abstract

Contamination of wood waste with wood treatment preservatives has greatly limited recycling of dimensional wood within the State of Florida. Many solid waste processing facilities throughout the State choose not to recycle dimensional wood and dispose the wood in either C&D or MSW landfills due to concerns about contamination from wood treatment preservatives. The objective of this proposed project is to develop an arsenic-specific stain for the detection of arsenical-treated wood (e.g. CCA). The proposed stain represents an improvement over the current stain, PAN Indicator. PAN Indicator detects copper in CCA and therefore cannot distinguish between wood treated with CCA and other copper-based wood treatment preservatives. The proposed stain will detect arsenic which is the chemical within CCA that causes wood waste to fail disposal guidelines most often. The arsenic-specific stain developed through this study will help wood recyclers distinguish between arsenical-treated wood versus copper-treated wood.

Introduction

At the end of 2003, wood treated with chromated copper arsenate (CCA) will no longer be manufactured for residential applications resulting in a 60 to 80% decrease in the sales of CCA-treated wood after this time (U.S. EPA 2002). CCA-treated wood contains high concentrations of arsenic (Table 1). The alternatives to CCA which currently share the bulk of the residential market (ACQ and CBA) do not contain arsenic. These preservatives contain copper and an organic co-biocide. It is anticipated that these alternatives will be observed shortly within the disposal stream, at first as a small fraction of the dimensional wood that is disposed but as time progresses wood products treated with copper (but not arsenic) will be found in a greater proportion, as ACQ- and CBA-treated structures are removed from service.

Disposal criteria are much stricter for arsenic containing wastes than for copper containing wastes (Table 1). For example, there is no Toxicity Characteristic limit for copper for wastes subjected to the Toxicity Characteristic Leaching Procedure (TCLP) (USEPA 2001). The Florida Groundwater Cleanup Target Level (GWCTL) is also much higher for copper than for arsenic (FDEP 1999). The largest differences are observed for Florida's Soil Cleanup Target Levels (SCTL). The residential SCTL for arsenic is 0.8 mg/kg whereas for copper it is 110 mg/kg (FDEP 1999).

These differences in regulatory guidelines suggest that recycling of copper containing wood may be feasible whereas the recycling of arsenic containing wood would be extremely limited. Primary markets for recycled dimensional wood within the State of Florida include the wood fuel and mulch markets (Solo-Gabriele and Townsend 1999). In order for wood to be utilized for these markets, the wood must be free from arsenical-preservative chemicals (Townsend et al. 2003). However, some leeway is possible for copper-based wood preservatives. For example, if the goal is for a mulch to meet the residential SCTL, then essentially no CCA-treated wood can be found in the mulch if it is to meet the residential SCTL for arsenic; however up to 9 % CCA-treated wood can be found in the mulch and it would still meet the residential guideline for copper. This will be significant in the future as copper-based preservatives begin to represent the dominant type of treated wood within the disposal sector.

Table 1: Comparison of CCA Metals Concentrations & FL Regulatory Guidelines

Metal	Residential SCTL (mg/kg)	Industrial SCTL (mg/kg)	TCLP (mg/L)	GWCTL (mg/L)	Untreated Wood		CCA-wood at 0.25 pcf		CCA wood at 2.5 pcf
					Total (mg/kg)	Leachate (mg/L)	Total (mg/kg)	Leachate (mg/L)	Total (mg/kg)
Cr	210	420	5	0.1	7	<0.1	1,930	1	19,300
Cu	110	76,000	None	1.0	4	<0.1	1,150	3	11,500
As	0.8*	3.7	5	0.05	2	<0.1	1,730	5	17,300

* The FDEP is considering raising this guideline level.

Facilities that recycle dimensional wood should have a system in place by which they can identify with certainty the presence of wood treatment preservatives, especially given that dimensional wood is frequently treated (SFPA 2001). Many facilities that recycle dimensional wood, sort wood based upon the hue or color of the wood or knowledge of the ultimate source of the wood (e.g. an outdoor fence, marine dock, etc…). In these cases, CCA-treated wood can be easily removed, but there are many cases for which the original uses of the wood are not known and the wood is weathered masking the appearance of the colors associated with treated wood. For these cases, it is very difficult for the wood recycler to identify whether or not the wood contains wood treatment preservatives and thus identification of CCA-treated wood in these cases needs to be augmented with technologies that are capable of identifying the presence of wood preservatives, in particular arsenical preservatives.

One option currently available to wood recyclers for identifying CCA-treated wood within dimensional wood boards and within non-colored mulches is a chemical stain called PAN Indicator (Blassino et al. 2002). PAN Indicator reacts with the copper in CCA-treated wood to produce a deep magenta color. Untreated wood produces a lighter orange color (See Figure 1). The reaction time is relatively fast (12 seconds) and the stain is found to be useful for spot-checking piles of wood and mulch. However, due to the impending increases in the disposal of dimensional wood treated with copper-based preservatives, there will be an increasing need in identifying wood treated with specifically arsenic given that it is subject to the strictest disposal guidelines. The existing PAN indicator stain will not be capable of making the distinction between CCA-treated wood and non-arsenical treated wood containing copper.

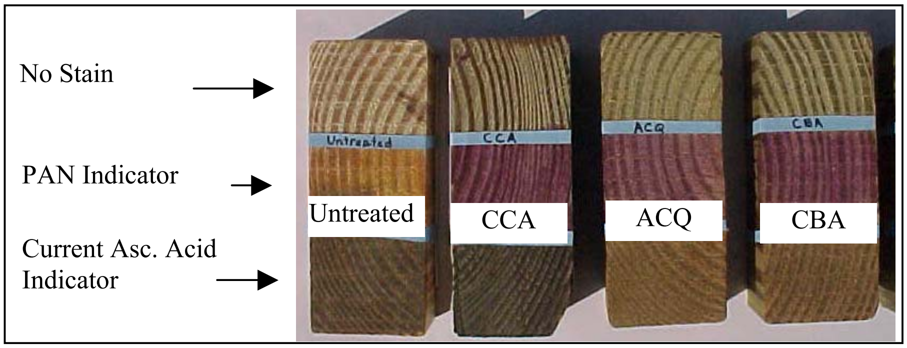

Figure 1: Performance of PAN Indicator and Ascorbic Acid Stain

<u>Objectives</u>

The objective of this proposal is to develop an arsenic-specific stain for identifying wood treated with arsenical preservatives, such as chromated copper arsenate (CCA). This stain will be useful for distinguishing CCA-treated wood from wood treated with other copper-based (non-arsenical) preservatives. Specifically, work will focus on modifying stains used for identifying phosphate in water. Preliminary experimentation has been successful but more work is needed in: a) decreasing the time for the stain to sorb into the wood and b) removing interferences observed in untreated wood. The optimum formula developed for the stain will be field tested to evaluate its suitability for use on weathered and soiled wood.

<u>Methods</u>

Phosphate and arsenate are very similar in their structure and in their chemical behavior and as a result analytical methods for phosphate in water are subject to interferences from waters that contain a significant amount of arsenate. Arsenate is the predominant form of arsenic within CCA-treated wood. The intent of the current proposal is to modify existing methods for analyzing phosphate for the analysis of arsenate in wood. There are two well known methods for analyzing phosphate: the stannous chloride method and the ascorbic acid method. Preliminary research with these two analytical methods for evaluating wood has shown that the "phosphate – water" methods can be utilized to evaluate arsenic in wood (See Figure 1), however more development of these methods is necessary in particular with respect to two drawbacks. These drawbacks include a long reaction time (1 hour) and interferences observed within untreated wood. These two drawbacks will be addressed through the following three tasks. Wood types to be evaluated in the laboratory include: untreated wood and wood treated with CCA, ACQ (alkaline copper quat), CBA (copper boron azole), CDDC (copper dimethyldithiocarbamate), and CC (copper citrate).

Task 1: Shorten the reaction time

The reaction time can be shortened by increasing the rate at which the stain chemicals soak into the wood. It has been observed that water does not soak into the wood very quickly. For treated wood, when water is placed on the wood sample it has a tendency to form a bubble. However, alcohols (which is the solvent used in the PAN Indicator solution) soaks into the wood within seconds. This is part of the reason for why the PAN Indicator stain develops color so quickly (12 seconds). The slow reaction time associated with the Stannous Chloride and Ascorbic Acid stain will be addressed by mixing the chemicals needed for this stain with alcohol as the solvent rather than water. Various proportions of alcohol and water will be tested during this phase of the experimentation. Other solvents evaluated will include the use of surfactants, which also soak into the wood rapidly.

Task 2: Reduce Interferences Observed in Untreated Wood

Untreated wood had a tendency to stain a faint blue, whereas CCA-treated wood stains a deep blue and the copper based alternatives do not stain blue. It is believed that the faint blue color observed on the untreated wood was due to low levels of phosphate and even perhaps arsenate within the wood structure. The faint blue color observed for the untreated wood will be addressed through this project by making the chemical stain less sensitive. The stain has more than enough sensitivity for identifying CCA. It is believed that this sensitivity will be reduced by decreasing the concentration of the chemicals in the stannous chloride and ascorbic acid stains. Furthermore, adding an alcohol or surfactant to the solvent will also likely decrease the sensitivity.

Task 3: Test Stain In Field

All laboratory testing (Tasks 1 and 2) will be conducted on new wood samples. In order to further document the effectiveness of the stain it will be important to document the performance of the stain under field conditions which will include hotter temperatures and soiled weathered wood. The stain will be field tested at a wood recycling facility to determine how useful it can be for sorting and spot-checking the presence of CCA within dimensional wood boards and within wood mulch. Field work will also include testing the stain at existing structures to determine whether or not it is useful for properly identifying the wood prior to demolition. The effectiveness of the stain will be cross-checked against an independent measure of arsenic concentration which can include analysis of sawdust in the laboratory or by the use of a field portable x-ray unit.

Separation of Work Among the Universities

Helena Solo-Gabriele of U.Miami will be responsible for all administrative activities required by the Center, and for all deliverables. She will also be responsible for directly supervising Phases I and II of the project. Tim Townsend of U.Florida will assist in supervising Phase III, by identifying an appropriate facility for testing the arsenic-specific stain and by participating in the sorting and documentation effort.

Timeline

Project Duration: 1.3 years
Project Start Date: July 1, 2004 Project End Date: October 31, 2005

Description	2004						2005									
	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O
Task 1: Shorten the reaction time	o	o	o	o	X											
Task 2: Reduce Interferences	o	o	o	o	o	o	o	o	X							
Task 3: Test Improved Stain In Field				o	o	o	o	o	o	o	o	o	X			
Progress Reports			X			X			X			X				
TAG Meetings							X						X			
Draft & Final Report												o	o	o	o	X

Deliverables

A technical awareness group (TAG) will be established for the project and will likely include the 20 members that participated during the year 2003 project. TAG members include representatives from the wood treatment industry, from the waste disposal sector, from regulatory agencies, and from academia. A listing of the TAG members is available at http://www.ccaresearch.org/tag14_membersupdate.htm. A minimum of two TAG meetings will be held per year. TAG meetings have been very successful in the past. The last three TAG meetings held on the CCA-treated wood research had between 40 to 50 attendees. The last meeting was held during the last day of the international conference sponsored by the Florida Center for Environmental Solutions, titled "Environmental Impacts of Preservative Treated Wood." This meeting was attended by 150 individuals including individuals from many other U.S. states and several different countries. Feedback received from the participants was excellent.

A final report will be prepared which documents the methods and results from both phases of the research. A draft of the final report will be available in August 2005. The report will be finalized by October 2005, after comments are received from the Center and from the TAG. Essential information will be included in the main body of the final report and less essential information will be included in an appendix. The current web site, www.ccaresearch.org, will continue to be maintained and updated throughout the duration of the project. Quarterly progress reports, minutes of the technical advisory group meetings, technology transfer plan, etc.. will be submitted to the Center as required.

Expected Technical Results

Sorption rates and reaction times for the ascorbic acid and stannous chloride stains will be documented within various wood types. A formula or recipe will be provided for the stain providing the best results. The "best" results correspond to those which are characterized by no interferences from untreated wood and those which are the most rapid. The use of the arsenic-specific stain will be documented in the field. As a result of this field study, the distribution between copper-treated versus arsenic-treated wood will be observed. This information will be useful for recycling programs which must comply with stricter regulatory criteria for arsenic as opposed to looser criteria for copper.

Anticipated Benefits for End Users

This project will directly help wood recyclers and regulators to identify CCA-treated wood within dimensional wood waste. The "sister" stain, PAN Indicator, which reacts with copper has found practical utility within the State. Over 50 PAN Indicator packets have been distributed by the research team. It is anticipated that there will be similar interest in the arsenic-specific stain. The arsenic-specific stain will be a low cost alternative for identifying arsenic-treated wood within wood waste. This stain will likely be suitable for sorting relatively small quantities of wood (less than a ton). The stain can be used for spot-checking loads and for regulatory purposes. For example, Broward County has utilized the PAN Indicator stain to identify copper-treated wood (which includes CCA). Once a "hit" is found with the stain, samples are then collected for laboratory analysis. Broward County has indicated that the stain has worked very well in this regard.

Related Work

The research team identified for this project has conducted a considerable amount of research focusing on sorting technologies for CCA-treated wood. They worked on developing the copper specific stains during 1998 and 1999 (Blassino et al. 2002). During 1999 they also focused on evaluating X-ray technologies (Solo-Gabriele et al. 2000). During 2000 to 2001, the team focused on field testing X-ray and laser technologies through a study sponsored by Sarasota County with support from the FDEP Innovative Recycling Grants program (Solo-Gabriele et al. 2004). A distribution program for the copper-specific stain was initiated in 2003. Currently the research team has collaborated with the Town of Medley in submitting an Innovative Recycling Grant proposal for evaluating an X-ray technology for "augmented" sorting at a wood recycling facility. This proposal is currently ranked first and should receive funding if the Florida legislature sponsors the Innovative Recycling Grants Program during this upcoming fiscal year. If funding is provided, the results from the stain developed through the proposed project can then be cross-checked against the X-ray technology for further verification of performance in the field.

Possible Follow-up

After this project, and assuming success, it would be useful to market the arsenic-specific stain for manufacture by chemical companies. The intent would be to enter into an agreement with the chemical company to manufacture the stain at a cost benefit to the Center. This stain can then be marketed to recyclers and individuals who would be interested in determining whether their wood, mulch, or wood structures contain arsenic. The research team has also been successful at obtaining funds from other agencies on complimentary CCA-treated wood projects funded by the Center. These agencies have included the National Institutes for Environmental Health Sciences, with subcontracts through Florida International University and Rutgers University and the Florida Department of Environmental Protection – Innovative Recycling Grants Program with subcontracts through Sarasota County. The research team has also received funding awards through the National Science Foundation for their recent conference focusing on the environmental impacts of preservative treated wood. Throughout the history of the CCA projects, funds from the Center have served as the "backbone" for the research focusing on CCA impacts. Without the continued support from the Center, funding from the other sources would not have been possible. Efforts will continue in soliciting funds from other agencies in efforts to build upon work directly sponsored by the Center.

References and Pertinent Literature

Blassino, M., Solo-Gabriele, H., and Townsend, T., 2002. "Pilot Scale Evaluation of Sorting Technologies for CCA-Treated Wood Waste." *Waste Management and Research*, 20: 290-301.

Florida Department of Environmental Protection, 1999. *Chapter 62-777, Contaminant Clean-up Target Levels*. FDEP, Tallahassee, FL. Available at: http://www.floridadep.com/waste/quick_topics/rules/default.htm#62-777.

Solo-Gabriele, H.M., and Townsend, T., 1999. "Disposal Practices and Management Alternatives for CCA-Treated Wood Waste. " *Waste Management Research*, 17: 378-389.

Solo-Gabriele, H., Townsend, T., Kormienko, M., Stook, K., Gary, K., and Tolaymat, T., 2000. *Alternative Chemicals and Improved Disposal-End Management Practices for CCA-Treated Wood, Report Number #00-03*. Florida Center for Solid and Hazardous Waste Management, Gainesville, FL.

Solo-Gabriele, H.M., Townsend, T.G., Hahn, D.W., Moskal, T.M., Hosein, N., Jambeck, J., and Jacobi, G., 2004. Evaluation of XRF and LIBS Technologies for On-Line Sorting of CCA-Treated Wood Waste. Waste Management. (In press).

Southern Forest Products Association (SFPA) 2001. *Treated Southern Pine Production Data*. Southern Forest Products Association, Kenner, LA

Tolaymat, T.M., Townsend, T.G., and Solo-Gabriele, H., 2000. Chromated copper arsenate Treated wood in recovered construction and demolition waste recycling facilities. *Environmental Engineering Science*, 17(1): 19-28.

Townsend, T.G., Solo-Gabriele, H.M., Tolaymat, T., and Stook, K., 2003. "Impact of Chromated Copper Arsenate (CCA) in Wood Mulch." *The Science of the Total Environment*, 309: 173-185.

U.S. Environmental Protection Agency, 2001. *Code of Federal Regulations, Title 40, Volume 20, Part 261, Identification and Listing of Hazardous Waste, Section 261.24, Toxicity Characteristics. 40CRF261.24*. U.S. Environmental Protection Agency, Washington D.C.

U.S. Environmental Protection Agency, 2002. *Federal Register, Notice of Receipt of Requests to Cancel Certain Chromated Copper Arsenate (CCA) Wood Preservative Products and Amend to Terminate Certain Uses of CCA Products (February 22, 2002)*, Volume 67, Number 36: 8244-8246.