



**US Army Corps
of Engineers**

Construction Engineering
Research Laboratory



USACERL Special Report M-91/26
September 1991

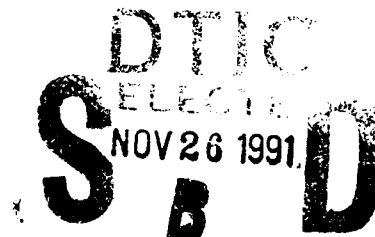
2

Applicability of Thermal Analysis to Characterization of Roof Membrane Materials: A Summary of the 28-29 March 1990 Workshop

by
Walter J. Rossiter, Jr.
Glen D. Gaddy

Although long used to characterize synthetic polymeric products, thermal analysis (TA) methods are not widely used to characterize roof membrane materials. In 1988, a Joint International Committee (CIB/RILEM) proposed to include TA methods with other test methods used to characterize roof membrane materials. The U.S. Army Construction Engineering Research Laboratory (USACERL) has begun a program to evaluate the performance of roof membrane materials, including the development of new or improved methods to determine their important properties. TA methods offer a means for such characterization, but whether they can be meaningfully incorporated into voluntary consensus standards for roofing membrane materials is unresolved.

Thirteen participants contributed to a workshop convened to address this issue. The consensus of workshop participants was that TA methods are valuable tools in the laboratory for research studies and troubleshooting, and for tracking manufacturing processes to check that they remain in control. However, participants concluded that TA methods do not have immediate use in consensus standards for roofing because they cannot alone predict how a product may perform in service, and because the high cost of TA equipment may prohibit general use of the methods, or make their incorporation in standards unattractive.



91-16307



Approved for public release; distribution is unlimited.

91 1122 040

The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official indorsement or approval of the use of such commercial products. The findings of this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

DESTROY THIS REPORT WHEN IT IS NO LONGER NEEDED

DO NOT RETURN IT TO THE ORIGINATOR

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.			
1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE September 1991	3. REPORT TYPE AND DATES COVERED Final	
4. TITLE AND SUBTITLE Applicability of Thermal Analysis to Characterization of Roof Membrane Materials: A Summary of the 28-29 March 1990 Workshop		5. FUNDING NUMBERS PE 62784 PR AT41 WU MA-CV0	
6. AUTHOR(S) Walter J. Rossiter, Jr., and Glen D. Gaddy			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Construction Engineering Research Laboratory (USACERL) PO Box 9005 Champaign, IL 61826-9005		8. PERFORMING ORGANIZATION REPORT NUMBER SR M-91/26	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) HQUSACE ATTN: CEMP-ES 20 Massachusetts Avenue, NW WASH DC 20314-1000		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Copies are available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Although long used to characterize synthetic polymeric products, thermal analysis (TA) methods are not widely used to characterize roof membrane materials. In 1988, a Joint International Committee (CIB/RILEM) proposed to include TA methods with other test methods used to characterize roof membrane materials. The U.S. Army Construction Engineering Research Laboratory (USACERL) has begun a program to evaluate the performance of roof membrane materials, including the development of new or improved methods to determine their important properties. TA methods offer a means for such characterization, but whether they can be meaningfully incorporated into voluntary consensus standards for roofing membrane materials is unresolved. Thirteen participants contributed to a workshop convened to address this issue. The consensus of workshop participants was that TA methods are valuable tools in the laboratory for research studies and troubleshooting, and for tracking manufacturing processes to check that they remain in control. However, participants concluded that TA methods do not have immediate use in consensus standards for roofing because they cannot alone predict how a product may perform in service, and because the high cost of TA equipment may prohibit general use of the methods, or make their incorporation in standards unattractive.			
14. SUBJECT TERMS roofs workshops thermal analysis		15. NUMBER OF PAGES 34	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT SAR

FOREWORD

This research was conducted for the Directorate of Military Programs, Headquarters, U.S. Army Corps of Engineers (HQUSACE) under Project 4A162784AT41, "Military Facility Engineering Technology"; Work Unit MA-CV0, "Evaluation of Roofing Materials Degradation Processes." The technical monitor was Mr. Rodger Seeman, CEMP-ES.

This work was monitored by the Engineering and Materials Division (EM) of the U.S. Army Construction Engineering Laboratory (USACERL). Mr. David M. Bailey was the principal investigator. Mr. Walter J. Rossiter is a research chemist for the National Institute of Standards and Technology (NIST) – Building and Fire Research Laboratory (BFRL) where the study was conducted. Mr. Glen D. Gaddy is a graduate student in the Materials Science and Engineering Department at Johns Hopkins University. Dr. Paul Howdyshell is Chief, USACERL-EM. The USACERL technical editor was Mr. William J. Wolfe, Information Management Office.

Special appreciation is owed to the participants in the Thermal Analysis Workshop, who gave freely of their time in attending, shared their experiences with thermal analyses, and joined enthusiastically in the discussions: Mr. Robert L. Alumbaugh (Naval Civil Engineering Laboratory), Mr. S.A. Banks (Exxon Chemical), Mr. Mark A. Berggren (Shell Development Company), Mr. Roger Blaine (DuPont Instrument Systems), Mr. Carl G. Cash (Simpson, Gumpertz and Heger), Mr. Thomas P. Danaher (Perkin-Elmer), Mr. Ruben G. Garcia (Manville Corporation), Mr. Richard Gillenwater (Carlisle Syn-Tec), Mr. Orlando Lobo (Carlisle Syn-Tec), Mr. Daniel R. McGillvary (Firestone Building Products), Mr. Theodore W. Michelsen (Manville Corporation), Mr. Peter C. Muller (Perkin-Elmer), Mr. Christopher F. Mullen (Sarnafil), Mr. Thomas L. Smith (National Roofing Contractors Assoc.), Mr. James Wells (Owens Corning Fiberglas). Special thanks are expressed to Mr. William C. Cullen, National Roofing Contractors Association (NRCA) Research Associate, for his valuable assistance as workshop moderator. Thanks are also extended to Ms. Karen Hozela (NIST) who made the arrangements for holding the workshop; Mr. Geoffrey Frohnsdorff (NIST), who provided valuable review and comments on a draft of this report; and Mr. Donald E. Brotherson, of the University of Illinois, and the University of Illinois Building Research Council for co-hosting the workshop.

COL Everett R. Thomas is Commander and Director of USACERL, and Dr. L.R. Shaffer is Technical Director.

CONTENTS

		Page
	SF298	1
	FOREWORD	2
1	INTRODUCTION	5
	Background	
	Objectives	
	Approach	
	Mode of Technology Transfer	
2	APPLICATIONS OF THERMAL ANALYSIS TO ROOFING MATERIALS	9
3	SUMMARY OF WORKSHOP DISCUSSIONS	11
	Utility of TA Methods	
	Limitations of TA Methods	
4	CONCLUSIONS	14
	REFERENCES	14
	APPENDIX A: CIB/RILEM Recommendations on Thermal Analysis Methods	16
	APPENDIX B: Overview of Thermal Analysis Methods	18
	APPENDIX C: Summaries of the Workshop Presentations	23
	DISTRIBUTION	

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By _____	
Distribution/ _____	
Availability Codes	
Dist	Special
A-1	



APPLICABILITY OF THERMAL ANALYSIS TO CHARACTERIZATION OF ROOF MEMBRANE MATERIALS: A SUMMARY OF THE 28-29 MARCH 1990 WORKSHOP

1 INTRODUCTION

Background

The Application of Thermal Analysis to Roofing

In 1983, an International Committee on Elastomeric, Thermoplastic, and Modified Bituminous Roofing was organized under the auspices of CIB and RILEM.* The committee's membership consisted of 39 experts from 18 nations representing the design, manufacturing, contracting, and technical segments of the international roofing industry. The committee's major objective was to recommend a test protocol to evaluate and characterize generic roof membrane materials before and after exposure to simulated aging conditions, and during service on roofs. The committee's recommendations were published in 1988.¹

Chief among the committee's recommendations was that thermal analysis methods be added to the inventory of test methods currently used to characterize roof membrane materials. Thermal analysis is "a general term covering a group of related techniques whereby the dependence of the parameters of any physical property of a substance on temperature is measured."² An advantage to characterizing roofing membrane materials (or other products) using thermal analysis methods is that highly reproducible results may be obtained with extremely small sample sizes.³ Appendix A contains a copy of the CIB/RILEM proposal. This proposal was based on the investigations of a task group established within the committee to study the feasibility of using thermal analysis methods for membrane characterization. Preliminary interlaboratory testing demonstrated the capability of thermal analysis to detect changes in material properties of ethylene-propylene-diene terpolymer (EPDM), polyvinyl chloride (PVC), and polymer-modified bituminous membrane materials upon aging. The tests used torsion-pendulum analysis, dynamic mechanical analysis, and thermogravimetry. However, the task group acknowledged that the preliminary experimentation was limited and that further research should be conducted to interpret the results of laboratory tests in relation to long-term in-service performance.

* Conseil International du Batiment pour la Recherche, l'Etude et la Documentation (International Council for Building Research Studies and Documentation); and Reunion Internationale des Laboratoires d'Essais et de Recherches sur les Matériaux et les Constructions (International Union for Testing and Research Laboratories for Materials and Structures).

¹ "Elastomeric, Thermoplastic, and Modified Bitumen Roofing: A Summary Technical Report of CIB W.83 & RILEM 75-SLR Joint Committee," *Matériaux et Constructions*, Vol 19, No. 112 (July-August 1986), pp. 323-329; Ruth I. Warshaw, "Summary of the RILEM/CIB Report on Performance Testing of Roof Membrane Materials," *International Journal of Roofing Technology*, Vol 1, Issue 1 (Spring 1989), pp. 10-11.

² W.W. Wendlandt, *Thermal Methods of Analysis*, 2d ed. (John Wiley and Sons, New York, 1974), p. 490.

³ W.W. Wendlandt and P.K. Gallagher, "Instrumentation," in *Thermal Characterization of Polymeric Materials* (Academic Press, New York, 1981), pp. 1-86.

Presently, the thermal analysis methods of prime interest to the roofing industry are:

- Thermogravimetry (TG), which measures mass change
- Differential Scanning Calorimetry (DSC), which measures relative heat flux and, in turn, the heat capacity and the glass transition temperature
- Thermal Mechanical Analysis (TMA), which measures changes in volume or length
- Dynamic Mechanical Analysis (DMA) and Torsion Pendulum (TP), which measure the modulus of a material and, in turn, the glass transition temperature.

A summary of these methods is given in Appendix B.

Thermal analysis methods have not been widely used to characterize roofing membrane materials, although they have been employed for more than three decades to characterize synthetic polymeric products.⁴ An early study on the use of DSC for the characterization of EPDM, PVC, neoprene, and chlorinated polyethylene (CPE) concluded that this thermal-analysis method could be used to identify the components in a single-ply sheet to differentiate between manufacturers, and to distinguish between exposed and new materials.⁵ More recent work⁶ supports the recommendations of the CIB/RILEM Committee. These studies reported on the characteristics of EPDM, PVC, and polymer-modified bituminous materials using TG, DSC, and DMA methods. In addition, Backenstow and Flueller described the application of torsion pendulum analysis to the characterization of these membrane materials. In a study that followed, in part, from the CIB/RILEM recommendations,⁷ TG, DSC, TMA, and DMA were used to determine the changes that black and white EPDM membrane materials experienced upon heat, ultraviolet (UV) radiation, and ozone conditioning in the laboratory, as well as upon limited exposure outdoors. These studies also compared the results of the thermal analysis measurements to changes in load-elongation properties of the rubber test specimens. The four papers associated with the CIB/RILEM work⁸ conclude that thermal analysis methods were useful for membrane characterization, and that investigations should continue to provide the technical basis for their incorporation in standards.

⁴ W.W. Wendlandt; W.W. Wendlandt and P.K. Gallagher.

⁵ C.G. Cash, "Thermal Evaluation of One-Ply Sheet Roofing," in *Single-Ply Roofing Technology*, ASTM STP 790 (American Society for Testing and Materials [ASTM], Philadelphia, 1982), pp. 55-64.

⁶ M.S. Farling, "New Laboratory Procedures To Evaluate the Durability of Roofing Membranes," Appendix D in *Performance Testing of Roofing Membrane Materials*, Recommendations of CIB W.83 and RILEM 75-SLR Joint Committee on Elastomeric, Thermoplastic, and Modified Bitumen Roofing (RILEM, November 1988); D. Backenstow and P. Flueller, "Thermal Analysis for Characterization," in *Proceedings, 9th Conference on Roofing Technology* (National Roofing Contractors Association, Rosemont, IL, May 1989), pp. 85-90.

⁷ Glen D. Gaddy, Walter J. Rossiter, Jr., and Ronald K. Eby, "The Application of Thermal Analysis Techniques to the Characterization of EPDM Roofing Membrane Materials," in Thomas J. Wallace and Walter J. Rossiter, eds., *Roofing Research and Standards Development, 2nd Volume: ASTM STP 1088* (ASTM, Philadelphia, 1990), in press; Glen D. Gaddy, Walter J. Rossiter, Jr., and Ronald K. Eby, *The Use of Thermal Mechanical Analysis to Characterize EPDM Roofing Membrane Materials*, in review.

⁸ D. Backenstow and P. Flueller; M.S. Farling; Glen D. Gaddy, Walter J. Rossiter, and Ronald K. Eby (1990, and in review).

The USACERL Program on Roof Membrane Characterization

Since the late 1970s, when elastomeric, thermoplastic, and polymer-modified bituminous roofing became popular in the United States, the U.S. Army Construction Engineering Research Laboratory (USACERL) has considered these roof systems as practical alternatives to built-up roofing (BUR). In 1979, USACERL initiated a program to evaluate innovative roofing systems and materials as alternatives for BUR, and to identify requirements to be included in guide specifications for selected alternative systems.⁹ As part of the program, construction of selected alternative systems, e.g., EPDM, PVC, and spray-in-place polyurethane foam, was performed at Army installations with different weather conditions.¹⁰

Not unexpectedly, the experimental field program found that membranes based on various polymeric resins underwent different degradation mechanisms in service. Better understanding of these mechanisms and the factors that affect changes in material properties would provide the knowledge needed to prepare specifications that minimize material degradation and reduce long-term maintenance and repair costs of Army roofing. In the long term, this same knowledge would also help to develop standard tests to predict the serviceability and performance of membrane roofing.

USACERL initiated a program entitled "Evaluation of Roofing Materials Degradation Processes" to provide methods to evaluate the quality and service life of membrane roofing systems and to contribute to the basis for standards and specifications.¹¹ One objective of this program was to develop new or improved methods to characterize important properties of membrane materials, and to evaluate their resistance to failure through common degradation processes. Thermal analysis methods for characterization of membrane materials, as recommended by the CIB/RILEM Committee, are one attractive way for meeting this task objective. To find out whether experts in thermal analysis methods believe that these methods could be usefully incorporated into voluntary consensus standards for membrane materials, USACERL sponsored a workshop on the applicability of thermal analyses methods to the characterization of roofing membranes. This report presents the results of the workshop.

Objectives

The objectives of this study were to determine whether (1) thermal analysis methods are applicable to the characterization of roofing membranes, and (2) thermal analysis methods can be usefully incorporated into voluntary consensus standards for membrane materials.

⁹ E. Marvin et al., *Evaluation of Alternative Reroofing Systems*, Interim Report (IR) M-263/ADA071578 (U.S. Army Construction Engineering Research Laboratory [USACERL], June 1979).

¹⁰ Myer J. Rosenfield and D.E. Brotherson, *Construction of Experimental Roofing*, Technical Report (TR) M-298/ADA109595 (USACERL, November 1981); Myer J. Rosenfield, *Construction of Experimental Polyvinyl Chloride (PVC) Roofing*, TR M-343/ADA145406 (USACERL, April 1984).

¹¹ Walter J. Rossiter, Jr. and Larry W. Masters, *Suggested Research Topics for the Construction Engineering Research Laboratory (CERL) Program, Evaluation of Roofing Materials Degradation Processes*, NISTIR 88-3870 (National Institute of Standards and Technology [NIST], Gaithersburg, MD, November 1988).

Approach

Invitations were extended to participants who: (1) had personal experience with applications of thermal analysis to roofing, and (2) were willing to share those experiences in an informal presentation. The number of invitations was limited to the number of presentations that could be conveniently made in a day.

The workshop extended over 1-1/2 days. A moderator was assigned to direct the activities. During the first day, 13 of the invited participants made informal presentations describing their experiences in applying thermal analysis methods to the analysis of questions or problems regarding roofing performance.

On the second day, a general discussion among all participants was held on the question of the applicability of thermal analysis methods to standards and guide specifications. These discussions provided the basis of the participants' conclusions on the subject.

The participants represented a cross-section of the U.S. roofing industry, including the manufacturing, contracting, consulting, and research segments, and presented a wide range of subjects. Specific interests covered all major types of flexible-membrane roofing (i.e., bituminous built-up and polymer-modified, elastomeric, and thermoplastic). Presentations addressed nonproprietary subjects. Participants were asked to consider the following topics for presentation:

1. The current status of testing roofing membrane products using thermal analysis methods
2. The applicability of thermal analysis methods to standards and guide specifications
3. The limitations and barriers which must be overcome to allow implementation of thermal analysis methods in standards and guide specifications
4. Research needed to overcome the identified limitations and barriers.

Mode of Technology Transfer

Results generated by this study will impact Corps of Engineers Guide Specifications for roofing systems.

2 APPLICATIONS OF THERMAL ANALYSIS TO ROOFING MATERIALS

The presentations of the first day of the workshop provided many examples of the application of thermal analysis to the characterization of roofing materials. The questions and discussions among the participants produced many comments on the methods, usefulness, and limitations of roofing material analysis. Appendix C summarizes the topics addressed during the individual presentations, and includes examples of thermal analysis applications to roofing and the lessons learned from performing those analyses. Some presentations were limited enough in scope to describe specific applications and their detailed results. Other presentations broadly listed the types of applications that had been carried out, without giving details of analyses or results. Most examples presented applications not yet published in the roofing literature. This may explain the perception in the industry that thermal analysis has had little use for the characterization of roofing materials.

Table 1 (based on Appendix C) summarizes the applications of thermal analysis to roofing products given during the presentations, and shows the substantial application to roofing materials thermal analysis has actually had. In fact, thermal analysis methods are already routine laboratory procedures for the characterization of other materials.¹² The applications have covered the range of thermal analysis methods of prime interest to the roofing industry, although most of the examples concerned TG and DSC techniques. The examples included not only analyses of roof membrane materials, but also characterization of coatings for spray-in-place polyurethane foam, additives for bitumens, bitumen-polymer blends, and purity of constituents used in synthetic membrane formulations. The complexity of the applications has ranged from routine determination of moisture in materials, to experimental development of a method to determine the efficiency of modifying asphalts with polymers.

In most cases, presenters indicated that the analyses provided meaningful data to help characterize the samples, particularly when used along with other methods (e.g., infrared, mechanical tests). For example, differences in properties were observed between new and exposed specimens, or between batches of a product in which a constituent was varied. However, in the former case, it was generally mentioned that the relationship between the changes observed on exposure and the performance of the material in service was not understood. The lesson learned from these examples was that thermal analysis methods are sound analytical tools that assist in the characterization of materials, and that they should be used where appropriate for solving the problem at hand.

Not all the examples given during the presentations described successful applications of thermal analysis to roofing. One presentation (p. 26) discussed changes in glass transition temperature that did not indicate the performance of coatings for spray-in-place polyurethane foam. Little change in glass transition temperature was observed over 5 years of service, although the performance of many of the coatings did deteriorate. Another presentation (p. 27) mentioned two additives for bitumen that were described as identical by TG and DSC analyses, but still produced blends with different physical characteristics. Such examples indicate that, although thermal analysis methods may have wide application for roofing materials, they may not always be the best method for characterizing particular aspects of a product's performance.

¹² W.W. Wendlandt, W.W. Wendlandt and P.K. Gallagher.

Table 1

Applications of TA Methods to Roofing Materials

Method	Applications
TG*	• Analysis of SBS polymer-modified bitumen specimens before and after heat exposure • Analysis of EPDM, PVC, and modified bitumens before and after heat exposure • Characterization of additives for bitumen • Determination of the ratio of constituents (polymers, carbon black, and ash) in rubbers of known composition • Analysis of new and exposed black and white EPDM • Studies of thermal stability • Studies of volatility of plasticizers • Analysis of types of plasticizers in membranes • Determination of the presence of moisture • Determination and analysis of fillers • Determination of PVC resin stability after extraction of plasticizer
DSC	• Analysis of SBS polymer-modified bitumen specimens before and after heat exposure • Characterization of acceptable polymer-asphalt blends • Characterization of elastomeric coatings used for spray-in-place polyurethane foam (PUF) roofing • Analysis of EPDM, PVC, and modified bitumens before and after heat exposure • Analysis of new and exposed black and white EPDM • Characterization of additives for bitumen • Determination of glass transition temperature of pure materials and of compatible and incompatible mixtures • Studies of thermal stability • Determination of glass transition temperatures • Determination of the presence of moisture • Determination of melting points • Identification of unknown membranes by generic polymeric type including EPDM, PVC, neoprene, and CPE, and in some cases, by producer of a given type
TMA	• Analysis of new and exposed black and white EPDM
DMA	• Characterization of SBS-asphalt blends to assess the efficiency of the modification • Characterization of additive-bitumen blends • Analysis of EPDM, PVC, and modified bitumens before and after heat exposure • Analysis of new and exposed black and white EPDM
TP	• Determination of mechanical properties • Determination of thermal expansion coefficients • Investigation of a possible method to replace the time-consuming test of cold-temperature flexibility

*TG (Thermogravimetry); DSC (Differential Scanning Calorimetry); TMA (Thermal Mechanical Analysis); DMA (Dynamic Mechanical Analysis); TP (Torsion Pendulum)

3 SUMMARY OF WORKSHOP DISCUSSIONS

The workshop's second day focused on discussion of "the applicability of using thermal analysis methods in standards and guide specifications." The examples and "lessons learned" (Appendix D) cited the previous day formed the basis for this discussion.

Utility of TA Methods

During the second day's discussions, it was generally agreed that thermal analysis has a place for materials characterization, quality control, and problem solving. The participants considered the methods to be important laboratory tools that, applied as needed, may help answer specific questions or solve specific problems. However, participants also agreed that TA methods should not be considered as exclusive means to measure changes in a material's properties. Examples of the comments made by the participants concerning the utility of TA methods

- TA methods are sound laboratory research tools that assist in understanding material behavior and complement other tests for characterizing materials.
- TA methods provide a group of sensitive research techniques suitable for comparative studies within a class of similar materials; reference samples are needed.
- TA methods have their place in evaluating materials, but no single test should be used as a sole measure of performance.
- TA methods are useful for quality control. Analyses of materials are conducted as a measure of compound purity, and contamination of products can be observed.
- TA methods, in conjunction with other appropriate laboratory techniques, provide a successful way to identify the causes of problems, although a considerable history and a database on the product or system under investigation are needed.
- A controlled sampling is required to have reproducible results; test parameters must be carefully set.

Limitations of TA Methods

A common opinion was that TA methods are not immediately applicable in standards because no single thermal analysis method can solely predict the expected field performance of a particular product. It is also difficult to identify a performance characteristic that only a thermal analysis method could measure. TA methods are no "cure-all"; they may not always be appropriate for answering any specific question. (To be fair, this is generally true of any test method used to evaluate a building material.) Finally, the high costs of TA equipment may seriously restrict development of roofing standards that

incorporate TA methods. The following illustrate the comments made by the participants concerning the limitations of TA methods:

- TA methods should not be taken as performance predictors.
- TA methods cannot always be used to predict results obtained from the analysis of the materials using other techniques.
- The methods may not provide unique techniques for measuring performance parameters.
- The state of aging among different roofing materials cannot be judged on the basis of absolute thermal analysis measurements.
- Before TA methods can be applied in standards, much work is needed in the areas of technique development, and in relating results of the measurements to performance.
- TA equipment may be too expensive for routine use.
- In response to the CIB/RILEM Committee recommendations, a database needs to be developed to determine changes in properties. Data are not available to connect an observed change in a property (measured by thermal analysis) to a particular performance property. The database should include an analysis of many samples before and after in-service exposure on roofs.
- Some doubt was expressed regarding the CIB/RILEM recommendation that an allowable change in glass transition temperature not exceeding 10 °C be used to indicate acceptable performance.
- Corrosion due to release of hydrochloric acid during heating of some materials resulted in equipment problems.

Nevertheless, several participants suggested possible thermal analysis applications. For example, a thermal analysis method might be used to determine the coefficient of linear expansion of roofing membrane materials. (A convenient method is not presently available to the U.S. industry.)

The majority opinion was that thermal analysis methods are not presently applicable to standards and guide specifications. Participants were polled on the likelihood that thermal analysis could be applied to roofing material standards. The question was expressed as follows:

What is the likelihood that, in the case of roofing materials, a direct application to the consensus standards process will be found for a thermal analysis method? Please answer on a scale from 0 to 10:

0 = highly unlikely, not at all
10 = highly likely.

Table 2 shows the results of the poll.

Table 2
Workshop Poll Results

Scale Value	No. of Responses
0	7
1	1
2	4
3	1
4	1
5	2
6-10	0

The vote clearly shows that most of the participants did not believe that thermal analysis methods were of direct application in consensus standards for roofing. This ballot result ended the discussions and the remainder of the workshop was devoted to formulating conclusions.

4 CONCLUSIONS

Conclusions were grouped into two categories: (1) areas of immediate use of thermal analysis methods, and (2) areas where the use is not immediate. Participants agreed that thermal analysis methods have immediate applicability to roofing technology in the following areas:

- **Research:** Thermal analysis methods provide sound analytical tools for characterizing materials and the changes that they may undergo in service. They should be considered as one of a number of techniques that the researcher may use to answer a question or solve a problem.
- **QA/QC:** Thermal analysis methods provide valuable tools for tracking manufacturing processes to check that they remain in control. TA methods may help to examine the variability of materials within a batch or between batches, or to analyze raw materials for the presence of contaminants.
- **Troubleshooting:** Materials experiencing problems in service may be analyzed in the laboratory using thermal analysis techniques among other methods of analysis. The data obtained may be compared to those from control specimens that were new or have performed well in service. A considerable databank assembled on past experience is invaluable when troubleshooting problems.

Participants concluded that TA methods do not have immediate applicability to roofing technology in the following area:

- **Standards:** Thermal analysis methods are not, in themselves, considered to predict the performance of a product in service. Moreover, the high cost of TA equipment can prohibit general use of the methods, which may make their use in standards unattractive.

REFERENCES

- Backenstow, D., and P. Flueller, "Thermal Analysis for Characterization," in *Proceedings, 9th Conference on Roofing Technology* (National Roofing Contractors Association, Rosemont, IL, May 1989), pp. 85-90.
- Cash, C.G., "Thermal Evaluation of One-Ply Sheet Roofing," in *Single-Ply Roofing Technology, ASTM STP 790* (American Society for Testing and Materials [ASTM], Philadelphia, 1982), pp. 55-64.
- "Elastomeric, Thermoplastic, and Modified Bitumen Roofing: A Summary Technical Report of CIB W.83 & RILEM 75-SLR Joint Committee," *Matériaux et Constructions*, Vol 19, No. 112 (July-August 1986), pp. 323-329.
- Farling, M.S., "New Laboratory Procedures To Evaluate the Durability of Roofing Membranes," Appendix D in *Performance Testing of Roofing Membrane Materials*, "Recommendations of CIB W.83 and RILEM 75-SLR Joint Committee on Elastomeric, Thermoplastic, and Modified Bitumen Roofing" (RILEM, November 1988).
- Gaddy, Glen D., Walter J. Rossiter, Jr., and Ronald K. Eby, "The Application of Thermal Analysis Techniques to the Characterization of EPDM Roofing Membrane Materials," in Thomas J. Wallace and Walter J. Rossiter, eds., *Roofing Research and Standards Development, 2nd Volume: ASTM STP 1088* (ASTM, Philadelphia, 1990), in press.

REFERENCES (Cont'd)

- Gaddy, Glen D., Walter J. Rossiter, Jr., and Ronald K. Eby, *The Use of Thermal Mechanical Analysis to Characterize EPDM Roofing Membrane Materials*, in review.
- LeChatelier, H., *Bull. Soc. Fr. Mineral. Cristallogr.*, Vol 10 (1887), pp. 204-211.
- Marvin, E., et al., *Evaluation of Alternative Reroofing Systems*, Interim Report (IR) M-263/ADA071578 (U.S. Army Construction Engineering Research Laboratory [USACERL], June 1979).
- Maurer, J.J., "Elastomers," in E.A. Turi, ed., *Thermal Characterization of Polymeric Materials* (Academic Press, New York, 1981), pp. 571-704.
- Roberts-Austin, W.C., "Fifth Report of the Alloys Research Committee," *Metallographist*, Vol 2 (1889), pp. 186-195.
- Rosenfield, Myer J., *Construction of Experimental Polyvinyl Chloride (PVC) Roofing*, Technical Report (TR) M-343/ADA145406 (USACERL, April 1984).
- Rosenfield, Myer J., and D.E. Brotherson, *Construction of Experimental Roofing*, M-298/ADA109595 (USACERL, November 1981).
- Rossiter, Walter J., Jr., and Larry W. Masters, *Suggested Research Topics for the Construction Engineering Research Laboratory (CERL) Program, Evaluation of Roofing Materials Degradation Processes*, NISTIR 88-3870 (National Institute of Standards and Technology [NIST], Gaithersburg, MD, November 1988).
- Stone, R.L., "Dynamic Gas Controlled Differential Thermal Analysis," *Bulletin—Ohio State University, Engineering Experimental Station*, Vol 146 (1951), pp. 1-77.
- Warshaw, Ruth I., "Summary of the RILEM/CIB Report on Performance Testing of Roof Membrane Materials," *International Journal of Roofing Technology*, Vol 1, Issue 1 (Spring 1989), pp. 10-11.
- Watson, E.S., "A Differential Scanning Calorimeter for Quantitative Differential Thermal Analysis," *Analytical Chemistry*, Vol 36 (1964), pp. 1233-1238.
- Wendlandt, W.W., *Thermal Methods of Analysis*, 2d ed. (John Wiley and Sons, New York, 1974), p. 490.
- Wendlandt, W.W., and P.K. Gallagher, "Instrumentation," in *Thermal Characterization of Polymeric Materials* (Academic Press, New York, 1981), pp. 1-86.

APPENDIX A: CIB/RILEM Recommendations on Thermal Analysis Methods

This Appendix reprints the recommendations of the CIB/RILEM Committee regarding the use of thermal analysis methods for membrane material characterization.¹³

Committee Recommendation for Test Method

Thermal analysis methods should be applied to the characterization of roofing membrane materials. Specifically, the dynamic mechanical properties from -100 to 100 °C should be determined using either the torsion pendulum or dynamic mechanical analyzer (DMA). The characterization should be conducted on both new and aged materials. In addition, thermogravimetry (TG) of new and aged materials should be reported.

Consideration may also be given to the use of differential scanning calorimetry (DSC) for membrane characterization.

Test Method Description

The test methods for dynamic mechanical properties are given in ASTM D 4065, "Standard Practice for Determining and Reporting Dynamic Mechanical Properties of Plastics" (1990). An ISO standard, No. 537: 1980, "Plastics—Testing With the Torsion Pendulum," which describes the torsional pendulum test is also available.

Principle of the Test Method

Thermal analysis is a technique that characterizes the properties of a material as a function of temperature. The DMA measures mechanical properties such as modulus and glass transition temperature. The TGA provides a measurement of the thermal stability of a material. Data may be provided, for example, on loss of mass as a function of temperature and changes in chemical composition due to aging.

The torsion pendulum test (ISO 537) measures the complex shear modulus of a material as a function of temperature. This method detects changes caused not only by aging (either artificial or natural), but even changes due to alterations in formulation.

Criteria

Only a preliminary proposal is given at this time for testing procedures and criteria for thermal analysis until further research is conducted to refine them.

¹³ M.S. Farling, *Recommendations of CIB W.83 and RILEM 75-SLR Joint Committee on Elastomeric, Thermoplastic, and Modified Bitumen Roofing* (RILEM, November 1988).

Preliminary guidelines that should be the subject of future review based on the results of continuing research are:

- TGA The change in the organic constituents after aging should not exceed ± 2 percent.
- DMA The change in the brittle point after aging should not be more than 10 °C of the original value; the modulus should not change by more than a factor of 10.
- Torsion
 Pendulum As with the DMA, shifts in brittle point or modulus can be determined as a function of exposure, and allowable changes can be assigned as the criterion.

Suggestion for Membrane Classification According to the Recommended Test Method

No proposal is given at this time.

Suggestions for Future Work

Suggestions for future Committee work include tests of new and aged (in-service) materials. In addition, a standard method for sample preparation for both laboratory and in-service exposure needs to be developed.

With regard to testing aged specimens, changes in properties as determined by thermal analysis should be measured as a function of exposure conditions. One approach suggested was to examine specimens from different areas of roofs such as ponded sections, exposed versus shaded sections, and those having different orientations (i.e., north and south exposure).

With regard to testing new materials, interlaboratory tests should be conducted after the materials have been subjected to outdoor or laboratory exposure. The materials selected should have a known performance history.

Sample Size

The Committee suggests that samples in the size of 60 by 10 mm by t (thickness in mm) be taken from roofing membranes for testing. The direction and exposure of the specimen should be recorded.

APPENDIX B: Overview of Thermal Analysis Methods

Introduction

Thermal analysis (TA) methods have only recently begun to be used to characterize roofing membrane materials. Thermal analysis is a generic term for a group of techniques that measure the change in physical properties as a function of temperature. These techniques can produce highly reproducible results with very small sample sizes. TA techniques also provide more diverse information than other methods, such as load elongation or low-temperature embrittlement, alone. The TA techniques described here are:

1. Thermogravimetry (TG), which measures mass change
2. Differential scanning calorimetry (DSC), which measures relative heat flux and in turn the heat capacity and the glass transition temperature
3. Dynamic mechanical analysis (DMA), which measures moduli and in turn the glass transition temperature
4. Thermal mechanical analysis (TMA), which measures changes in volume or length as a function of temperature
5. Torsion pendulum (TP), which measures the decay of a free oscillation in a material.

Thermogravimetry

Thermogravimetry (TG) measures the changes in mass over a temperature range and its derivative method (dTG) measures the change in mass per time change over a temperature range. Wendlandt¹⁴ lists a number of uses of TG and dTG, including measuring thermal oxidative degradation of polymeric substrates.

The components of a TG system can be optimized for different applications such as high temperature or low mass change. Additionally, various sample containers can be used to ensure that the sample does not become unstable during normal testing or when measuring associated properties such as vapor pressure during experimentation.¹⁵ The optimization of components helps to reduce the impact of error sources such as buoyancy effects, aerodynamic forces, condensation, chemical reaction with the device, spurious sample loss, electric and magnetic fields, and temperature induced balance changes.¹⁶

A typical modern TG consists of a thermobalance, balance control unit, furnace, furnace programmer unit, and a computer data recorder. The system is designed with the furnace beneath the microbalance with one pan of the balance extending into the furnace. These systems can be operated at pressures from 760 to 10^{-4} torr in oxidative, reducing, or inert atmospheres at flow rates up to 200 ml/min. A furnace with a platinum resistance wire is used, allowing for heating to 1000 °C at rates

¹⁴ W.W. Wendlandt.

¹⁵ W.W. Wendlandt and P.K. Gallagher.

¹⁶ H. LeChatelier, *Bull. Soc. Fr. Mineral. Cristallogr.*, Vol 10 (1887), pp. 204-211.

between approximately 0.3 and 300 °C/min. Using a computer, it is possible to control the instrument accurately and to follow its progress by the tenth of a degree. Computer use also allows an analysis of both the thermogram and the derivative thermogram from the same run. Several manufacturers produce similar systems capable of determining mass loss as a function of temperature. Each of these devices may operate in a different fashion.

A typical TG curve is shown in Figure B1. The temperature is plotted on the x-axis and the percent original weight is plotted on the y-axis. As the temperature is increased, the corresponding change in the sample's mass is recorded. The various curves reflect the composition of an EPDM roofing membrane material after exposure to a number of conditions.

Differential Scanning Calorimetry

The differential scanning calorimeter (DSC) and the closely related differential thermal analyzer (DTA) are the logical progression of the application of the thermocouple, resistance thermometer, and the optical pyrometer to chemical systems at elevated temperatures. LeChatelier was the first to show the use of heating-rate-change curves to identify materials. The differential temperature method was derived to eliminate the effect of heating rate by comparing the temperature of interest to an inert reference material.¹⁷ Modern DTA began with the introduction of the dynamic gas atmosphere DTA in

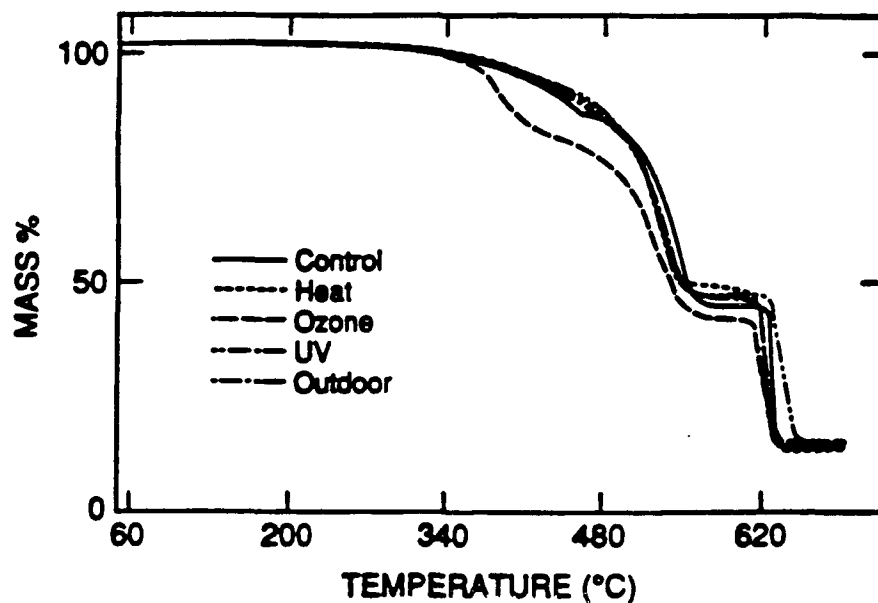


Figure B1. Typical TGA Curve.

¹⁷ W.C. Roberts-Austin, "Fifth Report of the Alloys Research Committee," *Metallographist*, Vol 2 (1889), pp. 186-195.

1951.¹⁸ This allowed for the manipulation of the atmosphere in the system, and lead to studies of reactions under various partial gas pressures.

The modern DSC was developed as an outgrowth of DTA by Watson and others.¹⁹ The rapid development of commercial systems was due to the adaptation of the equipment for use by polymer chemists after years of use solely by geologists. Polymer scientists found it possible to accurately determine parameters such as melting points, glass transition temperatures, rate of polymerization, and thermal oxidative reactions. The DSC made it possible to determine these parameters quickly and accurately with samples many times smaller than those required by other methods.

DSC comes in two readily available forms: power compensation and heat flux. Power compensation measures power input as a function of temperature change, while heat flux measures temperature difference as a function of temperature. DTA is a subset of this second DSC format.

Unlike the DTA the DSC apparatus maintains a sample temperature equal to a reference material by supplying heat to the sample or reference. The amount of heat required to maintain the isothermal condition is then recorded as function of time or temperature. Gas evolution can also be determined by collecting the exit gas from the system. To enable the system to measure heat input in two places, two control loops are used, one for average temperature and the other for differential temperature. The average temperature loop ensures that the average temperature of the system increases as programmed, while the differential loop compensates for differences between the sample and reference. By measuring this differential temperature, the amount of energy absorbed or liberated from the system is determined.

A DSC provides for a number of heating rates and a range of operating temperatures from approximately -175 to 725 °C. Additionally, the atmosphere is controlled and changeable. The system is housed in a dry box to avoid condensation and other problems of a wet environment. With computer control, it is possible to closely control the temperature of the system.

Figure B2 shows a typical unstandardized DSC curve for an EPDM. The temperature is plotted on the x-axis, and the heat capacity on the y-axis. The curve shows two transitions, a second order transition, in this case the glass transition, between -60 and -30 °C, and a first-order transition between 30 and 60 °C, reflecting melting of the diffuse crystalline structure present in the terpolymer.

Thermal Mechanical Analysis

Thermal Mechanical Analysis (TMA) measures the deflection of a material under a constant load as a function of temperature.²⁰ The sample is placed on a support perpendicular to a probe that rests on the sample surface. The probe is suspended so that a zero net load can be placed on the sample to measure expansion as a function of temperature or with a positive net load to measure penetration of the probe into the sample. Each of these, as well as other measurements, are accomplished using various probes in the same apparatus. The probe travels within a linear variable differential transformer (LVDT) that produces an output voltage according to the change in position of the probe.

¹⁸ R.L. Stone, "Dynamic Gas Controlled Differential Thermal Analysis," *Bulletin-Ohio State University, Engineering Experimental Station*, Vol 146 (1951), pp. 1-77.

¹⁹ E.S. Watson, "A Differential Scanning Calorimeter for Quantitative Differential Thermal Analysis," *Analytical Chemistry*, Vol 36 (1964), pp. 1233-1238.

²⁰ W.W. Wendlandt and P.K. Gallagher.

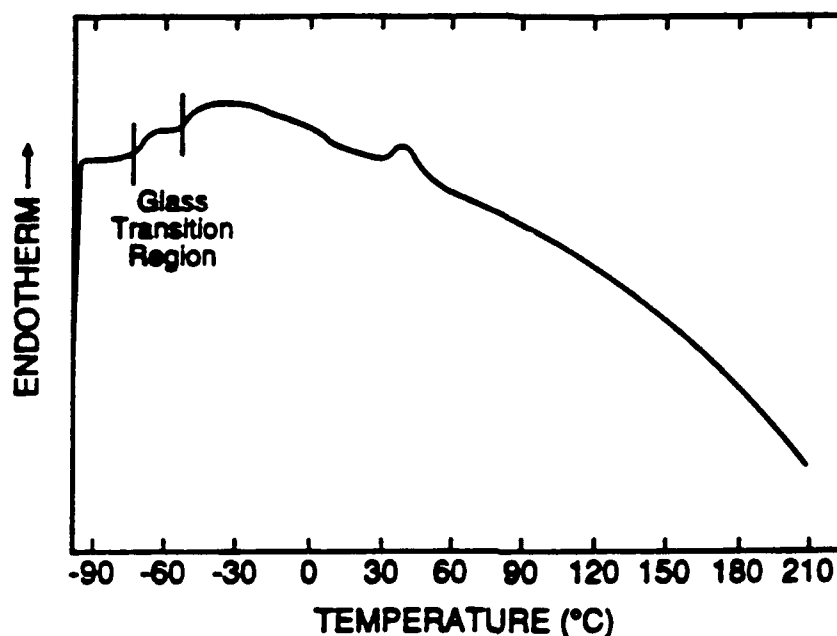


Figure B2. Typical DSC curve.

A typical apparatus measures displacement over the range of approximately -175 to 725 °C. Various probes can also be used to determine thermal expansion, compression, softening, and fiber measurements.

A typical TMA curve generated in the expansion mode would show the temperature on the x-axis and the change in length on the y-axis. Second order transitions (e.g., a glass transition) are shown as changes in the slope of the curve. A peak in the curve would indicate a first-order transition such as melting.

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) is a technique in which the dynamic modulus and/or the damping characteristics of a substance are measured under oscillatory load as a function of temperature.²¹ A DMA may oscillate a sample at its resonance frequency and measure the amount of energy required to maintain the oscillation, or it may oscillate at a fixed frequency and measure the energy lost by the oscillator. It is also possible to apply the load in shear and measure the shear moduli rather than the other moduli.

For this analysis, the sample is clamped between two arms: a passive support and a driven electromechanical transducer (an arm). The sample is bent by a slight rotation of the driven arm, and

²¹ W.W. Wendlandt and P.K. Gallagher.

then released to set the material into resonant oscillation. The frequency and amplitude are measured by an LVDT on the active member. This amplitude is fed back into the driver to provide the needed energy to feed the system. The system operates from -150 to 500 °C. The second method applies a load in the same fashion as the TMA, but cycles the load at a given amplitude, measuring the energy required to maintain that amplitude.

The DMA determines the storage modulus (E') and the loss modulus (E'') of the material. E' reflects the energy that the material converts into potential energy, and the loss modulus reflects the energy dissipated by the system, most commonly as heat. The E' and E'' are out of phase due to the time lag inherent in the dissipation of energy. Therefore, it is possible to determine a quantity, known as $\tan \delta$, which is the ratio E''/E' .

Figure B3 shows a typical DMA curve. It shows E' and E'' which decrease at different rates, and their ratio, $\tan \delta$. The peak in the $\tan \delta$ curve is taken to be the glass transition temperature.

Torsion Pendulum:

Torsion Pendulum (TP) is a technique in which a long thin sample of the material in question is extended with no net force and is twisted. The material is released and untwists. The frequency and decay of the oscillations are monitored. This method yields similar information to that generated by DMA. E' , E'' , and $\tan \delta$ can be determined.²²

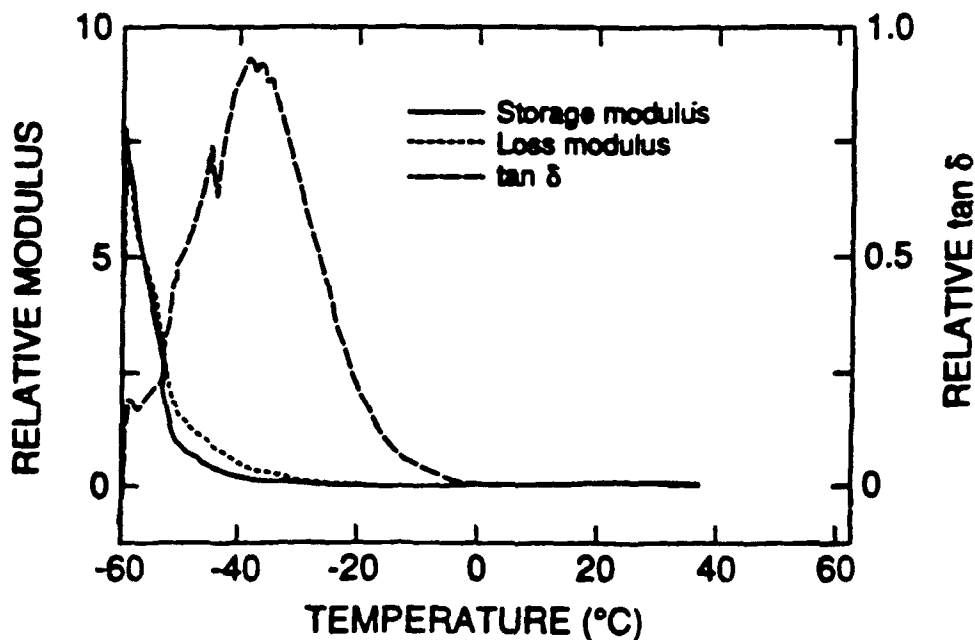


Figure B3. Typical resonance frequency DMA curve.

²² J.J. Maurer, "Elastomers," in E.A. Turi, ed., *Thermal Characterization of Polymeric Materials* (Academic Press, New York, 1981), pp. 571-704.

APPENDIX C: Summaries of the Workshop Presentations

This appendix gives a brief statement of the experiences with thermal analysis methods that each workshop participant mentioned during the first day of the workshop. It was beyond the scope of the workshop to have participants prepare papers for inclusion in a published "proceedings," but this appendix does give short examples of applications of thermal analysis methods to roofing technology.

An important aspect of the first day's activities was the commentary concerning the usefulness and limitations of thermal analysis to roofing. For this reason, each presentation is summarized in two parts: the "TA Experiences" of the specific presenters; and the "Lessons Learned," those key comments regarding the utility and limitations of thermal analysis to roofing.

Presenter: Mr. Theodore W. Michelsen, Manville Corp.

TA Experiences

Mr. Michelsen gave examples of the application of TG and DSC to the analysis of SBS polymer-modified bitumen specimens before and after exposure to heat aging. The results were compared to those obtained from other analytical techniques often conducted on bituminous membrane products.

Although the thermal analysis curves showed differences for the various specimens, they could not be used to predict the results from the other analytical techniques.

The thermal analysis methods were considered to be analytical tools to characterize properties of materials. They are sound laboratory research tools to help understand material behavior and to complement other methods. They should not be taken as performance predictors in themselves.

The methods may have utility for quality control.

The results of the thermal analysis tests described were dependent on the sampling technique used; sampling must be controlled to have reproducible results.

Presenter: Mr. Mark A. Berggren, Shell Development Co.

TA Experiences

Mr. Berggren gave an example of the use of DMA to characterize SBS-asphalt blends. The performance of modified bitumens was related to the quality of the modifier-asphalt network. This is often assessed using microscopy. In this case, DMA was investigated as a tool for assessing the efficiency of the modification process. The testing was conducted using SBS-asphalt blends at a constant frequency at four different temperatures. Results varied with different asphalts. It was found that a time-temperature superposition principle was valid over the range of -30 to 80 °C.

Lessons Learned

The use of the DMA method was considered useful to roofing applications because:

- "Benchmarks" for optimal SBS-asphalt performance could be set
- Compatible polymer-asphalt systems could be identified
- The effect of aging on the elasticity of the blend could be gauged.

To set benchmarks for optimal SBS-asphalt performance, data are needed from the field for both acceptable and unacceptable blends.

The procedure must carefully set test parameters such as frequency of cycling and strain applied so that meaningful data are obtained.

The method was applicable only to the modifier-asphalt blends and not to the composite reinforced membrane material. Many comments were offered that testing of the composite membrane material is complex and that the relative behavior of the components must first be understood.

Much work on system analysis is needed before this method achieves general applicability as a performance indicator.

Presenter: Mr. Christopher F. Mullen, Sarnafil

TA Experiences

Mr. Mullen gave an overview of his company's applications of TG, DSC, and TP methods. No data were presented. TG has been used for:

- Studies of thermal stability
- Studies of volatility of plasticizers
- Analysis of types of plasticizers in membranes
- Determination of the presence of moisture
- Determination and analysis of fillers
- Determination of PVC resin stability after extraction of plasticizer.

DSC has been used for:

- Studies of thermal stability
- Determination of glass transition temperatures
- Determination of the presence of moisture
- Determination of melting points.

TP has been used for:

- Determination of mechanical properties
- Determination of thermal expansion coefficients
- Investigating a possible method to replace the time-consuming test of cold temperature flexibility.

Lessons Learned

Thermal analysis provides a group of sensitive research methods suitable for comparative studies within a class of similar materials.

It is not possible to judge the state of aging among different roofing materials on the basis of absolute thermal analysis measurements. It is generally necessary to have reference samples or to make a series of comparative measurements.

Because thermal analysis methods cannot be used "absolutely," thermal analysis may never find its way into roofing standards.

Presenter: Mr. Thomas L. Smith, the National Roofing Contractors Association

TA Experiences

The National Roofing Contractors Association has supported investigations of the applicability of thermal analysis methods to the characterization of roofing membrane materials. They have not generated thermal analysis data directly.

Nearly a decade ago, with the influx of many new (and often untried) membrane products into the U.S. roofing market, the NRCA urged its members to retain samples of the materials being installed. The presenter reviewed this program in relation to the objectives of the Thermal Analysis Workshop. He indicated that, if research were to be conducted to determine thermal analytical properties of aged and unaged membrane materials, it might be possible to obtain membrane samples from roofs in cases where the original material had been retained. The retained materials could, thus, act as unaged controls for comparison of their properties with those of the membrane materials cut from roofs.

Lessons Learned

Samples of membrane materials retained for many years, even in a dark cabinet or other similar location, may still have undergone some changes in properties. This possibility must be considered before including such samples in a test program.

Presenter: Mr. Carl G. Cash, Simpson, Gumpertz, and Heger

TA Experiences

This presenter was one of the first researchers in the U.S. roofing industry to investigate thermal analysis for characterizing elastomeric and thermoplastic membrane materials. In 1982, he reported on the application of DSC to identifying unknown materials by generic polymeric type and by producer. The materials included EPDM, PVC, neoprene, and CPE.

Lessons Learned

This presenter could differentiate between material types and, in some cases, producers of a given type using TA methods. He could also detect differences between aged and unaged samples.

Equipment required for TA methods were too expensive for routine use. There were also equipment problems attributed to corrosion associated with the release of hydrochloric acid during heating of some of the materials under investigation.

The presenter stated that thermal analysis methods have their place in evaluating materials, but that no single test should be used as a measure of performance. The fact that distinctive mechanisms may degrade different materials must be considered in designing methods for performance assessment.

Presenter: Mr. S.A. Banks, Exxon Chemical

TA Experiences

This presenter discussed two areas of applied thermal analysis:

1. TA methods are used for "troubleshooting" problems that have arisen both in production and in the field. For troubleshooting purposes, thermal analysis is generally used along with other test methods.

2. The presenter's company uses DSC experimentally to determine if it is an appropriate method for characterizing acceptable polymer-asphalt blends. Enthalpies of fusion and melting point are compared to ring-and-ball softening point. These data relate to the application temperatures of the modified asphalt either in torch applications or with hot asphalt.

Lessons Learned

It was reported that thermal analysis, in appropriate combination with other laboratory techniques, has provided a successful means for troubleshooting the causes of problems. A limitation is that considerable history and a database on the product or system under investigation are needed.

Although the presenter had limited data on characterizing modified bitumens, he felt positive that thermal analysis has possibilities for characterizing the matrix of a polymer-asphalt blend. He also thought that the thermal analysis methods should be used in conjunction with other laboratory techniques for characterizing materials.

Presenter: Mr. Robert L. Alumbaugh, the Naval Civil Engineering Laboratory

TA Experiences

This presentation addressed the use of thermal analysis for the characterization of elastomeric coatings used for spray-in-place polyurethane foam (PUF) roofing systems, to relate changes in glass transition temperature (as determined using DSC) to the performance of the coating in service. PUF coatings were subjected to DSC analysis when new, and periodically (up to 5 years) in service.

Lessons Learned

The glass transition temperature was not found to be an indicator of performance. Most coatings showed little change in glass transition temperature in spite of variations in performance in service. In particular, a significant portion of one coating had eroded away. However, where the coating was still present, it showed essentially no change in glass transition.

There was a change in the specific heat of the glass transition for the coatings. It was hypothesized, but not shown, that the shape of the DSC curve in the area of the glass transition may relate to performance of the coating. Research is needed to test the hypothesis.

This presenter questioned the CIB/RILEM recommendation that an allowable change in glass transition temperature not exceeding 10 °C be considered as indicative of acceptable performance. Specific counter-evidence was the example of the coating (described above) that performed poorly, even though it showed essentially no change in glass transition temperature.

Presenter: Mr. James Wells, Owens Corning Fiberglass Corp.

TA Experiences

On the basis of limited experience with thermal analysis, this presenter gave two examples of the application of thermal analysis for characterizing products, one unsuccessful and another successful:

1. In the unsuccessful application, two additives for bitumen, which came from different sources, and which are considered to be the same, were analyzed using DSC and TG. These DSC and TG analyses showed no difference in the two products, even though bitumen blends with the two additives had different physical characteristics (i.e., tensile strength).

2. In the successful application, an additive was combined in increasing quantities with a bitumen, and the glass transition temperatures of the blends were determined using DMA. The analysis showed that, after a certain amount of additive was incorporated in the bitumen, no significant change in glass transition temperature was achieved with increased additive. Thus, the thermal analysis results were used as the basis for the amount of additive mixed in the blend.

Lessons Learned

This presenter confirmed other comments that thermal analysis is a valuable tool for material characterization, but that it should be used to complement other methods. He indicated that it is difficult to identify a performance characteristic that thermal analysis alone could measure. In general, conventional test methods are adequate to measure performance characteristics.

Thermal analysis may not always provide the method of choice for assessing a product. In these examples, thermal analysis alone was appropriate for conducting the characterization in one case, but was inappropriate in the other case.

Presenter: Mr. Richard Gillenwater, Carlisle Syn-Tec

TA Experiences

This presenter's organization conducts considerable thermal analysis including TG, DSC, and DMA. The tests have three purposes:

1. Troubleshooting: Thermal analysis methods are used to investigate problems. This example was similar to the experiences described in an earlier presentation (p. 26).
2. To determine the type of polymer in a compound or product: Results of thermal analysis are compared to those obtained from known materials.
3. Quality control: Thermal analyses of materials are conducted as a measure of compound purity. Product contamination can be observed.

The presenter also reported that his company had been involved in the work of the CIB/RILEM Committee. Data from the company's laboratory had been used, in part, for the basis of the CIB/RILEM recommendations.

Lessons Learned

The presenter indicated that most of his company's success with thermal analysis methods had been with troubleshooting and quality control. A database based on past tests is needed to compare these results to those obtained from other types of analyses.

The results of thermal analysis for polymer identification were described as only "fairly successful." Some analyses do not give positive identification. An advantage of thermal analysis for this application is that it can be a quick test, which can be complemented by other procedures (e.g., infrared analysis).

With regard to the recommendations of the CIB/RILEM Committee, the presenter indicated that a database needs to be developed as to what constitutes allowable changes in properties, as determined by thermal analysis. As yet, data are not available to indicate whether or not an observed change in a property has a meaningful relation to performance.

Presenter: Mr. Daniel R. McGillvary, Firestone Building Products

TA Experiences

This presenter's experiences were limited, but are expected to increase. In addition to having capability to conduct TG, DSC, and DMA analyses, his TG may be interfaced with Fourier transform infrared spectroscopy (FTIR) or mass spectrometry (MS).

The laboratory uses the TG method as a rapid technique for determining the ratio of constituents (polymers, carbon black, and ash) in rubbers of known composition. For quantitative analysis of constituents, classical methods are still employed because TA methods are not applicable.

The laboratory uses the DSC method to determine the glass transition temperature of pure materials, and also of compatible and incompatible mixtures. The laboratory plans to explore the method for other applications such as measurement of cross-link density, relative unsaturation, efficiency of accelerator systems, and reaction rates.

Testing with the DMA method is now beginning. The presenter believed that the more sophisticated DMA instruments will have more application for the measurement of dynamic hysteresis of the properties of rubber than the simpler (less expensive) apparatus.

Lessons Learned

TG, DSC, and DMA are valuable laboratory tools that help to solve problems, obtain materials property data, and perform process control. TG is an excellent control technique, but will not replace conventional analysis of unknown materials.

Much laboratory work needs to be done to develop the thermal methods for different materials. This is especially true for the methods interfaced with FTIR or MS.

Before thermal analysis can be applied in roofing standards, considerable work is needed in technique development, and in relating results of the measurements to performance.

The equipment required for thermal analysis is costly. Not all firms may be able to afford the equipment or to have the tests conducted.

**Presenter: Mr. Glen D. Gaddy, the Materials Science and Engineering
Department, Johns Hopkins University**

TA Experiences

This presenter summarized a specific study in which TG, DSC, DMA, and TMA were applied to the analysis of new and exposed black and white EPDM membrane materials. He subjected the test specimens to the exposure conditions given in ASTM D 4637, "Standard Specification for Vulcanized Rubber Sheet Used In Single-Ply Roof Membrane" (1987), and also to outdoor conditions at Gaithersburg for 9 months. The results of the thermal analyses were compared to those of load-elongation tests. The changes in thermal analytical properties were compared to the allowable changes suggested by the CIB/RILEM Committee.

Thermal analysis determined that both the black and white materials showed only slight changes under the exposure conditions. The changes were generally within the limits suggested by CIB/RILEM.

However, the percent elongation values of the materials displayed large changes. The differences may stem from the fact that the thermal analysis methods determined average properties influenced by the bulk polymer, whereas the elongation measurement was greatly influenced by the condition of the surface of the membrane sheets.

Lessons Learned

Thermal analysis techniques were found to be readily applicable to the black and white EPDM products.

In the case of EPDM membrane sheets, the thermal analysis methods complemented the load-elongation tests in that the former tested the bulk properties of the polymer, but the latter gave a measure of the surface properties of the sheet.

Before integrating thermal analysis methods in standards, much work must be done to determine those property changes that are and are not acceptable. This requires the analysis of many samples before and after their exposure in service on roofs.

Presenter: Mr. Peter C. Muller, Perkin-Elmer

TA Experiences

This presenter gave an overview of the application of DMA to various products, although none were specifically roofing membrane materials.

Lessons Learned

This presentation echoed those that stated that thermal analyses provide sound laboratory methods for the characterization of roofing products.

Presenter: Mr. Roger Blaine, DuPont Instrument Systems

TA Experiences

This presenter had experience with instrumentation and materials, as well as standards development. He is active in ASTM E 37 on "Thermal Measurements."

Although he had no direct experience with roof products, he summarized his ideas on the areas of applicability of thermal analysis to roofing. These included: problem solving regarding changes in products over time, process variability, product variability over time, and characterizing materials as a function of exposure in service.

Lessons Learned

He emphasized that the thermal methods are analytical tools for characterization and problem solving, and he offered the assistance of ASTM Committee E 37 in any activities that ASTM D 08 may undertake on roofing and thermal analysis.

USACERL DISTRIBUTION

Chief of Engineers
ATTN: CEHEC-IM-LH (2)
ATTN: CEHEC-IM-LP (2)
ATTN: CERD-L
ATTN: CECC-P
ATTN: CECW
ATTN: CECW-O
ATTN: CECW-P
ATTN: CECW-RR
ATTN: CEMP
ATTN: CEMP-M
ATTN: CEMP-R
ATTN: CEMP-C
ATTN: CEMP-E
ATTN: CERD
ATTN: CERD-C
ATTN: CERD-M
ATTN: CERM
ATTN: DAEN-ZCZ
ATTN: DAEN-ZCI
ATTN: DAEN-ZCM
ATTN: DAEN-ZCE

CEHSC
ATTN: CEHSC-ZC 22060
ATTN: CEHSC-F 22060
ATTN: CEHSC-TT-P 22060
ATTN: DET III 79906

US Army Engineer Districts
ATTN: Library (41)

US Army Engr Divisions
ATTN: Library (14)

US Army Europe
ODCS/Engineer 09403
ATTN: AEAEN-FE
ATTN: AEAEN-ODCS
V Corps
ATTN: DEH (11)
VII Corps
ATTN: DEH (15)
21st Support Command
ATTN: DEH (12)
USA Berlin
ATTN: DEH (9)
Allied Command Europe (ACE)
ATTN: ACSGEB 09011
ATTN: SHIHB/Engineer 09055
USASETAF
ATTN: AESE-EN-D 09019
ATTN: ACSEN 09168
ATTN: AESE-VE 09168

8th USA, Korea
ATTN: DEH (19)

ROK/US Combined Forces Command 96301
ATTN: EUSA-HHC-CFC/Engr

Pt. Leonard Wood, MO 65473
ATTN: ATZA-TE-SW
ATTN: Canadian Liaison Officer
ATTN: German Liaison Staff
ATTN: British Liaison Officer (2)
ATTN: French Liaison Officer

USA Japan (USARJ)
ATTN: DEH-Okinawa 96331
ATTN: DCSEN 96343
ATTN: HONSHU 96343

Area Engineer, AEDC-Area Office
Arnold Air Force Station, TN 37389

416th Engineer Command 60623
ATTN: Facilities Engineer

US Military Academy 10996
ATTN: Facilities Engineer
ATTN: Dept of Geography &
Environmental Engr
ATTN: MAEN-A

AMC - Dir., Inst., & Svcs.
ATTN: DEH (23)

DLA ATTN: DLA-WI 22304

DNA ATTN: NADS 20305

PORSCOM (28)
PORSCOM Engr, ATTN: Spt Det. 15071
ATTN: Facilities Engineer

HSC
Walter Reed AMC 20307
ATTN: Facilities Engineer
Pt. Sam Houston AMC 78234
ATTN: HSLO-F
Pittsmons AMC 80045
ATTN: HSHG-DEH

INSCOM - Ch. Inst. Div.
Vint Hill Farms Station 22186
ATTN: IAV-DEH
Pt Belvoir VA 22060
ATTN: Engr & Hsg Div

USA AMCCOM 61299
ATTN: Library
ATTN: AMSMC-RI

Military Dist of Washington
ATTN: DEH
Fort Lesley J. McNair 20319
Fort Myer 22211
Cameron Station (3) 22314

Military Traffic Mgmt Command
Bayonne 07002
Falls Church 20315
Sunny Point MOT 28461
Oakland Army Base 94626

NARADCOM, ATTN: DRDNA-F 01760

TARCOM, Pac, Div. 48090

TRADOC (19)
HQ, TRADOC, ATTN: ATEN-DEH 23651
ATTN: DEH

TSARCOM, ATTN: STSAS-F 63120

USAIS
Fort Ritchie 21719
Fort Huachuca 85613
ATTN: Facilities Engineer (3)

WESTCOM
Fort Shafter 96858
ATTN: DEH
ATTN: APEN-A

SHAPE 09055
ATTN: Infrastructure Branch, LANDA

HQ USEUCOM 09128
ATTN: ECI 4/7-LOE

Fort Belvoir, VA
ATTN: Australian Liaison Officer 22060
ATTN: Water Resource Center 22060
ATTN: Engr Studies Center 22060
ATTN: Engr Topographic Lab 22060
ATTN: CECC-R 22060

CECRL, ATTN: Library 03755

CEWBS, ATTN: Library 39180

HQ, XVIII Airborne Corps and
Pt. Bragg 28307
ATTN: APZA-DEH-EE

Chanute AFB, IL 61868
3345 CES/DE, Stop 27

AMMRC 02172
ATTN: DRXMR-AP
ATTN: DRXMR-WE

Norton AFB, CA 92409
ATTN: AFRCE-MX/DE

Tyndall AFB, FL 32403
AFESC/Engineering & Service Lab

NAVFAC
ATTN: Division Offices (11)
ATTN: Facilities Engr Cmd (9)
ATTN: Naval Public Works Center (9)
ATTN: Naval Civil Engr Lab 93043 (3)
ATTN: Naval Constr Battalion Ctr 93043

Engineering Societies Library
New York, NY 10017

National Guard Bureau 20310
Installation Division

US Government Printing Office 20401
Receiving/Depository Section (2)

US Army Env. Hygiene Agency
ATTN: HSHB-ME 21010

American Public Works Association 60637

Nat'l Institute of Standards & Tech 20899

Defense Technical Info. Center 22304
ATTN: DTIC-PAB (2)

325
1091

EMC Team Distribution

Chief of Engineers 20314
ATTN: CEMP-ZA
ATTN: CEMP-ZM (2)
ATTN: DAEN-ZCP

CEHSC 22060
ATTN: CEHSC-FB

US Army Engineer District
New York 10278
ATTN: Chief, Design Br
Pittsburgh 15222
ATTN: Chief, ORPCD
ATTN: Chief, Engr Div
Philadelphia 19106
ATTN: Chief, NAPEN-D
Baltimore 21203
ATTN: Chief, Engr Div
Norfolk 23510
ATTN: Chief, NAOEN-M
ATTN: Chief, NAOEN-D
Huntington 25701
ATTN: Chief, ORHED-G
Wilmington 28402
ATTN: Chief, SAWEN-D
Charleston 29402
ATTN: Chief, Engr Div
Savannah 31402
ATTN: Chief, SASAS-L
Jacksonville 32232
ATTN: Constr Branch
Mobile 36628
ATTN: Chief, SAMEN-D
ATTN: Chief, SAMEN-F
ATTN: Chief, SAMEN-C
Nashville 37202
ATTN: Chief, ORNED-P
Memphis 38103
ATTN: Chief, Constr Div
ATTN: Chief, LMMED-D
Vicksburg 39180
ATTN: Chief, Engr Div
Louisville 40201
ATTN: Chief, Engr Div
Detroit 48231
ATTN: Chief, NCEED-T
St. Paul 55101
ATTN: Chief, ED-D
ATTN: Chief, NCSED-GH
Rock Island 61204
ATTN: Chief, NCRED-G
St. Louis 63101
ATTN: Chief, ED-D
Kansas City 64106
ATTN: Chief, Engr Div
Omaha 68102
ATTN: Chief, Engr Div
New Orleans 70160
ATTN: Chief, LMNED-DG
Little Rock 72203
ATTN: Chief, Engr Div
Tulsa 74121
ATTN: Chief, Engr Div
Ft. Worth 76102
ATTN: Chief, SWFED-D

Galveston 77553
ATTN: Chief, SWGAS-L
ATTN: Chief, SWGCO-C
ATTN: Chief, SWGED-DC
Albuquerque 87103
ATTN: Chief, Engr Div
Los Angeles 90053
ATTN: Chief, SPLED-F
San Francisco 94105
ATTN: Chief, Engr Div
Sacramento 95814
ATTN: Chief, SPKED-D
ATTN: Chief, SPKCO-C
Far East 96301
ATTN: POFED-L
Portland 97208
ATTN: Geotech Engr Br
ATTN: Chief, FM-1
ATTN: Chief, EN-DB-ST
Seattle 98124
ATTN: Chief, NPSCO
ATTN: Chief, NPSEN-FM
ATTN: Chief, EN-DB-ST
Walla Walla 99362
ATTN: Chief, Engr Div
Alaska 99506
ATTN: NPAEN-G-M

US Army Engineer Division
New England 02254
ATTN: Chief, NEDED-T
ATTN: Laboratory
ATTN: Chief, NEDCD
North Atlantic 10007
ATTN: Chief, NADEN-T
Middle East (Africa) 22601
ATTN: Chief, MEDED-T
South Atlantic
ATTN: Laboratory 30060
ATTN: Chief, SADEN-TC 30335
ATTN: Chief, SADEN-TS 30335
Huntsville 35807
ATTN: Chief, HNDED-CS
ATTN: Chief, HNDED-M
ATTN: Chief, HNDED-SR
Lower Mississippi 39180
ATTN: Chief, LMVED-G
Ohio River 45201
ATTN: Laboratory
ATTN: Chief, Engr Div
Missouri River 68101
ATTN: Chief, MRDED-G
ATTN: Laboratory
Southwestern 75242
ATTN: Laboratory
ATTN: Chief, SWDED-MA
ATTN: Chief, SWDED-TG
South Pacific 94966
ATTN: Laboratory
Pacific Ocean 96858
ATTN: Chief, Engr Div
ATTN: FM&S Branch
ATTN: POFED-D
North Pacific
ATTN: Materials Lab 97060
ATTN: Chief, Engr Div 97208

HQ, Combined Field Army (ROK/US)
ATTN: CFAR-EN 96358

US Army Foreign Sci. & Tech Ctr
ATTN: Charlottesville, VA 22901
ATTN: Far East Office 96328

USA ARRADCOM 07801
ATTN: DRDAR-LCA-OK

HQ, USAMRDC 21701
ATTN: SGRD-PLC

West Point, NY 10996
ATTN: Dept of Mechanics
ATTN: Library

Ft. Leonard Wood MO 65473
ATTN: Clarke Engr School Library

Ft. Benning, GA 31905
ATTN: ATZB-DEH-BG
ATTN: ATZB-EH-E

Ft. Leavenworth, KS 66027
ATTN: ATZLCA-SA

Ft. Lee, VA 23801
ATTN: AMXMC-D (2)

Ft. McPherson, GA 30330
ATTN: AFEN-CD

Ft. Monroe, VA 23651
ATTN: ATEN-AD
ATTN: ATEN-FE-ME
ATTN: ATEN-FN (2)

Ft. Richardson, AK 99505
ATTN: AFVR-DE-E

Rocky Mountain Arsenal 80022
ATTN: SARRM-CO-FEP

USAWES 39180
ATTN: C/Structures
ATTN: Soils & Pavements Lab

Naval Facilities Engr Command 22332
ATTN: Code 2003

COMMANDER (CODE 2636) 93555
Naval Weapons Center

Little Rock AFB 72099
ATTN: 314/DEEE

Building Research Board 20418

Dept of Transportation Library 20590

Transportation Research Board 20418

7th US Army 09407
ATTN: AETTM DTT-MG-EH

107
+1
06/91

Roofing Team Distribution

Fort Drum, AFZS-EH-P 13602
ATTN: DEH/Construction

NAVFACENGCOM Atlantic Division 23511
ATTN: Code 406

U.S. Bureau of Reclamation 80225

Tyndall AFB 32403
ATTN: AFESC-DEMM

Williams AFB 85224
ATTN: 82 ABG/DE

NAVFACENGCOM 22332
ATTN: Code 461C

Federal Aviation Administration 60018
ATTN: AGL-436

USA Natick R&D Laboratories 01760
ATTN: STRNC-D

Norfolk Naval Shipyard 23709
ATTN: Code 440

U.S. Army Engr District
New York 01731
ATTN: Mail Stop 5
Baltimore 21203

U.S. Army Engr Division, Huntsville 35805

Cold Regions Research Laboratory 03755
ATTN: CECRL

Wright Patterson AFB 45433
ATTN: HQ-AFLC/DEEC

Naval Air Development Center 18974
ATTN: Public Works Office

NCEL 93043
ATTN: Code L53

U.S. Dept of Energy 97208
Code ENOA

Veterans Administration 20420
ATTN: Arch Spec Div