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Cleaning of Aged EPDM Rubber Roofing Membrane Material for Patching: Laboratory Investigations and Recommendations

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ABSTRACT

This study assessed the relative effectiveness of different surface cleaning methods used for preparing the surface of aged EPDM membranes for patching, and recommends procedures for use in the field. The effectiveness of the methods was evaluated using tests of short-term strength and long-term creep rupture in peel, and surface analytical techniques, namely, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and contact angle measurements. A section of an aged, ballasted EPDM membrane, sampled from a roof after 10 years in service, was used in the study. The majority of the cleaning methods evaluated was selected based on a review of procedures used in the field to prepare the surface of aged EPDM rubber before patching.

Cleaning the aged EPDM rubber surface removed the bulk of the contaminants and resulted in an increase of the exposed surface area of the EPDM rubber. This resulted in a decrease in the rubber's wettability by water, and a concomitant gain in the peel strengths of joints made with the cleaned rubber. All cleaning methods used in the study provided aged EPDM rubber surfaces that formed joints having peel strengths comparable to those of seams formed in the field between solvent-based adhesives and new EPDM rubber. Short-term strength and creep-rupture joints, prepared by tape-bonding the surface of heptane-cleaned aged EPDM to a surface of well-cleaned new EPDM, failed at the interface between the tape and the new rubber. But, no relationships between contact angle and cleaning method were found. In particular, the contact angles measured using methylene iodide varied only slightly as a function of cleaning method. The FTIR technique could distinguish the uncleaned surface of the aged EPDM from those which were well-cleaned and/or coated during cleaning. No major differences between the FTIR spectra of the specimens cleaned using the various methods were observed. SEM analysis was the only technique that distinguished particle-free surfaces from those which retained particles after cleaning. The rate of spreading of dimethyl formamide (DMF) droplets on the surface of the aged EPDM rubber was found to relate to the degree of surface cleanness.

Based on the results of this laboratory study on cleaning a section of an aged EPDM rubber membrane, it was concluded that such membrane materials may be suitably cleaned for patching. It was recommended that: (1) a number of cleaning methods may be used to prepare the surface of aged EPDM rubber membrane material before patching, and (2) the change in size over time of a droplet of DMF, placed on the aged EPDM rubber after cleaning, be used for preliminary assessment of the condition of the cleaned surface.

Key words: aged EPDM membrane; cleaning methods; contact angle; creep rupture; FTIR; low-sloped roofs; peel strength; roofing; scanning electron microscopy; seams; surface analysis; surface preparation methods; wettability

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (cont.)

EXECUTIVE SUMMARY

INTRODUCTION

The use of membranes made from vulcanized ethylene-propylene-diene terpolymer (EPDM) rubber as the waterproofing component of low-sloped roofing systems has become common in the United States. EPDMs are essentially non-polar, relatively inert rubbers. This makes the adhesive-bonding of sheets difficult. A factor affecting seam performance that has not been addressed in studies to date is the condition of the surface of aged EPDM rubber before bonding to it. This factor has importance, because as time passes, patches and splices to EPDM membranes in service may be needed.

Since 1979, the US Army Construction Engineering Research Laboratory (CERL) has been conducting field investigations of the performance of roofing systems such as EPDM as alternatives to built-up roofing (BUR). A key concern expressed by CERL is whether the surface characteristics of EPDM rubber are altered during weathering such that successful bonding of the aged material becomes more difficult than with unaged rubber. Thus, CERL requested that the National Institute of Standards and Technology (NIST) conduct a study of the effect of surface preparation on the surface characteristics of the cleaned sheet and the bond strength of seam specimens fabricated from it. This report presents the results of the study.

The laboratory research was carried out in two phases. In the preliminary phase, investigations were conducted on the use of surface analytical techniques for ascertaining whether the surface of aged EPDM rubber is properly cleaned before patches are bonded to it. The intent was to develop experimental procedures applicable to EPDM rubber based on existing analytical methods. It was found that scanning electron microscopy (SEM), contact angle measurement, and Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy were useful for general laboratory analysis of EPDM rubber sheets.

In the main phase of the study, short- and long-term peel tests and the surface analytical techniques were used to determine the effectiveness of different cleaning methods for removing contamination from the surface of an aged EPDM membrane sample taken from a roof. The major laboratory tasks conducted were:

1. The surface of the uncleaned, aged EPDM sample was analyzed using the contact angle and FTIR procedures developed in the preliminary phase of the study.

2. The surface of the aged sample was cleaned using a variety of surface cleaning methods. Subsequently, the surfaces of the cleaned specimens were analyzed using the surface analysis procedures to characterize the effectiveness of the cleaning methods for removing contaminants.

3. "Seam specimens" were prepared from the aged EPDM membrane material after the surface was cleaned using various methods; the bond strength of the seam specimens was measured as a function of cleaning method using a T-peel test.

4. The peel resistance under creep conditions of seam specimens prepared from the aged EPDM membrane material after cleaning were compared with that of specimens fabricated from new (unaged), well-cleaned EPDM rubber.

5. The results of the bond strength measurements were compared to the surface cleanness of the aged EPDM as determined by the surface analytical procedures as a function of the surface cleaning methods.

EXPERIMENTAL

A sample of aged EPDM membrane used in the cleaning experiments was cut from a ballasted roof system located in the mid-Atlantic area of the United States. It was a single sheet, about 10 years old, and had been covered with a talc-like release agent on both surfaces when manufactured. The surface of the sheet was completely covered with a layer of dirt when removed from the roof.

The procedure selected to clean the surface of the aged EPDM membrane material was based on use of the abrasion test apparatus described in ASTM D 4213, "Standard Test Method for Wet Abrasion Resistance of Interior Paints." The intent was to have a mechanical method for repeatedly scrubbing a brush or wiping a cloth in a reproducible manner across the surface of the EPDM sample. A cycle consisted of one back and forth stroke of the abrader across the sample. Two types of abraders were used: (1) a synthetic absorbent laboratory cleaning cloth, and (2) a brush with stiff nylon bristles. The cloth abrader was used when the cleaning agent was an organic solvent. The brush abrader was employed when the cleaning agent was an aqueous solution.

Samples of the aged EPDM sheet were subjected to surface cleaning using 16 different methods, 11 of which were akin to procedures normally used in the field. Four methods were experimental in that surface preparation agents were investigated to determine whether these products could modify the EPDM surface while it was being cleaned and, thus, possibly enhance adhesion. Finally, the 16th method was a procedure using manual scrubbing and solvent wiping of the surface that has been found to be a suitable laboratory method for preparing the surface of new EPDM rubber.

PEEL TEST RESULTS

In selecting a peel test as one measure of the effect of the various surface cleaning methods on the preparation of the surface of an aged EPDM membrane, an adhesive tape was selected for preparation of joint specimens instead of a solvent-based adhesive. The uncleaned rubber would not form a bond to the tape. However,

after removal of some of the contaminants, joint specimens having relatively low peel strengths could be formed with the tape.

A preliminary experiment was conducted wherein the aged EPDM rubber was cleaned to varying degrees with heptane or 75% heptane/25% methyl ethyl ketone (MEK) solution (v/v). The number of cleaning cycles was progressively doubled from 5 to 160. The effect of the number of cycles was visually apparent, as the surfaces became noticeably cleaner as the number increased. The strength of the joints increased with an increase in the number of cycles. The data analysis showed a linear relationship between strength and the log of the number of cycles over the range of cycles employed. Based on this experiment, subsequent cleaning tests were conducted at eighty cycles because such cycling produced a relatively high peel strength in a time that was experimentally practical.

The aged EPDM rubber sheet was subjected to each of the 16 surface cleaning methods. T-peel joints were made from the cleaned rubber using the adhesive tape. All cleaning methods provided aged EPDM rubber surfaces that formed joint specimens with the tape whose peel strengths were comparable to bonds formed between solvent-based adhesives and new EPDM rubber. Statistically significant differences between some cleaning methods were found. EPDM prepared by wiping with heptane, a method akin to the common field procedure of washing with unleaded gasoline, gave average joint strengths among the highest of those measured. Their strengths were higher than those of joints prepared by cleaning the aged rubber with water-based methods. Short-term strength and creep-rupture joints, prepared by tape-bonding the surface of the heptane-cleaned aged EPDM to a surface of well-cleaned new EPDM, failed at the interface between the tape and the new rubber.

CONTACT ANGLE RESULTS

The contact angle of a liquid with a solid surface is a convenient measure of wettability; it is an indicator of the affinity of a liquid for a solid. Contact angle and wettability are inversely related; that is, as one increases, the other decreases. The contact angle measurement is sensitive to the first 0.5-1 nm (5-10 Å) layer on the solid surface and, thus, its behavior reflects the chemical composition of the very top layer of the surface. Contact angle measurements (and wettability parameters derived from them) were used as a complementary method to the peel strength analysis. Thus, the effects of cleaning cycle on the contact angles of two liquids, water and methylene iodide, placed on the aged EPDM rubber samples were determined after cleaning for various numbers of cycles ranging from 5 to 160 using either heptane or the heptane/MEK solution as the cleaning method.

The results of these contact angle measurements showed that the uncleaned aged EPDM rubber was very wettable by methylene iodide (a relatively nonpolar liquid) and was not wettable by water (a highly polar liquid). Cleaning with heptane and the heptane/MEK solution decreased substantially the wettability by methylene iodide and increased the wettability by water. When determined using water,

the contact angle decreased with the first few cycles. After removal of the bulk of the contaminants by cleaning, it showed a slight increase, which was attributed to an increase of the exposed surface area of the less polar rubber. When measured using methylene iodide, after an initial increase with five cleaning cycles, the contact angle remained essentially constant. The results of this experiment supported the T-peel results for selecting the number of cycles to be used in conducting cleaning according to the 16 methods included in the study.

The contact angles of methylene iodide and water were measured for the aged EPDM rubber after cleaning using the 16 methods. The specimens for this experiment were the same as those used in the T-peel tests. No systematic relationships between contact angle and cleaning method were found. In particular, the methylene iodide contact angle varied only slightly as a function of cleaning method. This result implied that a number of cleaning methods would provide surfaces that would have similar wettability characteristics to nonpolar-solvent-based adhesives.

FTIR SPECTROSCOPY RESULTS

The surfaces of the aged EPDM rubber specimens cleaned using the 16 methods were analyzed using FTIR spectroscopy. The results indicated that the technique could distinguish the uncleaned contaminated surface of the aged EPDM from those which were well-cleaned. Only minor differences between the FTIR spectra of the specimens cleaned using the various methods were observed. It was found that specimens cleaned with water (and wiped with a dry cloth) and other polar solvents had residual water on their surfaces. However, the FTIR technique could not resolve whether or not the surfaces of the cleaned rubber specimens had a talc-like release agent on them.

SCANNING ELECTRON MICROSCOPY RESULTS

Cleaned surfaces of the aged EPDM rubber were subjected to SEM surface analysis. The most notable feature of the resulting photomicrographs was the presence of platelet particles indicative of release agent on the surfaces of the majority of the specimens. In the cases where these particles were visible, it was not possible by visual examination of the micrographs to ascertain whether the amount varied between specimens as a function of the cleaning method. Qualitatively, all the micrographs appeared to be comparable. The presence of platelet particles was not surprising in that the original rubber sheet had been coated with a release agent during its manufacture. During cleaning, the majority of the cleaning methods apparently removed relatively loose particles on the surface, while leaving behind those that were more strongly bonded to, or perhaps partially embedded, in the rubber surface.

Only in the case of two cleaning methods involving relatively vigorous abrasion were the rubber surfaces observed to be essentially free of platelet particles. Nevertheless, although the rubber surfaces were cleaned essentially free of release agent, the

peel strengths of the bonds formed with the tape were not significantly greater than those made on rubber which still contained release agent after washing with heptane.

COMPARISON OF THE RESULTS OF THE DIFFERENT TEST METHODS

The peel strength data for the cleaned aged rubber specimens were compared with the information obtained by the surface analytical techniques to look for evidence of systematic relationships. None were found between any of the wettability parameters and peel strength. Moreover, the SEM technique was not able to distinguish a surface that produced a relatively high peel-strength seam from a surface that gave rise to a relatively low peel-strength seam. Similarly, the FTIR technique could also not differentiate between surfaces providing bonds of different strength.

However, using the number of cleaning cycles as a measure of surface cleanness, after initial cycling, increases in the peel strength were accompanied by increases in the water contact angle. Consequently, the water contact angle could be used to assess the condition of the EPDM surface after cleaning. If substantial amounts of the loose surface particles and other contaminants have been removed from the EPDM, the water contact angle on the cleaned rubber should be greater than 55 degrees. However, use of such a criterion is not practicable for field use, because a method to provide a good estimation of the water contact angle on EPDM rubber in the field is not available.

It was known from the initial data obtained in the preliminary phase of the present study that the spreading of water increased as the level of contamination of new unaged EPDM increased. In other words, if the surface was not well cleaned, the water contact angle would decrease more rapidly with time as compared to that obtained for a well-cleaned surface. The decrease in contact angle with time would be observed as a spreading of a drop of water placed on the rubber. Thus, in the field, the rate of spreading, or the change in size of the droplet on the rubber surface, could be estimated, and allowable limits for a given period of time could be prescribed.

However, preliminary tests of the spreading tendency of water on the surface of the specimens cleaned in this study showed that water was not a suitable liquid. In particular, using the size of the drop as an indicator, it was not possible to discriminate variations in the spreading of water for the specimens cleaned to varying degrees as a function of cleaning cycles. Consequently, other liquids were investigated.

Dimethyl formamide (DMF) was found to be sensitive to differences in surface condition achieved with the various cycles of cleaning. In addition, drops of DMF placed on the surfaces of the specimens cleaned for 80 cycles using the various cleaning methods did not spread appreciably within 5 minutes. Although these results were obtained qualitatively, they were seen to be consistent for repeated tests.

Based on these limited data, it is suggested that a "droplet test", using the spreading of DMF as just described, be used in the field on an experimental basis as a simple test of the condition of aged EPDM after cleaning. It requires little skill and no costly equipment.

CONCLUSIONS AND RECOMMENDATIONS

Based on the results of this laboratory study on cleaning a section of an aged EPDM rubber membrane, it was concluded that such membrane materials may be suitably cleaned for patching. The following recommendations are, thus, given for field cleaning and assessment of the cleaned surfaces when patches or repairs are to be made:

1. All visible contaminants present on the surface should be removed and the dark black or bright white color, typical of well cleaned new black and white EPDM sheets, respectively, should be restored. This may be accomplished using solvent wipe or the detergent scrub techniques commonly used in practice. When using a solvent wipe technique, it is important to change cloths often as they pick up the contaminants from the rubber surface. In the case of the detergent scrub, it is important to rinse the brush often to remove contaminants picked up during the cleaning. When water is part of the cleaning procedure, the rubber surface should be dried (e.g., using a dry cloth) before solvent wiping.

2. As a preliminary step towards establishment of a simple test for assessing the condition of the EPDM surface after cleaning, the droplet test with dimethyl formamide (DMF) should be used on an experimental basis. This would provide a means for obtaining field data on the proposed test.

   In this regard, after cleaning, the surface condition of the EPDM rubber should be assessed by placing a droplet of DMF on it. This may be accomplished using an eye-dropper held vertically (e.g., about 90 degrees) about 5 mm above the rubber surface. The droplet should have an initial diameter of about 7 to 8 mm. If the surface is acceptably clean, the diameter of the droplet should not increase by more than 2 mm within a 5 min time period. The diameter of the droplet may be estimated using a ruler.

3. It is necessary to use vigorous mechanical abrasion, for example, a wire brush attached to an electric drill, if it is desired to have a rubber surface that is essentially free of release agent before making a patch.

1. INTRODUCTION

1.1 Background

The use of membranes made from vulcanized ethylene-propylene-diene terpolymer (EPDM) rubber as the waterproofing component of low-sloped roofing systems has become common in the United States. Current estimates indicate that over 93 million square meters (one billion square feet) are being applied annually [1,2]. EPDMs are essentially non-polar, relatively inert rubbers. This makes the adhesive-bonding of sheets difficult. Proper seam formation is a critical parameter associated with long-term performance of EPDM roofing systems [3-5]. Several studies based on short-term bond strength tests and long-term creep-rupture tests have been conducted on EPDM systems to provide baseline data on the factors affecting seam performance [6]. Factors addressed in these studies have included temperature, stress level, rate of loading, voids in the adhesive layer, pressure during application, contamination of the rubber surface, open time, and adhesive thickness. These laboratory studies have been conducted using seam specimens fabricated from new (unaged) EPDM rubber. Another factor affecting seam performance that has not been addressed in studies to date is the condition of the surface of aged EPDM rubber before bonding to it. This factor has importance because, as time passes, patches and splices to EPDM membranes in service may be needed.

Since 1979, the US Army Construction Engineering Research Laboratory (CERL) has been conducting field investigations of the performance of roofing systems such as EPDM as alternatives to built-up roofing (BUR) [7]. A key concern expressed by CERL is whether the surface characteristics of EPDM rubber are altered during weathering such that successful bonding of an aged material becomes more difficult than that of an unaged rubber [8]. For example, in the CERL study of EPDM roofing at Fort Benning, it was found that some repair patches delaminated within months after formation [8]. This may have been due to the use of improper repair materials and patching techniques. Nevertheless, it is illustrative of the need for developing a technical basis for standard methods used in preparing the surfaces of weathered EPDM. Thus, CERL requested that the National Institute of Standards and Technology (NIST) conduct a study of the effect of surface preparation on the surface characteristics of the cleaned sheet and the bond strength of seam specimens fabricated from it. This report presents the final results of the study.

1.2 Objective of the Study

The objective of the study was to evaluate methods for preparing the surface of aged EPDM rubber roofing membrane material for making patches or repairs. Laboratory research was conducted to provide the technical basis for determining whether the surface of aged rubber has been properly prepared before patches are applied.

1.3 Scope of the Study

The laboratory research was carried out in two phases. In the preliminary phase, investigations were conducted [9] on the use of surface analytical techniques for ascertaining whether the surface of aged EPDM rubber is properly cleaned before patches are bonded to it. The intent was to develop experimental procedures applicable to EPDM rubber based on existing analytical methods. It was found that scanning electron microscopy (SEM), contact angle measurements, and Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy were useful for general laboratory analysis of EPDM rubber sheets. Experimental procedures were developed for this purpose for use in the main phase of the study. The major findings from the preliminary phase are summarized in Appendix A.

In the main phase of the study, short- and long-term peel tests and the surface analytical techniques were used to determine the effectiveness of different cleaning methods for removing contamination from the surface of an aged EPDM membrane sample taken from a roof. The major laboratory tasks conducted in this phase were:

- The surface of the uncleaned, aged EPDM sample was analyzed using the contact angle and FTIR procedures[1] developed in the preliminary phase of the study.

- The surface of the aged sample was cleaned using a variety of surface cleaning methods. Subsequently, the surfaces of the cleaned specimens were analyzed using the surface analysis procedures to assess the effectiveness of the cleaning methods for removing contaminants.

- "Seam specimens" were prepared from the aged EPDM membrane material after the surface was cleaned using various methods; the bond strength of the seam specimens was measured as a function of cleaning method using a T-peel test.

- The peel resistance under creep conditions of seam specimens prepared from the aged EPDM membrane material after cleaning were compared with that of specimens fabricated from new (unaged), well-cleaned EPDM rubber.

- The results of the bond strength measurements were compared to the surface cleanness of the aged EPDM as determined by the surface analytical procedures as a function of the surface cleaning methods.

- Based on the study results, a recommendation for preparing aged EPDM membranes for bonding was made, and a simple test of cleanness was suggested for use on an experimental basis.

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[1]A thick layer of dirt on the surface of the sample precluded SEM analysis due to possible damage to the instrument.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Aged EPDM Membrane Material. The sample of aged EPDM membrane used in the cleaning experiments was cut from a ballasted roof system located in the mid-Atlantic area of the United States. It was a single sheet, approximately 3 x 3 m (10 x 10 ft) in area, which was in service about 10 years. The membrane material was non-reinforced, and had been covered with a talc-like release agent on both surfaces when manufactured. Table 1 gives the thickness and load-elongation data for the aged EPDM rubber sheet. The surface of the sheet, which was completely covered with a layer of dirt when removed from the roof, was not even, but contained dimples from its calendering.

In using this rubber sample for the evaluation of various cleaning methods for EPDM, the original sheet was divided into two 3 x 1.5 m (10 x 5 ft) sections. Each section was labeled distinct from the other and further cut into smaller test samples, having dimensions of 170 x 400 mm (6 3/4 x 16 in.). The small test samples were numbered to allow for random sampling during subsequent cleaning and testing experiments.

Table 1. Properties of the EPDM rubber test materials

Property	Units	EPDM Rubber Test Material	
		Aged	New
Nominal Thickness	mm (in.)	1.0 (0.04)	1.5 (0.06)
Stress at Break	MPa (lbf/in^2)	13.3 (1930)	10.7 (1550)
Elongation at Break	percent	450	680
Modulus at 300% Elong.	MPa (lbf/in^2)	3.6 (520)	2.0 (290)

NOTE: The mechanical properties were determined according to the procedures given in ASTM D 412. The "aged" and "new" EPDM rubber materials were not of the same batch, but were distinctly different.

2.1.2 New EPDM Membrane Material. New EPDM membrane material used in the preparation of seam specimens was a commercially available sheet, which was non-reinforced and had a talc-like release agent on its surfaces. Table 1 includes thickness and load-elongation data for this sheet rubber. One surface of the sheet was cleaned by sequentially scrubbing with detergent and water, rinsing with water and drying at ambient conditions. Immediately before use to

form seam specimens, the water-washed surface was cleaned by rubbing with a cloth which was soaked with reagent-grade heptane. This method has been previously shown to provide a well-cleaned EPDM surface [10].

2.1.3 Adhesive Tape. Adhesive tape used in making seam specimens was a butyl-based product that is commercially available for fabricating seams in EPDM roof membranes. The tape had a nominal thickness of 0.88 mm (0.035 in.). Both its surfaces were tacky for direct application between the two EPDM sheets to be bonded. To prevent unwanted adhering of the tape to itself or other objects during shipping and handling, the surfaces were protected with release paper. In the laboratory, this paper was removed just prior to use of the tape in forming joints.

2.2 Cleaning Aged EPDM Membrane Material

2.2.1 Procedure. The procedure selected to clean the surface of the aged EPDM membrane material was based on use of the abrasion test apparatus described in ASTM D 4213, "Standard Test Method for Wet Abrasion Resistance of Interior Paints" [11]. The intent was to have a mechanical method for repeatedly scrubbing a brush or wiping a cloth in a reproducible manner across the surface of the EPDM sample. Figure 1 shows the abrasion test apparatus with a brush placed on the surface of a dirty EPDM roofing membrane sample, which was held flat in place using a vacuum. Note that the brush did not scrub the entire surface of the sample. Before placing the rubber sample in the apparatus, the backside surface[2] was wiped thoroughly with a heptane soaked cloth.

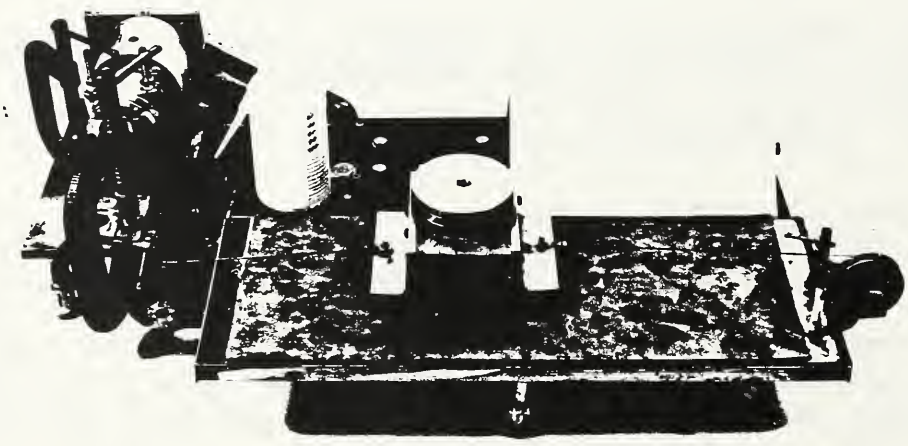

Figure 1. Abrasion apparatus and the aged EPDM membrane specimen used in the evaluation of surface preparation methods

[2]Although wiped thoroughly with solvent, for purposes of this paper, the backside surface was considered as "uncleaned." This was done to distinguish it from the frontside surface which was subjected to cleaning using any of the selected methods.

The size of the sample was 170 x 400 mm (6 3/4 x 16 in.), as cut from the large membrane sections. For safety reasons when inflammable solvents were used as the cleaning agent, a compressed air-driven motor was used to cycle the abrader (i.e., brush or cloth) across the sample surface. A cycle consisted of one back and forth stroke of the abrader on the long dimension of the sample. The average speed of the abrader was 4 cycles/min.

The contact area of the abrader surface with the sample surface was 70 x 112 mm (2 3/4 x 4 1/2 in.). Two types of abraders, held in clamping devices for attachment to the abrasion test apparatus, were used: (1) a synthetic absorbent laboratory cleaning cloth, and (2) a brush with stiff nylon bristles (Figure 1). In both cases, the mass of the abrader-clamp assembly was 1.1 kgm (2.5 lbm). Throughout cycling, the surface of the EPDM sample was kept wet with the cleaning agent which was applied from a laboratory wash bottle. In general, over the course of an 80-cycle cleaning (i.e., the number used in most experiments), about 50 ml of an aqueous solution were used, whereas for organic solvents, about 200 ml were employed.

The cloth abrader was used when the primary cleaning agent was an organic solvent. A cloth was only used for 10 cycles after which it was replaced with another clean one.

The brush abrader was employed when the primary cleaning agent was an aqueous solution. After every 10 cycles of cleaning, the brush was removed from the abrasion test device and rinsed profusely (about 2L in 15 s) under running tap water. After the predetermined number of cycles with the brush abrader were completed, the remaining aqueous cleaning agent was removed from the sample surface. This was accomplished by conducting two cycles of cloth abrasion using a clean dry cloth followed immediately by two cycles with another cloth saturated with reagent-grade heptane.

2.2.2 Resultant Specimens for Testing and Analysis. A 150 x 275 mm (6 x 11 in.) section of the EPDM sample removed from the abrasion apparatus was cut such that its cleaned surface area had dimensions of 106 x 275 mm (4 1/4 x 11 in.), as shown in Figure 2. The uncleaned portion of this section provided for handling and labeling. The section was divided into 11 strips, each with dimensions of 25 x 150 mm (1 x 6 in.). Using random sampling, four strips were used for peel tests, one was taken for contact angle measurements, and another was used for FTIR spectroscopy and SEM observation.

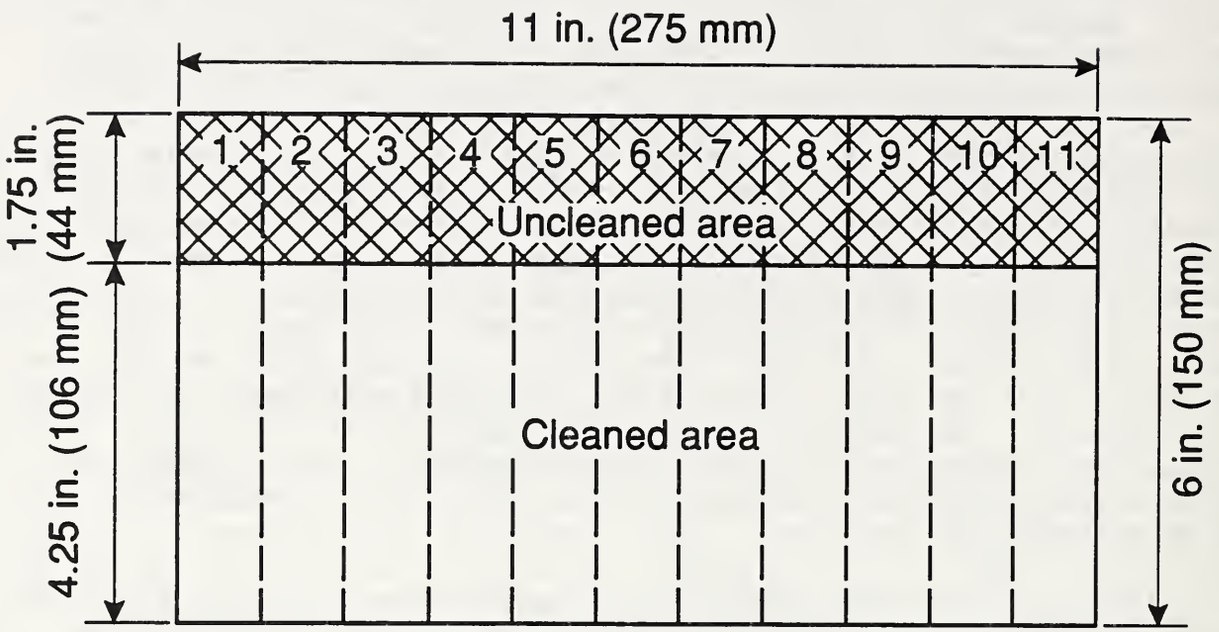

Figure 2. Sampling pattern used to select sections of the cleaned EPDM specimen for use in the peel tests, and the wettability, FTIR, and SEM analyses

2.2.3 Surface Cleaning Methods. Table 2 summarizes some typical procedures used in the field to prepare the surface of aged EPDM rubber before patching. The summary was based on field experiences gained from sampling EPDM systems [12,13], and from conversations with contractors experienced in installing EPDM roofing [14]. The majority of the surface cleaning methods evaluated for effectiveness in the present study were selected with consideration of the procedures described in Table 2.

Table 3 presents the 16 surface cleaning methods to which samples of the aged EPDM sheet were subjected. The first 11 methods were akin to the procedures normally used in the field for cleaning aged EPDM rubber. Four (Nos. 1-4) used a cloth wipe with common solvents, five (Nos. 5-9) were based on brushing with water with or without detergent, one (No. 10) was a combination of scrubbing followed by a solvent wipe, and another (No. 11) employed an electrically-powered brush scrub with water and a detergent. Cleaning Methods Nos. 12-15 were experimental in that a proprietary silane coupling agent and a proprietary aromatic hydrocarbon tackifier were investigated to determine whether these products could modify the EPDM surface while it was being cleaned and, thus, possibly enhance adhesion. Finally, Method No. 16 was the laboratory procedure using manual scrubbing and solvent wiping of the surface that has been found to be a suitable laboratory method for preparing the surface of new EPDM rubber [10].

Table 2. Typical field procedures for cleaning aged EPDM

Type of Cleaning	Procedure
Solvent Wipe	This is the most common; the procedure is akin to that used to form seams in the application of new EPDM membranes. An absorbent rag is soaked with unleaded gasoline or a similar solvent, and wiped on the surface to be patched. Some solvent may be poured on the membrane. As the rag becomes dirty, it is replaced with a clean one. Wiping is continued until the mechanic considers that the surface is adequately clean.
Detergent Scrub Followed by a Solvent Wipe	This is often done when the roof has much dirt on the surface. A detergent (often a household product) is added to water. The surface of the aged membrane is scrubbed by hand with the aqueous detergent solution using a stiff bristle brush. After drying, a solvent wipe is carried out.
Detergent Scrub Followed by a Water Rinse and Solvent Wipe	This is the same as the procedure above except that the scrubbed surface is rinsed with water before carrying out the solvent wipe. Rinsing is recommended by many contractors, but the extent to which it is done may depend on the availability of water on the roof. In some extreme cases, a water hose may be used.
Mechanical Scrub Followed by a Water Rinse and Solvent Wipe	This is essentially the same procedure as that described above except that mechanical action such as an electrical floor scrubber is used. It is done less often than manual scrubbing, and may only be used if the contractor considers that an extensive area of the membrane surface is too dirty to clean by hand.

Table 3. Surface cleaning methods used in the study

Method No.	Type of Abrasion	No. of Cycles	Cleaning Solution[a]
1	Wipe	80	Reagent-grade heptane
2	Wipe	80	25% reagent-grade methyl ethyl ketone (MEK) in 75% reagent-grade heptane (v/v)
3	Wipe	80	25% reagent-grade heptane in 75% reagent-grade MEK (v/v)
4	Wipe	80	Proprietary wash solution used for EPDM
5	Brush	80	Tap water without detergent[b]
6	Brush	80	Tap water with household detergent #1
7	Brush	80	Tap water with household detergent #2
8	Brush	80	Tap water with household detergent #1; after every 10 cycles the rubber sample was rinsed under running tap water (flow of about 2L/min for 3 min.)
9	Brush	80	Tap water with a laboratory detergent
10	Brush/ Wipe	80	Tap water with household detergent #1 (40 cycles) followed by 25% MEK/75% heptane (40 cycles)
11	Electric Brush[c]	5	Tap water with household detergent #1; after scrubbing, the surface was wiped manually using a cloth soaked in heptane.
12	Wipe	80	Experimental cleaning agent #1: an aromatic hydrocarbon tackifier (2% by mass) and a silane coupling agent (2% by mass) in reagent-grade heptane; the silane was not soluble but dispersed.

[a]Unless otherwise indicated, all steps were conducted at ambient temperatures (about 72°F or 22°C).
[b]Samples cleaned with a method involving water were dried by two cycles of cloth abrasion using a clean dry cloth followed immediately by two cycles with a cloth saturated with heptane.
[c]Performed with a wire brush attached to an electric drill.

Table 3. Surface cleaning methods used in the study (cont.)

Method No.	Type of Abrasion	No. of Cycles	Cleaning Solution
13	Wipe	80	Reagent-grade heptane followed by experimental cleaning agent #2: a silane coupling agent (5% by mass) in ethyl alcohol was wiped on the surface of the rubber which was then heated in an oven at about 158°F (70°C) for 5 min.
14	Wipe	80	Experimental cleaning agent #3: an aromatic hydrocarbon tackifier (2% by mass) in heptane; a silane coupling agent (5% by mass) in ethyl alcohol was wiped on the surface of the rubber which was then heated in an oven at about 158°F (70°C) for 5 min.
15	Wipe	80	Experimental cleaning agent #4: a silane coupling agent (2% by mass) in water along with a laboratory detergent; the cleaned rubber was then heated in an oven at about 158°F (70°C) for 5 min.
16	Manual Brush/ Wipe	NA[a]	The sample was extensively scrubbed in a sink with a brush and detergent, rinsed under running tap water, and allowed to dry by setting on a laboratory bench over night; this step was followed by wiping the dried surface with a cloth soaked with heptane.

[a]NA indicates not applicable.

2.3 Test Methods and Data Analysis

The test methods, i.e., T-peel test, contact angle measurement, FTIR-ATR spectroscopy, and SEM analyses, used to evaluate the effectiveness of the various surface cleaning methods are given in Appendix B. Data were recorded in a computer file and analyzed using a graphics program called "DATAPLOT" [15].

3. RESULTS AND DISCUSSION

3.1 Peel Tests

The bond strength of a seam, as determined by the force required to separate a unit of the bonded area, is a useful criterion to assess the quality of the seam formation process. In the case of EPDM roofing, the ultimate strength (in peel) of seam specimens prepared from new rubber and solvent-based adhesive has been found to be dependent on the surface cleanness of the rubber sheet [3,6].

3.1.1 Use of Tape for Preparation of Peel Specimens. In selecting a peel test as one parameter for evaluating the effect of the various surface cleaning methods on the preparation of the surface of an aged EPDM membrane, it was necessary to fabricate joints for testing. In practice, solvent-based adhesives are the primary bonding agents for making seams, although in recent years, an increase in the use of tapes has occurred [16]. For the present study, use of a solvent-based adhesive had a number of disadvantages which were overcome by use of a tape:

1. During application of the solvent-based adhesive, the solvent might interact with the surface of the cleaned specimens (in an unknown way) such that effects attributable to the cleaning methods might not be observed.

2. Control of thickness during application of solvent-based adhesives (a difficult procedure) would be necessary because peel strength is dependent upon adhesive thickness [6,17]. As a factory-produced material, a tape has a relatively constant thickness.

3. The specimen failure mode had to be interfacial. Butyl-based adhesives for EPDM roofing sheets fail cohesively in peel when the sheet surface is reasonably well cleaned [3,6]. This factor raised the possibility that quantitative differences between some cleaning methods would be unobservable if they were sufficiently effective to bring about cohesive failure of the test joint.

Consequently, a tape was selected for preparation of joint specimens. Using the joint specimen configuration shown in Figure B1, the specimens failed interfacially between the cleaned rubber surface and the tape. Preliminary experiments using new, cleaned (Method No. 16) EPDM rubber were conducted (data not shown) to determine the key parameters that needed to be controlled in the preparation of the specimens. It was found that strength was dependent on the pressure and the time over which it was applied during joint formation, and also the dwell time (i.e., time elapsed between joint formation and peel testing). Specimen preparation conditions were selected, in part, based on the results of the preliminary tests. Optimization of the three parameters was beyond the scope of the study. It was shown, however, that strengths of joint specimens having 7-day dwell time were not significantly different from those with a 4-day dwell time.

3.1.2 Preliminary Tests. In using the abrasion test apparatus for cleaning the surface of the aged EPDM sheet, it was necessary to set a criterion for judging the effectiveness of the cleaning method used. Two choices were apparent:

1. The number of cycles used in abrading the surface for a given cleaning method could be variable. In this case, the criterion for assessing the effectiveness of the method would be the number of cycles at which the peel strength of the joint specimen reached a maximum. A low number of cycles would signify a more effective cleaning method.

2. The number of cycles used for all surface cleaning methods would be constant. In this case, the criterion for assessing the effectiveness of the cleaning method would be the peel strength achieved by the joint specimen. A high peel strength would signify a more effective cleaning method. From a practical standpoint, this option was considered advantageous in that the number of cycles involved in the cleaning method would be minimized.

To assist in making a choice between the two criteria, a preliminary experiment was conducted using the aged EPDM rubber specimen cleaned under Methods Nos. 1 and 2. The number of cycles was progressively doubled from 5 to 160. Only one rubber sample was cleaned, but four joint specimens were prepared and tested in peel for each given number of cycles for each cleaning method. The effect of increasing the number of cycles was visually apparent, as the surfaces became noticeably cleaner as the number increased (Figure 3).

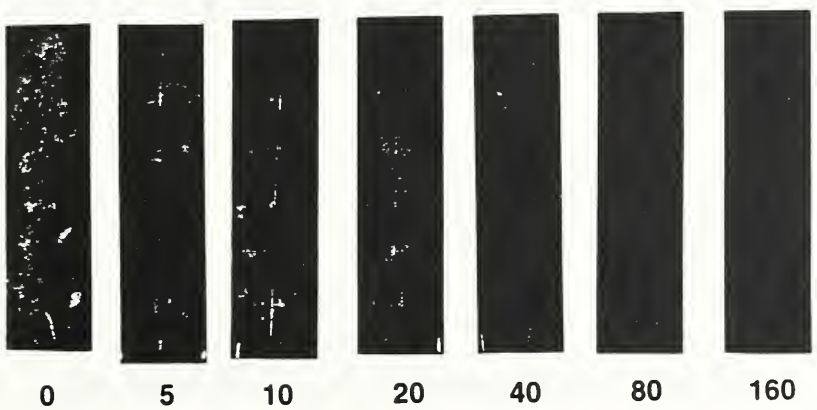

Figure 3. Surface appearance of the cleaned (Method No. 1) aged EPDM as a function of cycles

The results for the preliminary experiment are given in Figure 4, where the peel strength of the joint specimens is plotted versus the number of cycles (Figure 4a) and the log of the number of cycles (Figure 4b). As is evident in these figures, the strength of the joints increased with an increase in the number of cycles. No data are given for 0 cycles (i.e., the as-received sheet), because the tape would not bond to the uncleaned EPDM surface. Statistical analysis of the data indicated that, for the total data set, there was no significant effect attributable to the cleaning method. As a consequence, as given in Figure 4, only a single curve or line was fit to the data points. The data analysis showed a linear relationship between strength and the log of the number of cycles over the range of cycles employed. In general, each time the number of cycles was doubled, an incremental increase in strength of about 0.1 kN/m (0.8 lbf/in.) occurred. This finding suggested that further cleaning experiments be conducted using at least 320 cycles for both cleaning Methods Nos. 1 and 2. However, this was not carried out because it was not practicable to extend the surface cleaning to such large numbers of cycles.

Consequently, it was decided to conduct subsequent cleaning experiments at a constant number of cycles and judge effectiveness on the basis of the relative strength achieved by the joint specimens prepared using the cleaned sheet. Eighty cycles were selected because the preliminary experiments showed that such cycling produced a relatively high peel strength in an experimentally reasonable time.

3.1.3 Results for the Various Surface Cleaning Methods. Two randomly sampled (Section 2.1.1) pieces of the aged EPDM rubber sheet were subjected to each of the surface cleaning methods given in Table 3. In turn, for each cleaned piece, a set of four replicate tape-joint specimens (Figure B1) was prepared for peel testing. The duplicate sets of peel specimens for a given cleaning method were assigned the designations "Set 1" and "Set 2." All peel specimens with the designation "Set 1" were taken from one half of the large piece of EPDM rubber, while the peel specimens designated "Set 2" were sampled from the other half. The number of peel specimens was 128 (16 cleaning methods X 2 sets per method X 4 replicate peel specimens per set).

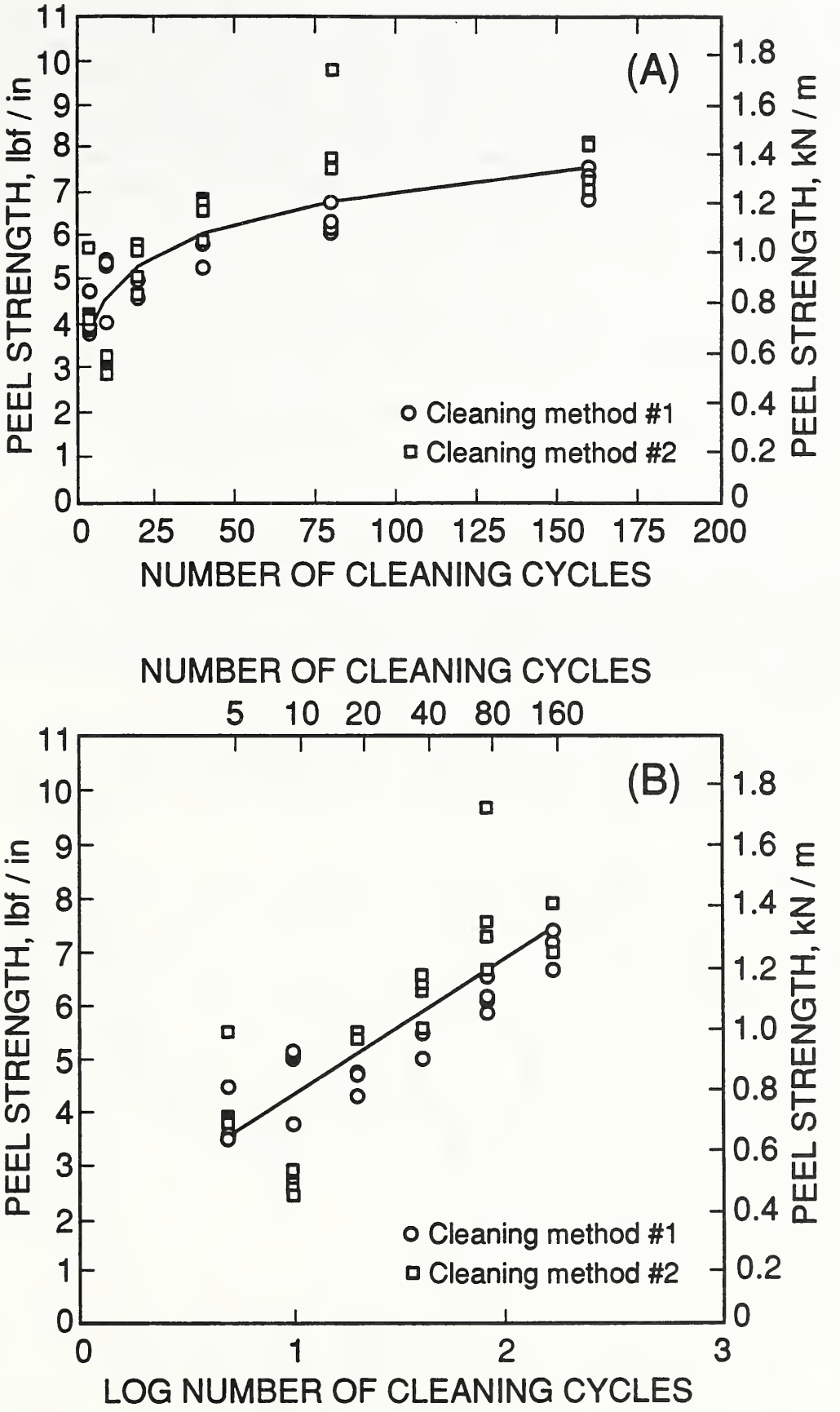

Figure 4. Peel strength of joints prepared from the aged EPDM versus: (a) the number of cleaning cycles, and (b) log of the number of cleaning cycles

The results of the peel strength measurements are given in Figure 5 for each set of tests per cleaning method. An analysis of variance was performed on the data set, and indicated significant differences in peel strength among the various surface cleaning methods. Moreover, there were significant differences in strength between some sets for the same cleaning method. However, examination of the data uncovered no patterns in the data and, consequently, the model proposed for further data analysis was that any given response (i.e., peel strength value) is the sum of three items:

1. an average (mean) strength characteristic of the cleaning method used,

2. a random effect characteristic of the particular set of peel specimens, and

3. a measurement error.

The means were assumed to be characteristic of the effectiveness of the various surface cleaning methods. The set effects and measurement error were assumed to be drawn randomly from distributions with means equal to zero so that they could be characterized by the standard deviations of their respective distributions.

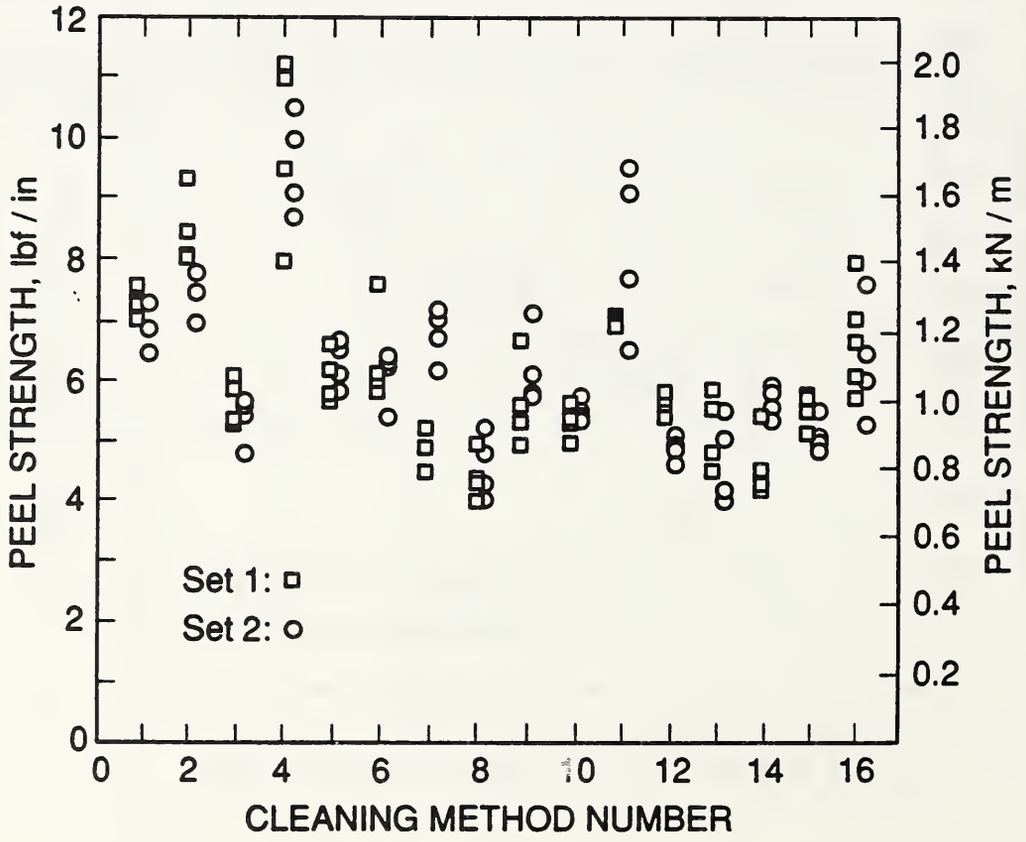

Figure 5. Peel strength as related to the surface cleaning method

Using this analysis model, conclusions were derived for the set effects and the cleaning method effects. In the former case, because all peel specimens in "Set 1" were taken from one half of the original rubber sheet, while those of "Set 2" were sampled from the other half, it was of interest to determine whether a difference existed between the two pieces of rubber. The analysis produced no evidence that the two rubber pieces were significantly different.

Table 4 gives the results of the analysis of the effects of the various surface cleaning methods. The approach taken in presenting the results was to give an average strength for all peel specimens for a given cleaning method, and to compare these averages with two cleaning methods (Nos. 1 and 16) which were designated, for purposes of the study, as controls. Method No. 1 (wiping the surface with a heptane solvent) was a method akin to that most commonly used in practice whereby the roofing mechanic wipes the EPDM surface with a cloth soaked with unleaded gasoline. On the other hand, Method No. 16 (scrubbing with detergent and water followed by a solvent wipe) was taken as a control because, as indicated, it was known to be effective for the laboratory preparation of the surface of new (unaged) EPDM rubber [10]. No statistical difference in the average strengths of the peel specimens cleaned as controls was observed (Table 4).

The peel strengths of the tape-joint specimens ranged from 0.8 to 1.7 kN/m (4.6 to 9.8 lbf/in.), depending on the cleaning method used. This range of values was comparable to the peel strengths of field seams fabricated from solvent-based adhesives and new EPDM rubber [12].

Only three of the surface cleaning methods (Nos. 2, 4, and 11) produced average peel strengths greater than the controls (Table 4). With the exception of Method No. 11 compared with Control No. 1, these differences were statistically significant. Method No. 2 was a solution of 75% heptane/25% MEK. In this case, no practical significance was attributed to the higher strength, because the preliminary cycling experiment showed no overall difference between cleaning with heptane (Method No. 1) and the 75% heptane/25% MEK solution (Method No. 2). Method No. 4 involved cleaning with a proprietary wash solution. Its effect may have been due to the presence of bond-promoting agents in the solution (see SEM discussion in Section 3.4). Finally, Method No. 11 was an aqueous detergent wash of the EPDM surface using a wire brush attached to an electric hand drill. Although, based on peel-strength measurements, the mechanical abrasion with the wire brush resulted in more effective surface preparation than manual scrubbing followed by a solvent wipe (Method No. 16), it was not more effective than wiping with heptane alone (Method No. 1).

As mentioned earlier, the surface of the aged EPDM sample, taken from a ballasted roof, was covered with a heavy layer of dirt. Thus, in planning the cleaning experiments, it was considered that washing with aqueous detergent solutions might be an important step in a surface cleaning method. Using peel strength as a benchmark

Table 4. Peel strengths of the joint specimens for the various surface cleaning methods

Cleaning Method No.	Peel Strength Average lbf/in.	Peel Strength Average kN/m	COV[a] %	Comparison Versus Controls[b] Method #1 Diff.	Method #1 Sign.	Method #16 Diff.	Method #16 Sign.
1-control	7.1	1.2	4.0	NA[c]	NA	+	No
2	7.9	1.4	6.5	+	Yes	+	Yes
3	5.6	1.0	7.0	-	Yes	-	Yes
4	9.8	1.7	12.6	+	Yes	+	Yes
5	6.2	1.1	6.5	-	Yes	-	No
6	6.3	1.1	10.6	-	Yes	o	No
7	5.9	1.0	6.3	-	Yes	-	No
8	4.6	0.8	9.9	-	Yes	-	Yes
9	6.0	1.1	11.6	-	Yes	-	No
10	5.4	0.9	4.1	-	Yes	-	Yes
11	7.2	1.3	12.0	+	No	+	Yes
12	5.3	0.9	3.8	-	Yes	-	Yes
13	5.0	0.9	13.6	-	Yes	-	Yes
14	5.1	0.9	9.0	-	Yes	-	Yes
15	5.3	0.9	5.6	-	Yes	-	Yes
16-control	6.3	1.1	11.3	-	No	NA	NA

[a]Coefficient of variation for the combined peel data of Sets 1 and 2. It was calculated as the root mean square of the individual coefficients of variation for each set. This approach was taken because, in the case of some cleaning methods, significant differences were observed between the strengths of the Set-1 and Set-2 specimens.

[b]The comparison was based on whether a difference (Diff.) was found between the average strength of a control and that for a given cleaning method. The symbol, o, indicates that no difference was found. The symbols, + and -, indicate whether an observed difference was an increase or a decrease, respectively, in average strength versus that of a control. Whether or not an observed difference was statistically significant (Sign.) at the 0.05 level is denoted by "Yes" and "No," respectively.

[c]NA indicates "not applicable."

for judgment, this was not found to be the case. As is evident in Table 4, with the exception of Method No. 11 versus Control No. 16, none of the methods involving an aqueous detergent solution (Nos. 5-11) produced higher bond strengths than the controls. In the case of Methods Nos. 5-9, it might be assumed that the aqueous-based procedure with only a little solvent wiping was biased toward removing the dirt and other polar contaminants from the surface, while leaving non-polar and low-polarity contaminants. However, Method No. 10 was a combination of brushing with an aqueous detergent followed by a wipe with the 75% heptane/25% MEK solution. This combination was not more efficient than wiping solely with heptane. One interpretation of these results was that residual water on the surface of the cleaned EPDM probably contributed to a lowering of the strength of the bond between the rubber sheet and the tape. This possibility was not investigated through further experiments in the study, although the FTIR analyses (Section 3.3) supported the hypothesis.

Finally, the results of the cleaning methods using the experimental agents (Nos. 12-15) are noted. The use of a proprietary aromatic tackifier or a proprietary silane coupling agent either in the cleaning solvent or as an additional step to solvent cleaning did not enhance bond strength. The four methods resulted in bond strengths that were among the lowest of those achieved.

3.2. Contact Angle Measurements

3.2.1 Background. The contact angle (Figure 6) of a liquid with a solid surface is a convenient measure of the affinity of a liquid for a solid. This affinity is often referred to as wettability. Contact angle and wettability are inversely related; that is, as one increases, the other decreases. A wide range of surface sensitive techniques have been developed in the last decade to probe the surface characteristics of solids. Although extremely useful, many are sophisticated, high-vacuum techniques, which are

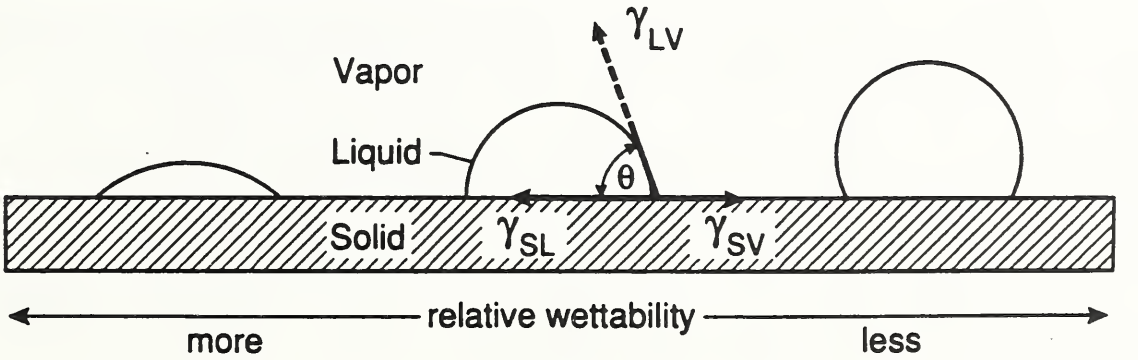

Figure 6. Contact angle and interfacial tensions for a drop of liquid resting on a solid surface: θ - contact angle, γ_{lv} - liquid/vapor interfacial tension, γ_{sv} - solid/vapor interfacial tension, γ_{sl} - solid/liquid interfacial tension

expensive, require highly skilled analysts, and are incompatible with liquids that are volatile under vacuum. In contrast, contact angle measurements are relatively inexpensive and require less analytical skill. Furthermore, the contact angle measurement is sensitive to the first 0.5-1 nm (5-10 Å) of the solid surface and, thus, its behavior reflects the chemical composition of the topmost atomic layers of the surface. Consequently, a layer of atomic thickness of a substance deposited on the surface of a test specimen is adequate to change the wetting characteristics.

In addition to contact angle, wettability parameters used in the study were calculated from the contact angle measurements:

1. γ_s -- This is the surface free energy (surface tension) and is the sum of γ^p_s and γ^d_s. The higher the value of γ_s, the more energetic (reactive) is the surface.

2. γ^p_s -- This is the polar component of the surface free energy, and is an indicator of the level of polarity of a surface. In comparing materials having the same γ_s, higher values of γ^p indicate more polar surfaces.

3. γ^d_s -- This is the nonpolar (dispersion) component of the surface free energy which results from the interactions of the instantaneous dipole moments produced by molecules with or without a permanent dipole moment. This component signifies the nonpolar characteristics of a surface. For surfaces having the same γ_s, higher values of γ^d indicate less polar surfaces. This component drops off more rapidly than γ^p with increasing molecular distance between the adhesive and substrate. Thus, for example, in the case of adhesive bonding, substrates having only a γ^d component (i.e., no polar component) are normally more difficult to bond with an adhesive than those containing some level of polarity.

4. Polarity -- This is the ratio between γ^p_s and γ_s. It is a measure of the polar nature of the surface.

3.2.2. Effects of Cleaning Cycle on Contact Angle Measurements. Contact angle measurements were used as a complementary method to the peel strength analysis to assist in the selection of a practicable, yet effective, number of cleaning cycles for evaluating the various surface cleaning methods. Thus, the effects of cleaning cycle on the contact angles of two liquids, water and methylene iodide, placed on the aged EPDM rubber samples cleaned under Methods Nos. 1 and 2 (Table 3) were determined. Four contact angles were measured for each cycle for each cleaning method, except for the 0 (as-received) and 80 cycles, where 8 and 12 measurements were taken, respectively.

Table 5 and Figures 7 and 8 present the effects of cleaning cycle on the contact angles and wettability parameters of water and methylene iodide on the aged EPDM rubber after cleaning by Methods Nos. 1 and 2. For purposes of comparison, Table 5 also includes the results for specimens of the aged and new EPDM rubber sheets cleaned using Method No. 16.

Table 5. Contact angles and wettability parameters of the aged EPDM rubber as a function of cleaning cycles[a]

Cleaning Method	Cycles No.	Contact Angle[b] degrees CH_2I_2	degrees H_2O	Surface Free Energy mJ/m^2 γ^d_s	γ^p_s	γ_s	Polarity γ^p_s/γ_s
NA[c]	0[d]	8	98	63.3	0.8	64.1	0.01
1	5	48	65	23.2	16.6	39.8	0.42
1	10	49	73	25.5	10.9	36.4	0.30
1	20	48	60	21.1	21.7	42.8	0.51
1	40	47	47	17.3	34.5	51.8	0.67
1	80	51	50	16.1	33.0	49.1	0.67
1	160	48	64	22.4	18.2	40.6	0.45
2	5	29	95	52.1	0.0	52.1	0.00
2	10	36	97	48.3	0.0	48.3	0.00
2	20	40	65	27.5	14.8	42.3	0.35
2	40	51	56	17.8	26.8	44.5	0.60
2	80	50	62	20.6	20.6	41.2	0.50
2	160	53	39	12.1	46.0	58.0	0.79
16	NA	51	71	23.5	12.9	36.4	0.35
new EPDM rubber 16	NA	52	75	24.3	10.4	34.7	0.30

[a]Data for well-cleaned (Method No. 16) aged and new EPDM rubbers are included for purposes of comparison.
[b]Average of eight measurements; CH_2I_2 and H_2O indicate methylene iodide and water, respectively.
[c]NA indicates not applicable.
[d]The measurements were conducted on the uncleaned aged EPDM.

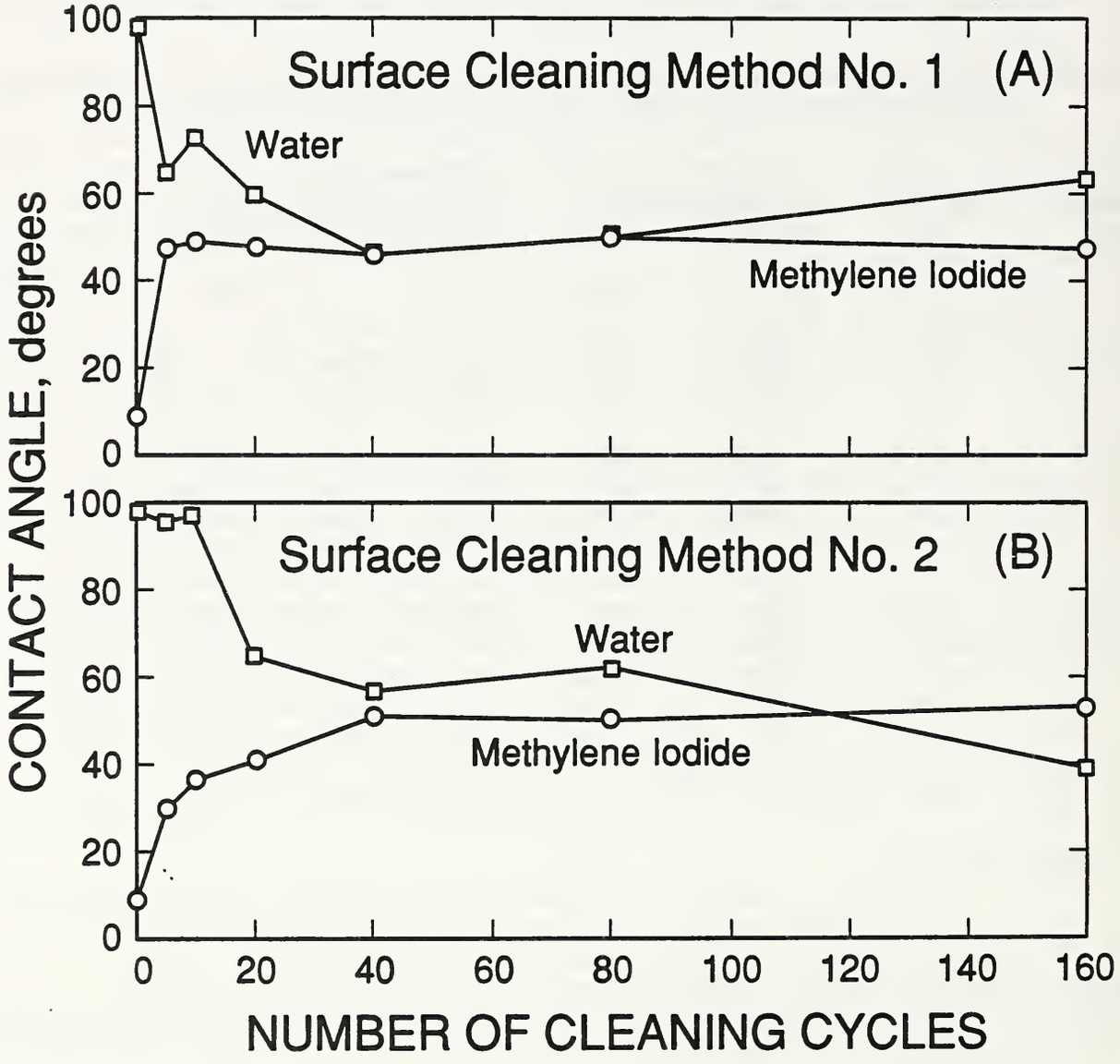

Figure 7. Water and methylene iodide contact angles of the aged EPDM as a function of the number of cleaning cycles: (a) surface cleaned with Method No. 1 and (b) surface cleaned with Method No. 2

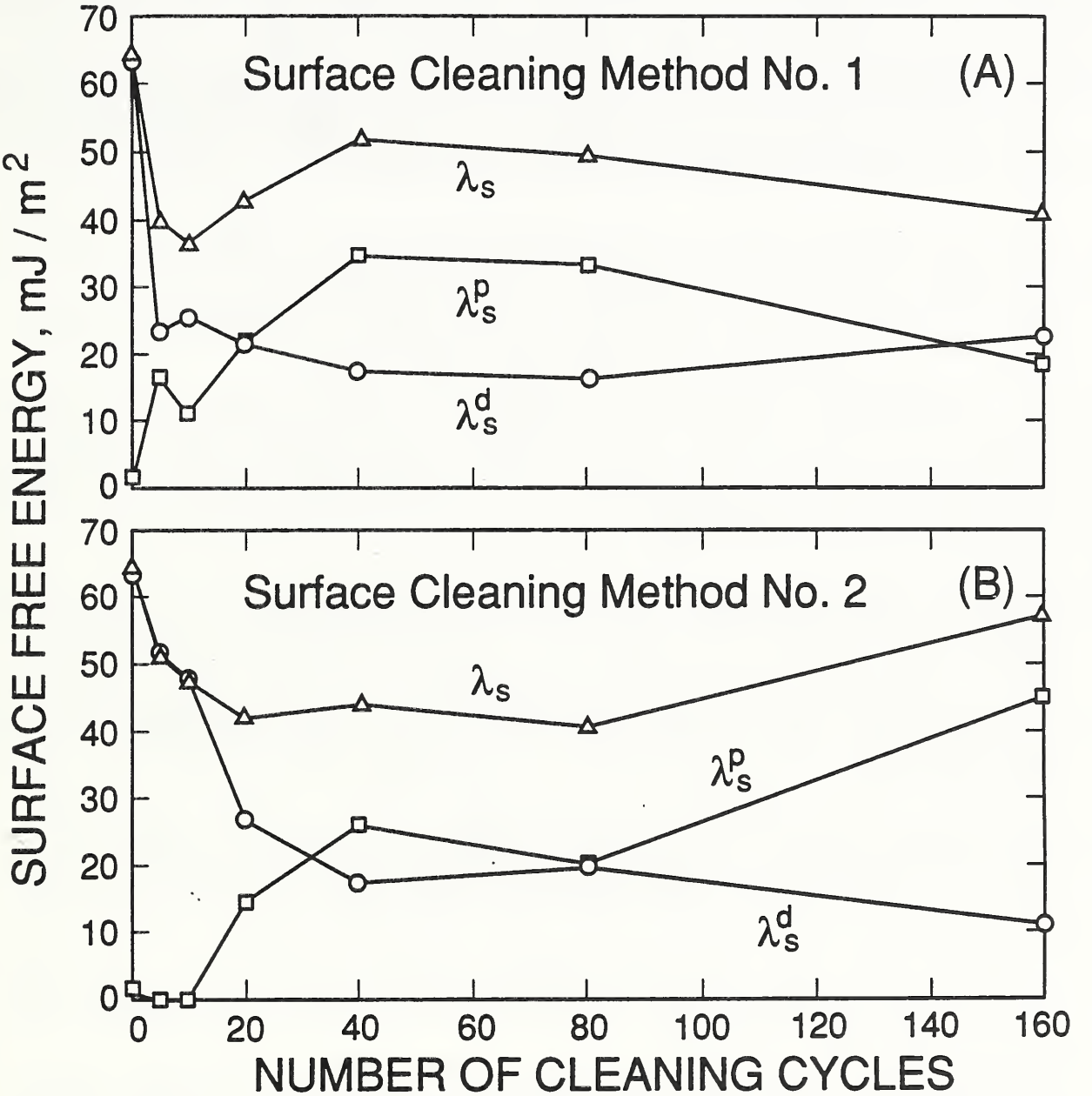

Figure 8. Surface free energies of aged EPDM as a function of the number of cleaning cycles: (a) surface cleaned with Method No. 1 and (b) surface cleaned with Method No. 2

The key features of the results in Table 5 and Figures 7 and 8 are summarized below. Interpretation of the data is discussed in the paragraphs after the summary.

1. The uncleaned aged EPDM rubber was very wettable by methylene iodide (a relatively nonpolar liquid) and was not wettable by water (a highly polar liquid).

2. Cleaning with heptane (Method No. 1, a nonpolar solvent) and 75% heptane/25% MEK (Method No 2, a slightly polar solvent) decreased substantially the wettability by methylene iodide and increased the wettability by water.

3. After five cycles of cleaning Method No. 1, the wettability by methylene iodide remained essentially constant; in contrast, the wettability by water increased (i.e., the contact angle decreased) up to 40 cycles; thereafter, the wettability by water appeared to decrease.

4. For Method No. 2, as the number of cleaning cycles increased up to 40, the wettability by methylene iodide decreased, whereas that by water increased. Then both appeared to level off except for the wettability by water at 160 cycles, whose value showed a decrease.

5. With regard to surface free energy parameters, increasing the number of Method No. 1 cleaning cycles beyond 5 did not appear to affect the nonpolar component (γ^d_s) of the aged EPDM. However, its polar component (γ^p_s) and total surface free energy (γ_s) increased as a function of cleaning with the nonpolar heptane solvent to 40 cycles. Then they appeared to decrease.

6. In the case of cleaning Method No. 2, the polar component increased and the nonpolar component decreased up to 40 cycles. Thereafter, the former increased, while the latter decreased.

7. For cleaning with either of Methods Nos. 1 and 2, the surface free energy values, as a function of cycles, followed the polar component values.

8. The cleaned, aged EPDM rubber was somewhat more polar than the cleaned, new rubber. (It should be cautioned that, since an unexposed sample of the aged EPDM was not available, it is not known whether this difference was due to formulation or aging effects.)

As an initial point of discussion, the contact angle data provide for characterization the contaminants on the surface of the aged EPDM rubber and how they behaved due to cleaning. The polar and nonpolar components and the polarity results indicated that the surface of the contaminants of the uncleaned, aged EPDM rubber was nonpolar. Note the polarity which was essentially zero (Table 5). This suggested that no polar sites were exposed on the uncleaned

surface. The magnitude of the nonpolar component of the uncleaned aged surface was much higher (63 mJ/m^2) than that of organic compounds, which are generally nonpolar and have nonpolar components in the range of 18-40 mJ/m^2 [18,19]. On the other hand, the nonpolar components of inorganic oxides are much higher than those of hydrocarbons. For example, the nonpolar components of SiO_2 and Al_2O_3 are 78 and 100 mJ/m^2, respectively [19]. Based on a comparison to these literature data, the contaminants on the uncleaned, aged EPDM were apparently inorganic materials. However, because the measured nonpolar component of the surface of the uncleaned aged EPDM was lower than that of inorganic oxides, some of the nonpolar sites on this surface were probably covered by some organic materials.

As the aged EPDM rubber was cleaned with a nonpolar solvent (Method No. 1), the polar component of the surface free energy and polarity increased (Table 5). This was observed even after only five cycles of cleaning. This increase in polar component and polarity indicated that some of the nonpolar and low-polarity materials on the surface of the uncleaned aged rubber were removed and that polar sites were exposed. Since five cycles of cleaning left a rubber surface that was still substantially covered with particles (Figure 3), it was assumed that the increase in polarity was due, in part, to exposure of polar sites of the inorganic contaminant. The increase of the polar component and the polarity as the number of cleaning cycles increased (up to 40 cycles) indicated that the nonpolar and low-polarity organic materials were further removed by the repeated cleaning.

The low contact angle (high wettability) value of water after 160 cycles using Method No. 2 may have been due to residual water on the surface of the specimen at the time of the measurement. This sample, which was considered to be reasonably well cleaned, displayed a higher value of the polar component as compared to that of the well-cleaned (Method No. 16), aged rubber. Consistent with this supposition of water on the surface, FTIR results (Section 3.3) of specimens cleaned using the heptane/25% MEK solution indicated the presence of water molecules. Consequently, the contact angle data for 160 cycles of cleaning with Method No. 2 were not considered representative of the cleaned surface.

3.2.3. Contact Angle Results for Various Surface Cleaning Methods. Specimens used for the contact angle measurements as a function of the different surface cleaning methods were taken from the same cleaned aged EPDM samples used for peel strength measurements. Four contact angles were obtained on two duplicate specimens (Set 1 and Set 2) for each surface cleaning method. Thus, eight contact angle measurements were obtained for each liquid (i.e., water and methylene iodide) per cleaning method.

Figures 9a and 9b present the results of the contact angles of water and methylene iodide, respectively, on the aged EPDM rubber after cleaning by the 16 different methods listed in Table 3. The contact angles in these figures are the individual values from the Set-1 and Set-2 samples and indicate the reproducibility of the

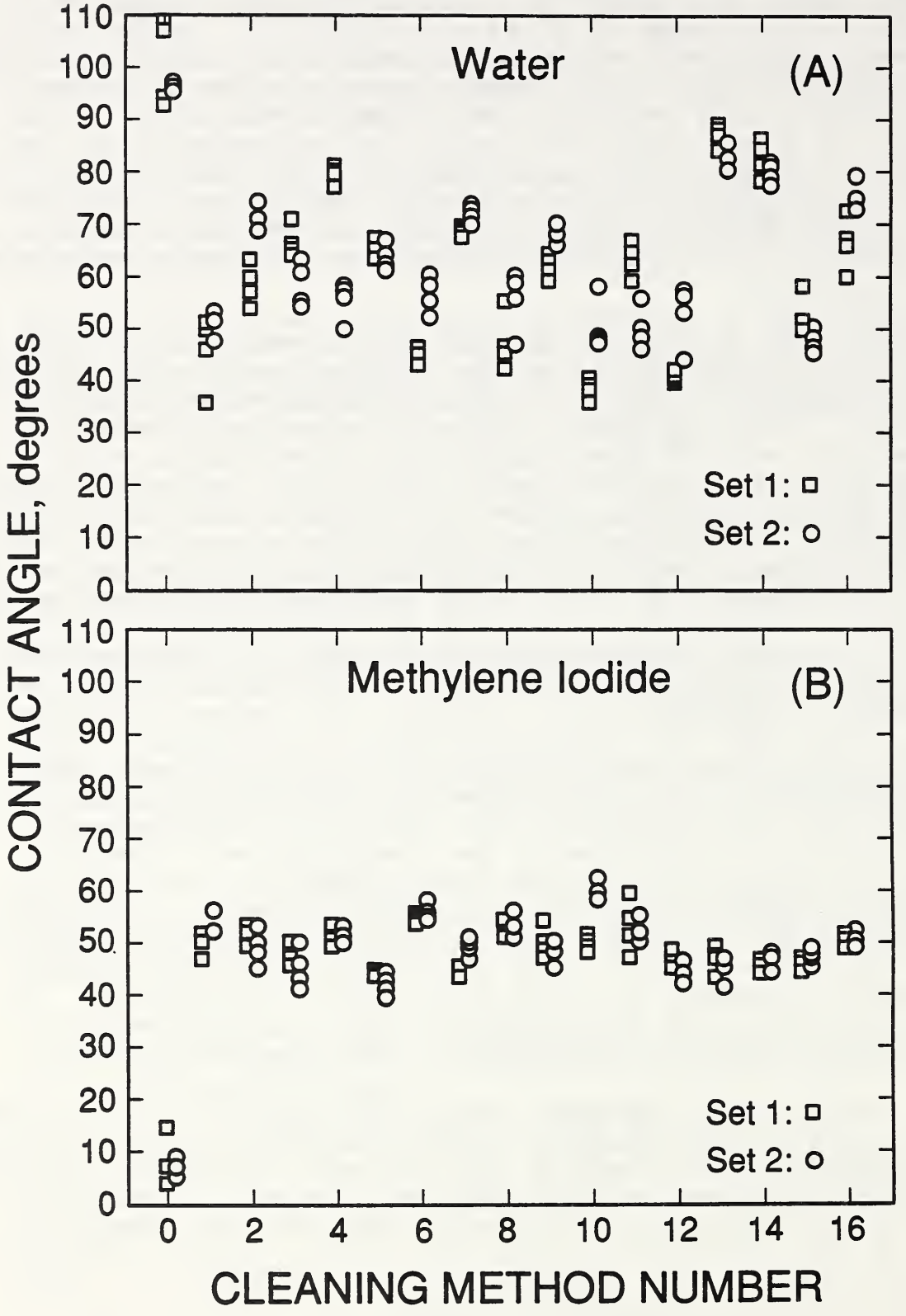

Figure 9. Contact angle as related to the cleaning method: (a) measured with water and (b) measured with methylene iodide

measurement within and between sets[3]. Within any of the sets, the coefficients of variation were 15 and 10 percent or less for water and methylene iodide, respectively. With regard to the between-set variation, more variability was observed for water than for methylene iodide. In the case of the water contact angles, for the majority of the cleaning methods, the two data sets were statistically different (0.03 level or less). Only for Methods Nos. 1, 5, and 14 were no differences between sets found. In contrast, for the methylene iodide contact angles, no statistical differences (0.07 level or greater) were observed for all but three of the cleaning methods (Nos. 1, 7, and 10). The analysis of the overall data indicated that no significant difference existed between the two sections of rubber from which the Set-1 and Set-2 specimens were taken. In analyzing the data in Figures 9a and 9b, no relationships between contact angle and cleaning method were found.

Table 6 summarizes the contact angle results and wettability parameters for the different surface cleaning methods. For each cleaning method, the listed values are the averages of all eight specimens.

Table 6. Summary of the contact angles and wettability parameters for the surface cleaning methods

Cleaning Method No.	Contact Angle[a] degrees		Surface Free Energy mJ/m^2			Polarity
	CH_2I_2	H_2O	γ^d_s	γ^p_s	γ_s	γ^p_s/γ_s
1	52	48	14.5	36.3	50.8	0.71
2	51	65	20.8	18.8	39.6	0.46
3	47	62	22.3	19.2	41.5	0.46
4	51	68	22.0	17.5	39.5	0.41
5	44	65	25.5	15.8	41.3	0.38
6	56	50	13.5	35.7	49.2	0.72
7	48	70	25.1	12.7	37.8	0.34
8	54	51	14.9	33.3	48.2	0.69
9	50	65	21.7	17.9	39.6	0.45
10	56	45	12.3	40.6	52.9	0.77
11	54	57	16.6	27.7	44.3	0.62
12	46	47	17.8	34.1	51.9	0.65
13	47	84	33.0	3.4	36.4	0.09
14	47	81	31.0	5.2	36.2	0.14
15	47	51	18.3	30.7	48.9	0.62
16	51	71	23.5	12.9	36.4	0.35

[a]Average of eight measurements; CH_2I_2 and H_2O indicate methylene iodide and water, respectively.

[3]Some data points are not seen for some sets because they were identical or very close to other values.

As given in Table 6, all cleaning methods produced aged EPDM rubber surfaces having average contact angles by methylene iodide ranging between 43-56 degrees. This suggested that the interactions of the cleaned surfaces, irrespective of the cleaning method used, with an essentially nonpolar liquid were rather comparable. This result has practical significance for it implies that a number of cleaning methods would provide surfaces that would have similar wettability characteristics to nonpolar-solvent-based adhesives.

The lowest methylene iodide contact angle (43 degrees) was from cleaning with tap water without a detergent (Method No. 5). This result suggested that this cleaning method left more nonpolar or low-polarity organic contaminants on the surface than the other methods. The suggestion was supported by the relatively high value of the nonpolar component.

The average contact angles for water varied more widely than those for methylene iodide, ranging from 45 to 84 degrees (Table 6). In the case of wetting with water, the lower contact angles indicate more polar surfaces. With the exception of the experimental silane solutions (Nos. 12-15), the lowest contact angles were obtained with specimens cleaned with Methods Nos. 1, 6, 8, and 10, suggesting that these methods were relatively effective in removing nonpolar contaminants. In support of this suggestion, the polar components were also relatively high, indicating very polar surfaces. The polar nature of the surfaces may have been either due to removing a substantial amount of nonpolar organic contaminants from the aged EPDM (Method No. 1) or to the presence of residual water on the surface (Methods Nos. 6, 8, and 10). As will be discussed, the FTIR results indicated that specimens cleaned with water and other polar solvents left residual water on the surface (Section 3.3).

In the case of the experimental cleaning methods (Nos. 12-15), differences in the contact angle data among the four were observed. However, since the peel test results for the EPDM rubber specimens cleaned using these four methods indicated that they did not enhance adhesion, further investigation of their effects on the surfaces of the cleaned aged rubber was not conducted. Consequently, an explanation of the differences in the contact angle data for the experimental cleaning methods is not offered.

3.3 FTIR Spectroscopy

Before conducting the FTIR analyses on the surfaces of the aged EPDM rubber specimens that were cleaned by the different methods, the chemical nature of the contaminants and of the contaminant-free, aged EPDM surface was investigated. Figure 10a presents the FTIR transmission spectrum of the removed contaminants. The spectrum showed the bands between 2800-3000 cm^{-1}, due to CH stretchings of hydrocarbons. This finding indicated that the contaminants included organic materials, which was consistent with the wettability data. The broad bands between 3200 and 3500 cm^{-1} are normally due to the OH (and NH) stretchings, which was an indication that the contaminants likely contained polar materials

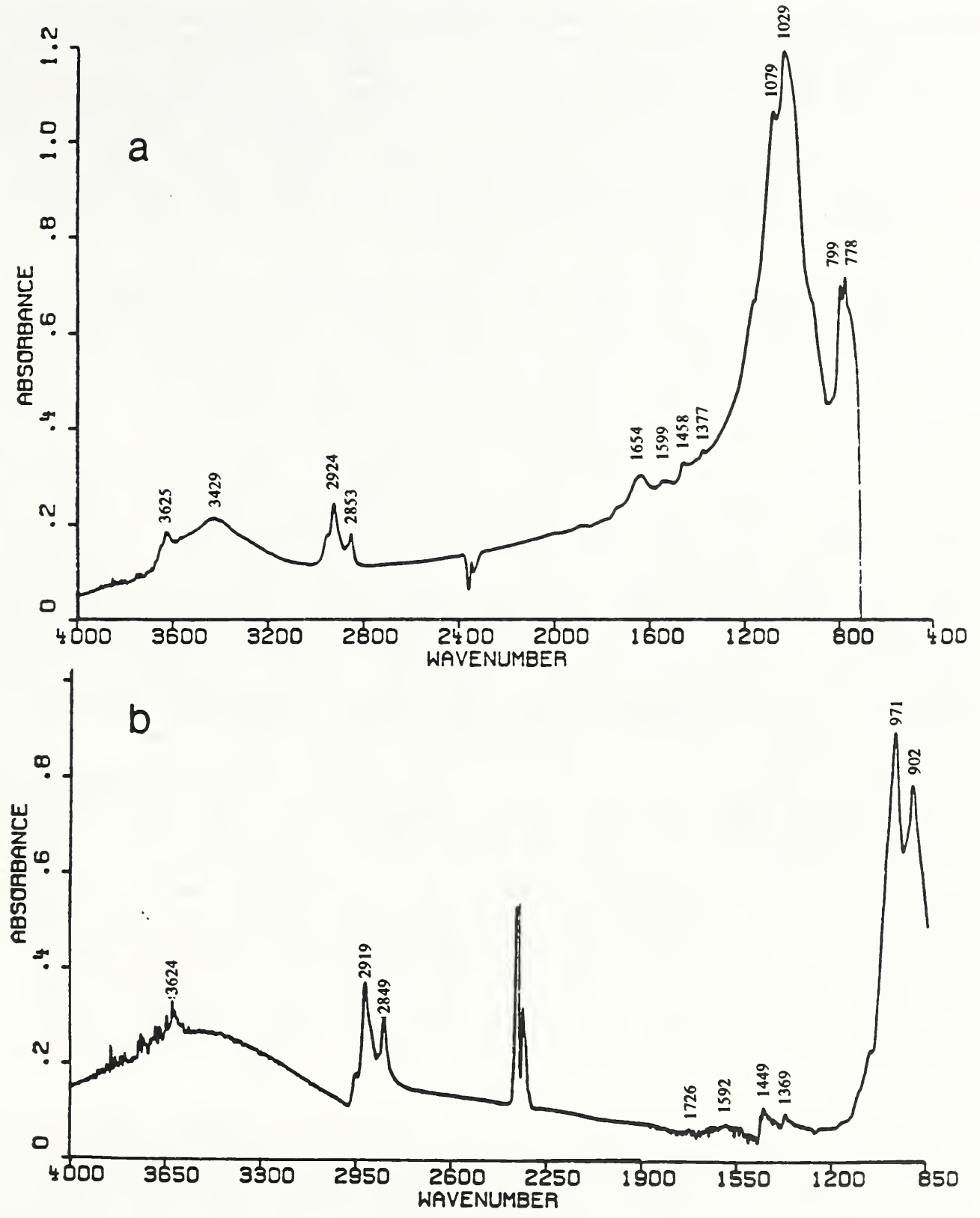

Figure 10. FTIR spectra: (a) transmission spectrum of the contaminants removed from aged EPDM rubber, and (b) ATR spectrum of cleaned (Method No. 11) aged EPDM

having hydroxyl groups. The presence of these bands supported the wettability data which showed the high polar component and high polarity after removing the nonpolar organic contaminants from the surface of the uncleaned, aged EPDM rubber. The sharp band near 3625 cm^{-1} in Figure 10a is probably due to isolated, adsorbed water molecules on the inorganic contaminants; bands associated with hydrogen-bonded adsorbed water molecules occur in the 3200-3500 cm^{-1} region. Finally, the broad bands near 1000 cm^{-1} are normally characteristic of silicates and phosphate inorganic materials.

Figure 10b is the FTIR-ATR spectrum of a cleaned (Method No. 11), aged EPDM rubber. The surface of this specimen was essentially free of platelet particles with the rubber being quite visible, as evidenced from its SEM image (Section 3.4). Figure 10b shows strong absorption bands in the 2800-3000 and 850-1050 cm^{-1} regions. Again, the bands in the 2800-3000 cm^{-1} region are due to the CH stretchings. The band peaking at 970 cm^{-1} may be due to the CH out-of-plane deformation of the vinylidene group of the unsaturated monomer used for cross-linking. For example, the CH deformation of the vinylidene group in 1,4-hexadiene occurs at 966 cm^{-1} [20]. The strong band at 904 cm^{-1} was not assigned at this time. The band near 3625 cm^{-1} suggested that water was present on this cleaned surface. The broad band in the 3100-3600 cm^{-1} region and the very weak band occurring near 1725 cm^{-1} indicated the presence of OH and C=O groups, respectively. Careful examination of FTIR-ATR spectra (not shown) of cleaned, new EPDM rubbers did not detect these bands. Thus, their presence in the aged rubber suggested possible oxidation of the surface of the EPDM sheet with time; however, further study is needed to provide conclusive evidence.

FTIR-ATR spectra were obtained on specimens of the aged EPDM rubber cleaned using Methods Nos. 1-10. Figures 11a, 11b, 11c, and 11d present representative spectra and compare specimens which were: uncleaned, heptane cleaned (Method No. 1), cleaned with a proprietary wash solution (Method No. 4), and tap water cleaned (Method No. 5), respectively. In general, there were only minor differences in the spectral characteristics of the cleaned aged specimens, as illustrated in Figures 11b, 11c, and 11d. The spectral characteristics of the cleaned specimens included the bands in the 2800-3000 cm^{-1} region and the bands peaking at 970 and 904 cm^{-1}. These bands were assigned as previously discussed for cleaned aged EPDM.

In comparison to the spectra of the cleaned specimens, the spectrum of the uncleaned aged EPDM (Figure 10a) also showed bands peaking at 983 and 914 cm^{-1}. Because these bands were not present in the spectra of the cleaned specimens, they probably resulted from contaminants on the uncleaned EPDM. Note, however, the closeness of these bands of the contaminants and bands at 970 and 904 cm^{-1} of the aged cleaned EPDM rubbers. This closeness complicates the interpretation of the spectra of specimens cleaned by the different methods. For example, it was shown using SEM analysis (Section 3.4) that many of the surfaces of the cleaned specimens contained platelet particles typical of release agent. Because the release agents are silicate materials (talc or mica), they would be

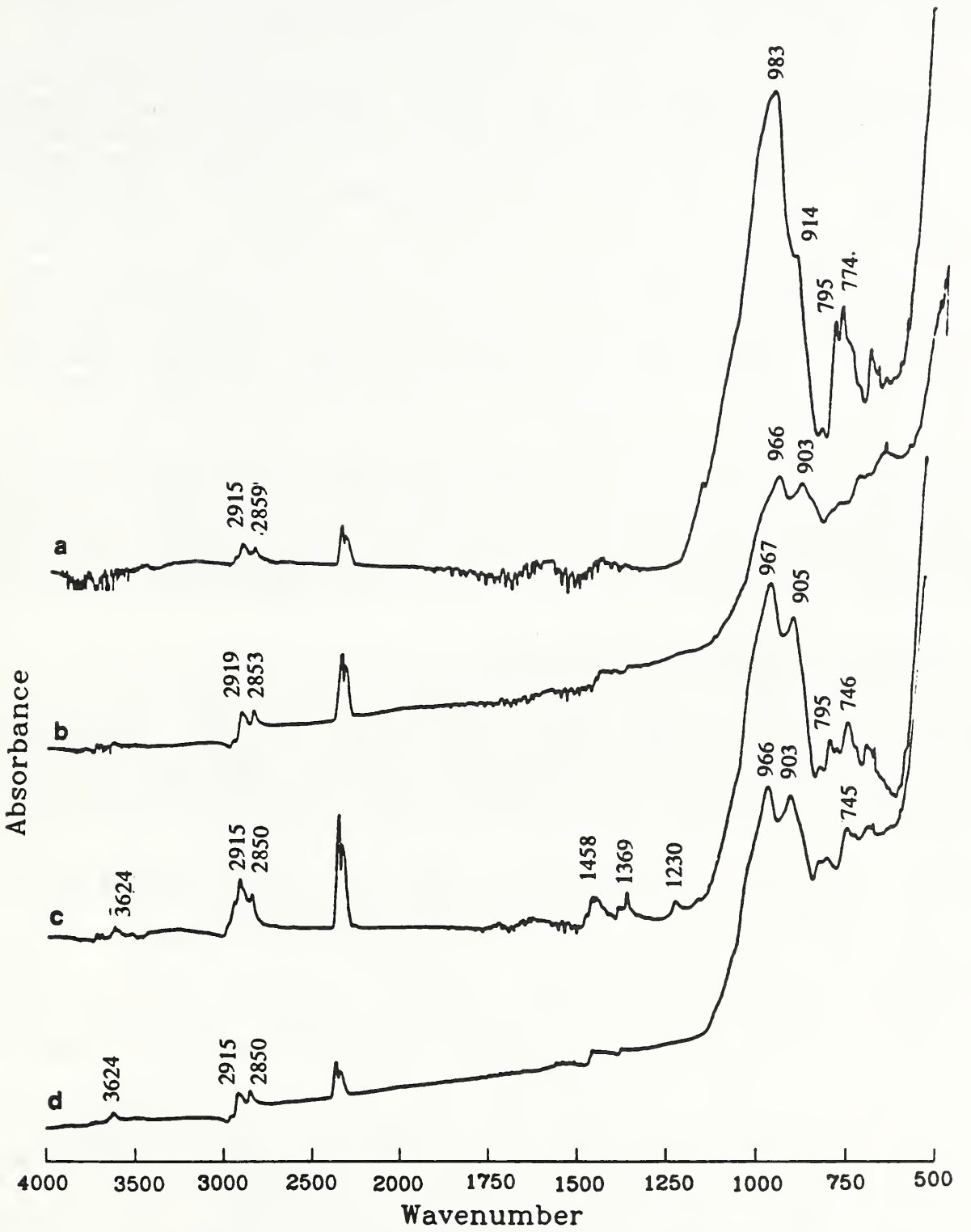

Figure 11. FTIR-ATR spectra of aged EPDM rubber: (a) uncleaned, (b) heptane cleaned (Method No. 1), (c) proprietary wash solution cleaned (Method No. 4), and (d) tap-water cleaned (Method No. 5)

expected to have a band in the region of 1000 cm^{-1}. However, this band overlaps the higher frequency end of the 970 cm^{-1} band associated with the EPDM. Consequently, the FTIR analysis could not resolve whether or not the surfaces of the cleaned rubber specimens had a talc-like release agent on them.

The spectra of the specimens cleaning using Methods Nos. 2-10 contained a band near 3625 cm^{-1}. This band was due to molecular water as stated earlier. Its presence was attributed to cleaning with methods that included polar solvents or water. The band was not present in the spectrum of the surface cleaned with heptane (Method No. 1).

The specimen cleaned with Method No. 4 produced a spectrum that had several additional bands in the 1200-1500 cm^{-1} region. In this case, the band shapes in the 2800-3000 cm^{-1} were also different. The additional bands may have been due to the coating deposited on the surface of the aged EPDM rubber when cleaned using Method No. 4 (Section 3.4).

In summary, FTIR-ATR is useful for distinguishing the cleaned from the uncleaned, aged EPDM. It may also provide valuable information on whether a cleaning method has modified the surface, such as leaving behind a polymeric coating or residual water. No major differences between the FTIR spectra of the specimens cleaned using the various methods were observed.

3.4 Scanning Electron Microscopy

A section of each of the rubber specimens that were cleaned using surface cleaning Methods Nos. 1-12, and No. 16 were subjected to SEM surface analysis. The SEM observations, based on visual examination of the photomicrographs, are summarized in Table 7.

Table 7. Summary of the SEM observations on the cleaned EPDM rubber for the various cleaning methods

Cleaning Method No.	SEM Observations
1 - 3, 5 - 10	Surface substantially covered with platelet particles indicative of release agent.
4	Surface was smooth and appeared to be coated or covered with a residue; platelet particles covered with the residue could be observed.
11 & 16	The rubber surface was plainly visible and essentially free of platelet particles.
12	Surface appeared to be coated or covered with a residue; in some locations, platelet particles covered with residue could be observed.

The most notable feature was the presence of platelet particles indicative of release agent on the surfaces of the majority of the specimens (Methods Nos. 1-3 and 5-10). Figure 12a presents a typical photomicrograph showing the surface of a specimen covered with the platelet particles. In the cases where platelet particles were visible, it was not possible by visual examination of the micrographs to ascertain whether the amount varied between specimens as a function of the cleaning method. Qualitatively, all the micrographs appeared to be comparable regardless of the cleaning method employed.

The presence of platelet particles on the surfaces of these specimens was not surprising in that the original rubber sheet had been coated with a release agent during its manufacture. In service, the release agent was not washed free due to rain or other means, but remained in place covered with the layer of dirt which accumulated in time. The SEM observations indicated that the specimens were not totally cleaned under Methods Nos. 1-3 and 5-10 to provide a release-agent-free surface for bonding. In the present study, the majority of the cleaning methods apparently removed relatively loose particles on the surface, while leaving behind those that were more strongly bonded to or perhaps partially embedded in the rubber surface. As a consequence, the peel specimens made using the aged EPDM rubber cleaned with Methods Nos. 1-3 and 5-10 contained release agent at the interface of the tape and the rubber surface.

Only in the case of cleaning Methods Nos. 11 and 16 were the rubber surfaces observed to be essentially free of platelet particles (Figure 12b). In contrast to the methods where particles remained intact after cleaning, these two methods (Nos. 11 and 16) involved relatively vigorous mechanical abrasion. Method No. 11 used a wire brush attached to an electric drill, and Method No. 16 included extensive hand scrubbing with a stiff bristle brush (Table 3). Nevertheless, although the rubber surfaces were cleaned essentially free of release agent, the peel strengths of the bonds formed with the tape were not significantly greater (Table 4) than those made on rubber which still contained release agent after washing with heptane. That is, the tape formed a bond with the rubber surface having platelet particles (after cleaning) whose peel strength was comparable to that formed by the tape with the platelet-particle-free rubber surface.

For the specimens that had been cleaned using Methods Nos. 4 and 12, the SEM analyses indicated that a coating, which generally covered the release agent particles, had been deposited on the specimen surfaces (Table 7). In these cases, in forming the peel specimens, the tape was adhered to this coating. For cleaning Method No. 4, the effect of the coating was positive in that the average peel strength of the specimens was the highest of any of those measured for the various cleaning methods (Table 4). In contrast, the average peel strength of the specimens cleaned under Method No. 12 was among the lowest measured for the specimen sets.

Figure 12. SEM photomicrographs: (a) typical cleaned rubber surface with platelet particles, and (b) a cleaned (Method No. 11) surface which was essentially free of platelet particles

3.5 Creep-Rupture Experiment

Martin et al. [3] have reported that creep-rupture tests of joint specimens in a peel configuration offer a sensitive method for assessing factors affecting the performance of seams. In a creep-rupture experiment, a joint specimen is placed under load, and the time over which it sustains the load before total delamination is measured. This time period is called the time-to-failure for the specimen.

In the present study, joint specimens (Figure B.2) prepared from one strip of cleaned aged rubber (Method No. 1) and a second strip of cleaned new rubber (Method No. 16) were subjected to creep-rupture testing. This set of laboratory specimens was considered comparable to field patches (i.e., new rubber bonded to aged rubber) and was designated CR1. Heptane was selected to clean the aged rubber because it produced a relatively high peel strength in the comparative cleaning experiments (Table 4) and was akin to the most common method used in the field to clean aged EPDM before patching or splicing. As a control for the creep-rupture experiment, joint specimens were also prepared using two new strips of cleaned rubber (Method No. 16). This set of specimens was considered comparable to new field seams (i.e., new rubber bonded to new rubber) and was designated CR2.

Before conducting the creep-rupture tests, the short-term peel strengths of five replicate joint specimens from each set (CR1 and CR2) were determined. The two sets of specimens performed comparably in the tests. The average strengths of the CR1 and CR2 sets were 0.77 and 0.82 kN/m (4.4 and 4.7 lbf/in.), respectively (Table 8), and were not significantly different (0.05 level). The locus of failure of the five CR1 specimens was at the interface of the tape and the new rubber. These results indicated that cleaning the aged EPDM rubber by wiping the surface with a cloth soaked with heptane (Table 3) produced bonds with the tape which were, under the peel-test conditions, stronger than those obtained with new cleaned rubber and the tape.

Table 8. Summary of results for the creep-rupture experiment

	Short-term Peel Tests			Creep-rupture Tests			
	range	av	COV[a]	load	load ratio[b]	time-to-failure	
	lbf/in.			lbf		mean	s.d.[c]
Design.	(kN/m)		%	(N)	%	min	min
CR1	4.2 - 4.6	4.4	4	0.94	21	247	29
	(0.74 - 0.81)	(0.77)		(4.2)			
CR2	4.4 - 5.1	4.7	7	0.94	20	420	99
	(0.77 - 0.89)	(0.82)		(4.2)			

[a]Coefficient of variation.
[b]Ratio of the load applied under creep-rupture conditions to the average short-term peel strength.
[c]Standard deviation.

For each of the two sets (CR1 and CR2), 14 joint specimens were subjected to creep-rupture testing under a load of 4.2 N (0.94 lbf). This was approximately 20% of the average short-term strength of the specimens (Table 8). The results of the creep-rupture tests are given in Figure 13 wherein it is evident that the two specimen sets performed differently under the creep conditions. As just described, this finding was in contrast to that of the short-term strength tests where the CR1 and CR2 specimens performed comparably. Consistent with the short-term peel strength tests, the CR1 specimens failed at the interface of the new cleaned rubber with the tape. Cleaning the surface of the aged EPDM rubber by wiping with a cloth soaked with heptane provided a bond with the tape that was more resistant to peel under creep conditions than that of the new cleaned rubber.

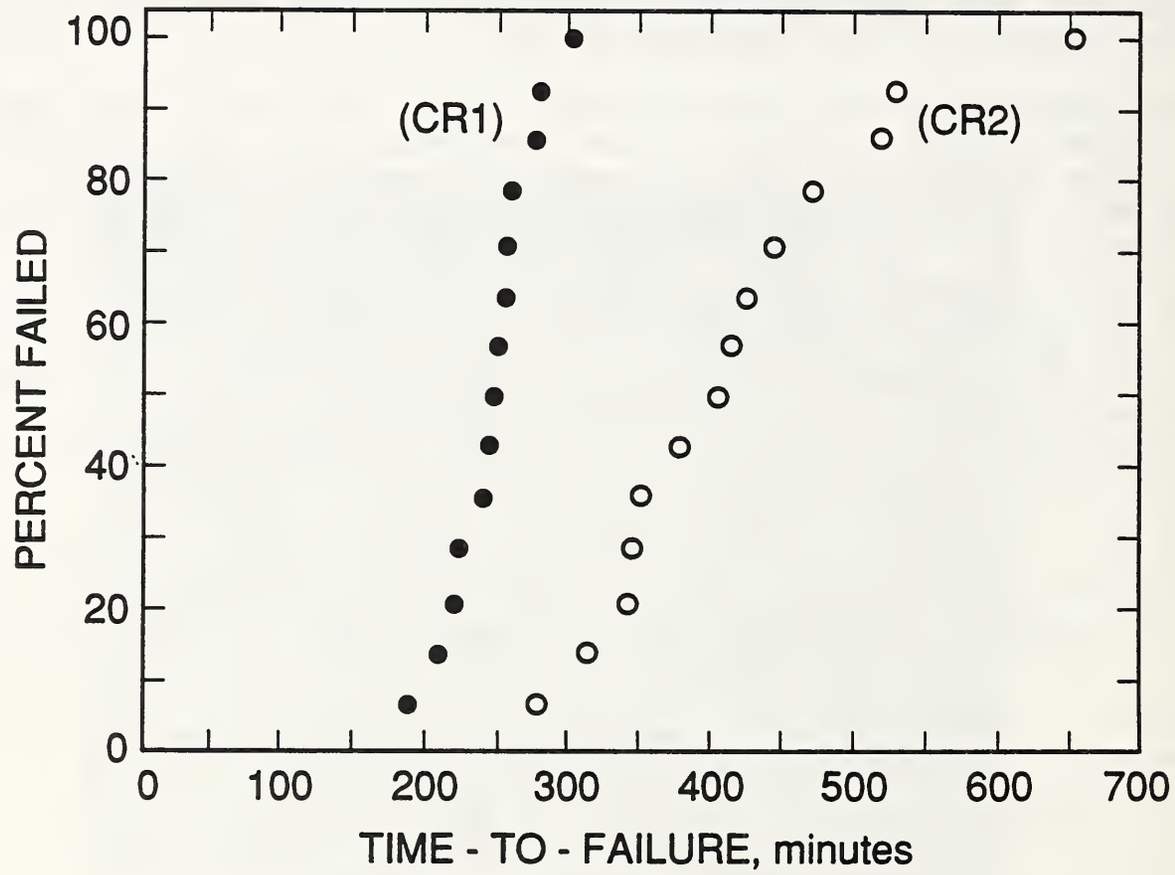

Figure 13. Results of the creep-rupture experiments: (CR1) new rubber bonded to aged rubber, and (CR2) new rubber bonded to new rubber

Martin et al. [3,21] have shown that creep-rupture times-to-failure of EPDM joint specimens fabricated from solvent-based adhesives fit a Weibull distribution which has the form:

$$F(t) = 1 - \exp(-t/\beta)^{\alpha}) \text{ for } t > 0$$

where: (1) F(t) is the Weibull distribution function and 100 times F(t) equals the cumulative percent failed,
(2) $\alpha > 0$ and is the Weibull shape parameter,
(3) $\beta > 0$ and is the Weibull scale parameter, and
(4) t is time.

Statistical analysis of the CR1 and CR2 creep-rupture data in the present study showed that each data set displayed a good fit to the Weibull distribution function. Moreover, the analysis verified the distinctive nature of the two data sets evident in Figure 13. For the CR1 data set, the values of the α and β parameters were 9.8 and 260, respectively; whereas for the CR2 data set, they were 5.3 and 454, respectively. For the two data sets, the differences between the α and β parameters were statistically significant.

Reasons why the data for the two specimen sets (CR1 and CR2) were different in the creep-rupture tests, while being indistinguishable for the short-term strength tests, were not investigated in the study. It may be that subtle differences in the mechanics of peel testing due to factors such as the stiffness or thickness of the EPDM strips comprising the joint specimens were amplified under creep testing in the peel configuration. Such factors can influence adhesion tests [18,19]. Note in Table 1 the difference in thickness and modulus values between the new and aged rubbers.

Although an explanation of these results is not given here, the observation illustrates Martin et al.'s [3] proposition that creep-rupture testing is a more sensitive method than short-term strength tests for assessing factors affecting seam performance. Although all specimens in both the CR1 and CR2 sets failed at the interface of the tape and the new EPDM rubber, some factor caused the CR2 specimens to have significantly longer times-to-failure than the CR1 specimens. An understanding of this observation might provide further insight into means for extending seam creep-rupture life.

SEM analysis was conducted on the sections of the cleaned surfaces of both the aged and new rubbers used in the creep-rupture experiments. The results were similar to those obtained from the SEM analyses of the rubber samples subjected to the various cleaning methods (Table 4). In the creep-rupture experiment, the aged rubber cleaned using Method No. 1 was found to have platelet particles on its surface. In contrast, the new rubber cleaned under Method No. 16 was seen to have a surface essentially free of release agent. These observations indicated that, under the conditions of both the short-term strength and creep-rupture tests, the interface between the release-agent free surface of the new rubber and the tape was more prone to failure than that between the surface of the aged rubber with release agent and the tape. Reasons for this observation were not explored.

4. COMPARISON OF THE RESULTS OF THE DIFFERENT TEST METHODS

Peel tests of bond strength can be time consuming, and more importantly, are destructive. Although peel tests are a routine exercise for laboratory evaluation, these factors are a serious limitation to the use of peel testing in the field. On the other hand, surface characterization by some other techniques may provide important information for assessing the surface condition of aged EPDM rubbers before making patches. For this reason, the peel strength data for the cleaned aged rubber specimens were compared with the information obtained by the surface analytical techniques, particularly contact angle, to look for evidence of systematic relationships. Table 9 is a summary of the results of the peel strengths and surface analyses of the rubber cleaned using the various methods.

From a comparison of the peel strengths with the SEM results, it was concluded that the SEM technique was not able to distinguish a surface that produced a relatively high peel-strength seam from a surface that gave rise to a low peel-strength seam. Similarly, in comparing the peel strengths with the FTIR spectra, it was found that the FTIR-ATR technique could also not differentiate between surfaces providing bonds of different strength.

An attempt was made to relate the peel strengths to the contact angle data for the 16 surface cleaning methods. In this regard, reports of good relationships between bond strength and contact angle parameters for homogeneous substrates have been published [18]. However, in the present study, no evidence of relationships was observed between any of the contact angles (or wettability parameters) and peel strength. One reason may be that the local chemical and topographical differences of the surfaces prepared by the different cleaning methods provide inhomogeneous substrates and, thus, have a strong effect on the contact angle measurements. In contrast, the bond strength measurements, which average out the entire surface area, are probably more forgiving to local inhomogeneities. Another reason is that the wettability parameters are derived from the theoretical and ideal interaction between a liquid and a solid [18], whereas the peel strength between a substrate and a solid adhesive tape depends not only on the interaction of the two solid bodies but also on the interfacial defects and conditions used in seam formation.

Table 9. Summary of the peel strength, contact angle, FTIR and SEM results for the various cleaning methods

Cleaning Method No.	Peel Strength Average lbf/in.	Peel Strength Average kN/m	Contact Angle[a] degrees CH_2I_2	Contact Angle[a] degrees H_2O	FTIR[b] Spectroscopy	SEM[c] Observations
1	7.1	1.2	52	48	no water	platelets
2	7.9	1.4	51	65	water	platelets
3	5.6	1.0	47	62	water	platelets
4	9.8	1.7	51	68	water	coated
5	6.2	1.1	44	65	water	platelets
6	6.3	1.1	56	50	water	platelets
7	5.9	1.0	48	70	water	platelets
8	4.6	0.8	54	51	water	platelets
9	6.0	1.1	50	65	water	platelets
10	5.4	0.9	56	45	water	platelets
11	7.2	1.3	54	57	water	plate. free
12	5.3	0.9	46	47	not run	coated
13	5.0	0.9	47	84	not run	not run
14	5.1	0.9	47	81	not run	not run
15	5.3	0.9	47	51	not run	not run
16	6.3	1.1	51	71	not run	plate. free

[a] CH_2I_2 and H_2O indicate methylene iodide and water, respectively.
[b] With the exception of the presence of residual water (as indicated below), no major differences between the FTIR spectra of the specimens cleaned using the various methods were observed.
[c] The major observations from the SEM analyses were; (1) a surface covered with platelet particles indicative of release agent, (2) a coated surface, and (3) a surface free of release agent.

When peel strength and contact angle of water were plotted as a function of the number of cleaning cycles, the relationship in Figure 14 was found. In this figure, with one exception, all strength and contact angle data points for each cleaning-cycle number were the average values obtained from both cleaning Methods Nos. 1 and 2. In the case of the contact angle value at 160 cycles, only data from cleaning Method No. 1 were used. As previously discussed, the contact angle measurement of water after cleaning with Method No. 2 for 160 cycles appeared to be unduly influenced by the presence of water molecules on the surface and, thus, was not considered to be truly representative of the cleaned surface.

Figure 14 shows that as the number of cleaning cycles was increased from 0 to 40, the water contact angle decreased and the peel strength increased. With further cycling, both the contact angle and the peel strength increased.

Figure 14 provides an explanation of the increase in peel strength as a function of cycles from a surface analytical point of view. During the initial cycling (0 to 40 cycles), the more nonpolar and low-polarity contaminants were removed from the surface of the rubber, exposing a more polar surface having lower water contact angles. This change in polarity, together with a continuing reduction of the loose particles on the rubber surface, produced a relatively rapid increase in the peel strengths of the seam specimens. Subsequently, after the bulk of the loose particles were removed (>40 cycles), further cycling resulted in a surface having more nonpolar characteristics and produced, consequently, a slight increase in the water contact angle. This increase in the water contact angle was attributed to exposure of greater surface

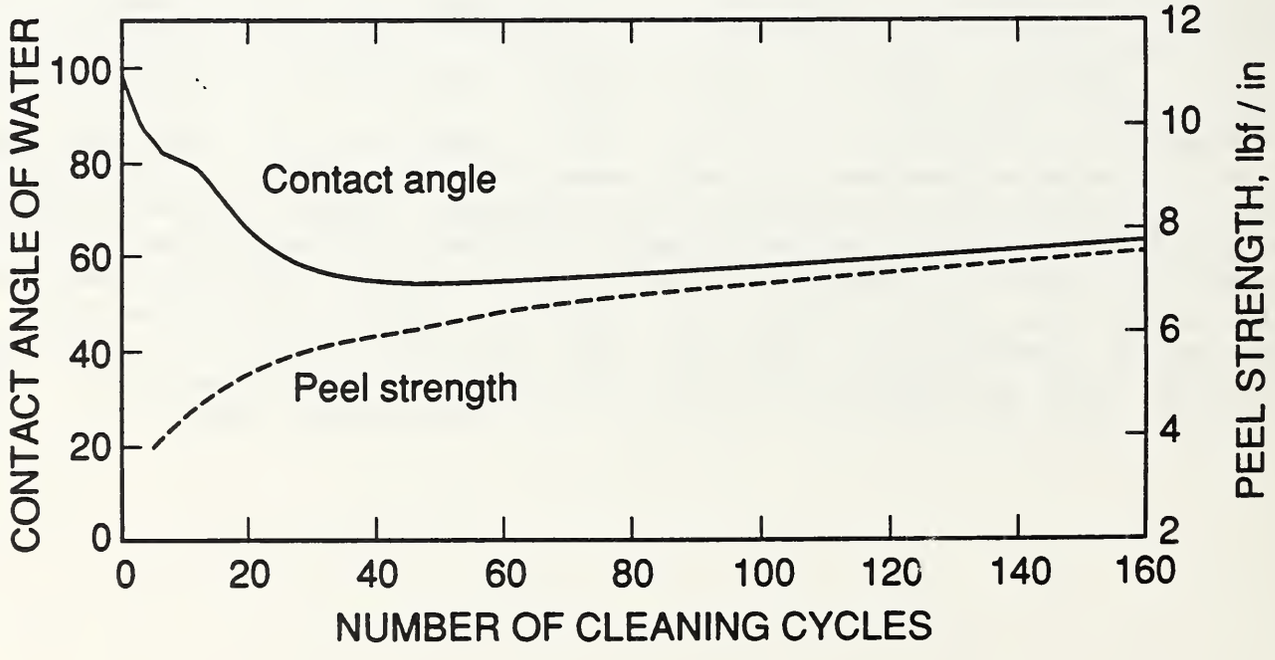

Figure 14. Relationship between peel strength and water contact angle as a function of cleaning cycles

area of the less polar EPDM rubber. This was accompanied by an increase in the peel strength, but at a relatively lower rate.

The data in Figure 14 suggested that contact angle of water could be used in the field to assess the condition of the EPDM surface after cleaning. Based on these data, after removal of the substantial amount of the loose surface particles and other contaminants, the water contact angle on the cleaned rubber should be greater than 55 degrees. However, use of such a criterion was not practicable, because a method to provide a good estimation of the contact angle on EPDM rubber in the field is not available.

It was known from the initial data obtained in the preliminary phase of the present study [9] that the spreading coefficient of water increased as the level of contamination of new unaged EPDM increased. In other words, if the surface was not well cleaned, the water contact angle would decrease more rapidly with time as compared to that obtained for a well-cleaned surface. The decrease in contact angle with time would be observed as a spreading of a drop of water placed on the rubber. If the spreading coefficient of water was used as a criterion of cleanness, there would be no need to measure the contact angle. Instead, the rate of spreading, or the change in size of the droplet on the rubber surface as a function of time, could be estimated, and allowable limits for a given period of time could be prescribed.

Preliminary tests of the spreading tendency of water on the surface of the specimens cleaned in this study showed that water was not a suitable liquid. In particular, using the size of the drop as an indicator, it was not possible to discriminate variations in the spreading of water for the specimens cleaned to varying degrees as a function of cleaning cycles.

Consequently, other liquids were investigated. Dimethyl formamide (DMF) was found to be sensitive to differences in surface condition achieved with the various cycles of cleaning. In particular, when the rubber was reasonably well cleaned (80 and 160 cycles), the size of a 7-8 mm drop of DMF was essentially unchanged after 5 minutes or more. When the number of cycles was 20 and 40, the drop spread to greater than 10 mm in about 5 minutes or less. Finally for the uncleaned and slightly cleaned surfaces (5 and 10 cycles), the drop spread spontaneously upon placing it on the surface. In addition, drops of DMF placed on the surfaces of the specimens cleaned for 80 cycles according to the various cleaning methods (Table 3) did not spread appreciably within 5 minutes. Although these results were obtained qualitatively, they were seen to be consistent for repeated tests.

Based on these limited data, as a preliminary step towards establishment of a simple test of the condition of the EPDM surface after cleaning, it is suggested that the "droplet test," using the spreading of DMF as just described, be used in the field on an experimental basis. This would provide a means for obtaining field data on the proposed test which has not yet been investigated in the field.

5. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

5.1 Summary

This study investigated the relative effectiveness of different cleaning methods used for preparing the surface of aged EPDM rubber for patching. The effectiveness of the methods was evaluated using tests of short-term strength and long-term creep rupture in peel, and surface analytical techniques, namely, scanning electron microscopy, Fourier transform infrared-attenuated total reflection spectroscopy, and contact angle measurements. A section of an aged ballasted EPDM membrane, cut from a roof after 10 years in service, was used in the study. Surface cleaning of the rubber was conducted using a mechanical abrasion device that repeatedly scrubbed a brush or wiped a cloth in a reproducible manner across the surface of the EPDM sample. Different surface cleaning methods were used including aqueous and solvent based solutions. The majority of these cleaning methods were based on procedures conducted in the field to prepare the surface of aged EPDM rubber before patching.

A summary of the key findings of the study is as follows:

1. The uncleaned, aged EPDM rubber surface was covered with contaminants whose outermost layer was nonpolar. The uncleaned rubber would not form a bond to an adhesive tape that has been used in practice to fabricate EPDM seams. After removal of some of the contaminants, joints having relatively low peel strengths could be formed with the tape.

2. As the number of cleaning cycles increased using nonpolar and low-polarity solvents, the peel strength of the joints increased. The water contact angle decreased (i.e., the nonpolar surface free energy component increased) with the first few cycles. After removal of the bulk of the contaminants due to a larger number of cycles, the contact angle showed a slight increase. This was attributed to an increase of the exposed surface area of the less polar rubber.

3. All cleaning methods provided aged EPDM rubber surfaces that formed joints with the tape whose peel strengths were comparable to bonds formed between solvent-based adhesives and new EPDM rubber. Statistically significant differences between some of the cleaning methods were found. Joints prepared by wiping with heptane, a method akin to the common field procedure of washing with unleaded gasoline, gave strengths that were among the highest measured. The strength of these joints were statistically higher than those prepared by cleaning the aged rubber using methods which involved water. Short-term strength and creep-rupture joints, prepared by tape-bonding the surface of the heptane-cleaned aged EPDM to a surface of well-cleaned new EPDM, failed in peel at the interface between the tape and the new rubber.

4. No relationships between contact angle and cleaning method were found. In particular, the methylene iodide contact angle varied only slightly as a function of cleaning method. This result implied that a number of cleaning methods would provide surfaces that would have similar wettability characteristics to nonpolar-solvent-based adhesives.

5. The FTIR technique could distinguish the uncleaned contaminated surface of the aged EPDM from those which were well-cleaned and/or coated during cleaning. Only minor differences between the FTIR spectra of the specimens cleaned using the various methods were observed.

6. SEM analysis was the only technique that distinguished particle-free surfaces from those which retained release-agent particles after cleaning. When particles were still present after cleaning, SEM analysis could not distinguish between the methods. Through SEM analysis, it was found that vigorous mechanical abrasion was the only cleaning method which provided a surface of the aged EPDM that was essentially free of release agent.

7. No relationships were observed between peel strength and the SEM, FTIR, and contact angle data for the surfaces cleaned using the various methods. However, contact angle measurements provided an explanation of the increase in peel strength as a function of cleaning cycles from a surface analytical point of view. This explanation was that the contact angle for water increased with larger numbers of cycles as the area of exposed (i.e., contaminants removed) EPDM rubber increased.

8. The rate of spreading, or the change in size over time, of a liquid droplet placed on the aged EPDM rubber was suggested as a means for setting a criterion for assessing the condition of its surface after cleaning. Dimethyl formamide (DMF) appeared to be suitable for this purpose as it was sensitive to differences in surfaces having various levels of cleanness. Water was not suitable. The use of a surface-cleanness criterion based on the rate of spreading, or change in the size, of a droplet of DMF placed on the aged EPDM rubber after its cleaning might be suitable for use in the field.

5.2 Conclusion and Recommendations

Based on the results of this laboratory study on cleaning a section of an aged EPDM rubber membrane, it was concluded that such membrane materials may be suitably cleaned for patching. The following recommendations are given for field cleaning of aged EPDM rubber membranes and assessment of the cleaned surfaces when patches or repairs are to be made:

1. All visible contaminants present on the surface should be removed and the dark black or bright white color, typical of well cleaned new black and white EPDM sheets, respectively, should be restored. This may be accomplished using solvent wipe or the detergent scrub techniques commonly used in practice. When using a solvent wipe technique, it is important to change cloths often as they pick up the contaminants from the rubber surface. In the case of the detergent scrub, it is important to rinse the brush often to remove contaminants picked up during the cleaning. When water is part of the cleaning procedure, the rubber surface should be dried (e.g., using a dry cloth) before solvent wiping.

2. As a preliminary step towards establishment of a simple test for assessing the condition of the EPDM surface after cleaning, the droplet test with dimethyl formamide (DMF) should be used on an experimental basis. This would provide a means for obtaining field data on the proposed test.

   In this regard, after cleaning, the surface condition of the EPDM rubber should be assessed by placing a droplet of DMF on it. This may be accomplished using an eye-dropper held vertically (e.g., about 90 degrees) about 5 mm above the rubber surface. The droplet should have an initial diameter of about 7 to 8 mm. If the surface is acceptably clean, the diameter of the droplet should not increase by more than 2 mm within a 5 minute time period. The diameter of the droplet may be estimated using a ruler.

3. It is necessary to use vigorous mechanical abrasion, for example, a wire brush attached to an electric drill, if it is desired to have a rubber surface that is essentially free of release agent before making a patch.

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APPENDIX A. SUMMARY OF THE MAJOR FINDINGS OF THE PRELIMINARY PHASE OF THE STUDY

In the preliminary phase, investigations were conducted [9] on the use of surface analysis techniques for ascertaining whether the surface of aged EPDM rubber is properly cleaned before patches are bonded to it. It was found that scanning electron microscopy (SEM), contact angle measurement, and Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy were found to be useful for general laboratory analysis of EPDM rubber sheets. Experimental procedures were developed for this purpose for use in the main phase of the study. The major findings were as follows.

A.1. Scanning Electron Microscopy (SEM)

Scanning electron microscopy analysis was able to differentiate between the amount of release agent on the surface for three degrees (slight, medium, and heavy) of contamination with a talc-like release agent. When the sample contained only a slight deposit, the micrograph showed areas of the rubber surface visible between particles of release agent. As the amount of release agent on the rubber surface increased, the areas of rubber surface that could be seen decreased.

A.2. Contact Angle

The preliminary results suggested that the water contact angle, the spreading rate of water on the EPDM rubber, and the polarity or the polar component of the EPDM rubber might provide useful indicators of the extent of surface cleanness of the rubber. For EPDM rubber surfaces with varying degrees of contamination with release agent, it was found that the cleaner sheets had greater contact angles and lower polarities.

A.3. Fourier Transform Infrared Spectroscopy (FTIR)

Investigations were limited to the development of a satisfactory experimental procedure for using FTIR for characterizing surface chemical compositions of EPDM membrane materials. It was found that FTIR-ATR using two reflections or less was useful for characterizing carbon black-filled EPDM roofing membrane material.

APPENDIX B. TEST METHODS

B.1 Test Methods

B.1.1 Peel Tests. T-peel test specimens, having dimensions of 150 x 25 mm (1 x 6 in.), were prepared using the cleaned rubber strips and the commercially available butyl-based tape (Figure B1). The dimensions of the bonded area delaminated in peel were 25 x 100 mm (1 x 4 in.). To prepare a test specimen, 25 x 100 mm (1 x 4 in.) and 25 x 150 mm (1 x 6 in.) pieces of butyl-based tape were adhered to the cleaned and uncleaned surfaces of an EPDM rubber strip (described in Section 2.2.2), respectively. The release paper was left in place on the surfaces of the tape not adhered to the EPDM strip. The resulting rubber/tape composite was placed in a laboratory press at 1.4 MPa (200 lbf/in.^{2}) for 5 minutes. After removal from the press, it was allowed to remain at ambient laboratory conditions (about 22°C or 72°F and 45-50% RH) for 7 days. Then, the release paper was removed from the two exposed surfaces of the butyl tape, and replaced with strips of fiberglass packing tape. The fiberglass tape was used to prevent excessive elongation of the specimens during peel testing.

As shown in Figure B1, the specimen was clamped in a universal testing machine such that one grip held only a section of fiberglass packing tape, while the other grip clasped a section comprised of the cleaned rubber strip, butyl-based tape, and fiberglass packing tape. When the specimen was subjected to peel delamination in the testing machine, the failure was interfacial between the cleaned surface of the rubber strip and the 25 x 100 mm (1 x 4 in.) piece of butyl-based tape. Peel tests were conducted at ambient laboratory conditions at a rate of 50 mm/min (2 in./min). The universal testing machine was equipped with microcircuitry that calculated the average peel strength.

B.1.2 Contact Angle Measurements. Contact angle measurements are made in various ways, but all essentially refer to the equilibrium of a drop of a liquid resting on a plane solid surface under the actions of three surface tensions: 1) liquid/vapor interface (γ_{lv}), 2) solid/liquid interface (γ_{sl}) and 3) solid/vapor interface (γ_{sv}). Figure 6 (in the main text) shows these interactions.

Essentially the use of contact angle in assessing wettability reduces to the fact that contact angle is a measure of the tendency for a given mass of liquid to spread and adhere to a solid; the smaller the contact angle, the greater the spreading tendency. Since contact angle measurement is very sensitive to the first 0.5-1 nm (5-10 Å) layer on the solid surface, its behavior reflects the composition of the very top layer of the surface.

Contact angles of a polar liquid (deionized, distilled water) and a nonpolar liquid (reagent grade methylene iodide) on cleaned and uncleaned, aged EPDM rubbers were measured using a goniometer. The goniometer was equipped with an eye piece and a protractor that

allow contact angles to be measured within 0.5 degree. A chromatograph microsyringe was used to place a droplet of 5 μl on the surface of the specimens. Preliminary experimentation indicated that the contact angles of water on "dirty" EPDM rubber surface decreased as a function of time after the droplets were placed on the specimen surface. For that reason, in this experiment, all contact angles were taken exactly one minute after the droplets were placed on the surface. Four contact angle values from droplets placed at four different locations on a 1 x 6 in. (25 x 150 mm) specimen were obtained for each liquid. As indicated earlier, one specimen taken from each of the two sets was used for contact angle measurement. Thus, for each surface preparation method, the value of contact angle of each liquid was the average of eight measurements.

Wettability parameters derived from contact angle measurements, namely: polarity, polar and nonpolar (dispersion) components, and total surface free energies of the cleaned and uncleaned EPDM rubber surfaces were also calculated using the harmonic mean equation [18]:

$$\gamma_{lv}\,(1 + \cos\theta) = \frac{4\gamma^d_l\,\gamma^d_s}{\gamma^d_l + \gamma^d_s} + \frac{4\gamma^p_l\,\gamma^p_s}{\gamma^p_l + \gamma^p_s}$$

where θ is the contact angle, γ^d_l and γ^p_l are the nonpolar and polar surface free energy components of the liquid, and γ^d_s and γ^p_s are the nonpolar and polar surface free energy components of the substrate. The polarity is the ratio between the polar component and the total surface free energy. The latter is the sum of γ^d and γ^p. γ^d_s and γ^p_s values were derived by substituting into the above equation the γ^d and γ^p values of water and methylene iodide, which were taken from the literature [18], and the measured contact angles of these two liquids on each specimen surface.

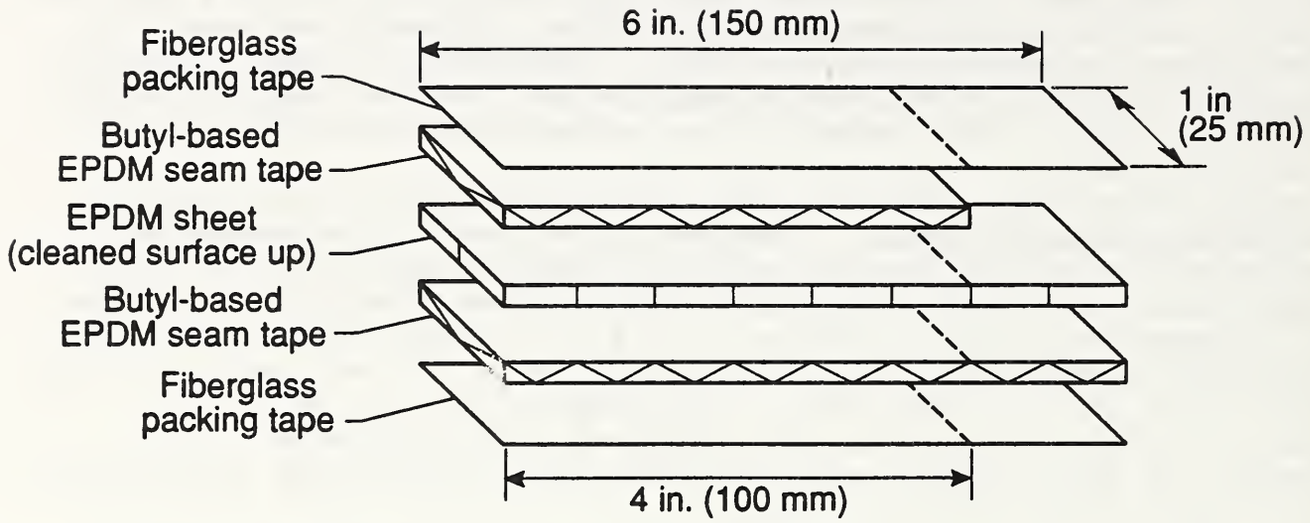
B.1.3 Fourier Transform Infrared Spectroscopic Measurements. Preliminary experimentation indicated that, for highly carbon-black-filled EPDM, Fourier transform infrared spectroscopy in the attenuated total reflection (FTIR-ATR) mode using single reflection produced the highest quality spectra. For that reason, unless otherwise stated, single reflection FTIR-ATR was used in this study. FTIR-ATR was carried out using an FTIR spectrometer and a single reflection ATR accessory. The sections, 15x15 mm, for FTIR-ATR analysis were cut from the same cleaned EPDM rubber strips used for SEM analysis. The surface of the specimen was pressed against a ZnSe ATR prism and the contact between the specimen and the prism was controlled by a mechanical device. Care was taken to ensure that approximately the same pressure was applied for all specimens. All spectra were taken at 4 cm^{-1} resolution using 100 scans and at an incident angle of 45 degrees. In the case of the cleaned, aged EPDM rubber, the FTIR-ATR spectrum was obtained using two reflections and a KRS-5 prism plate.

The FTIR spectrum of the contaminants, removed from the aged EPDM rubber surface using a spatula, was obtained using conventional transmission spectroscopy. A 1-mm thick KBr pellet was made and the spectrum was obtained using 16 scans and 4 cm^{-1} resolution.

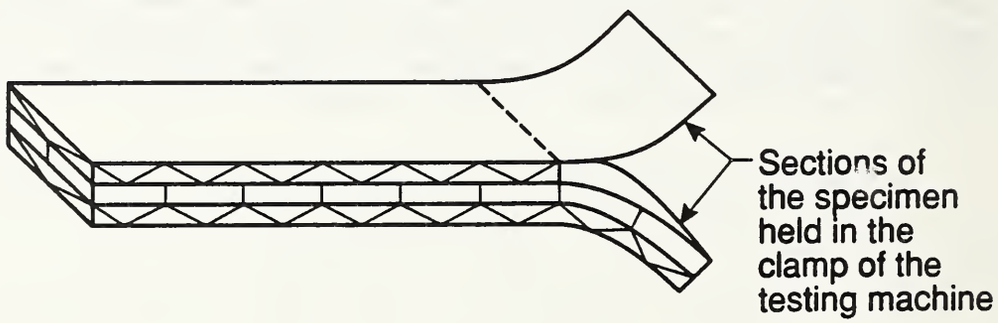
B.1.4 Scanning Electron Microscopy (SEM) Analysis. The sections for SEM analysis were cut from the cleaned rubber strips squares having about 8 to 10 mm (0.3 to 0.4 in.) sides. The cut pieces were adhered to SEM specimen mounting stubs with an epoxy adhesive. The mounted specimens were sputter coated with a nominal 20 nm (8×10^{-7} in.) gold conductive film to prevent surface electron charging during SEM analysis. The surfaces were examined in the SEM using an acceleration voltage of 10 kV at magnifications from x20 to x1000. Photographs were generally taken at x100 and x500 magnifications.

B.1.5 Creep-Rupture Tests. Creep-rupture tests were conducted according to the procedure described by Martin et al. [3]. Figure B2 illustrates the seam specimen configuration. Butyl-based tape, having dimensions of 25 x 100 mm (1 x 4 in.), was adhered between the cleaned surface of the aged EPDM rubber strip and that of a new (unaged) EPDM strip. The resulting specimen was placed in a laboratory press at 1.4 MPa (200 $lbf/in.^2$) for 5 minutes, whereafter it was kept at ambient laboratory conditions (about 22°C or 72°F and 45-50% RH) for 7 days.

For the given cleaning method, 14 replicate peel specimens were placed under a load of 4.2 N (0.94 lbf) at a temperature of 22 ± 1°C (72 ± 2°F) and a relative humidity of 45 ± 5%. The times under load over which the seam specimens completely separated were monitored electronically for each specimen. The separation caused deactivation of the electronic clock assigned to the specimen, and the recording of the time-to-failure [3]. The accuracy of the times-to-failure was within 1 second.

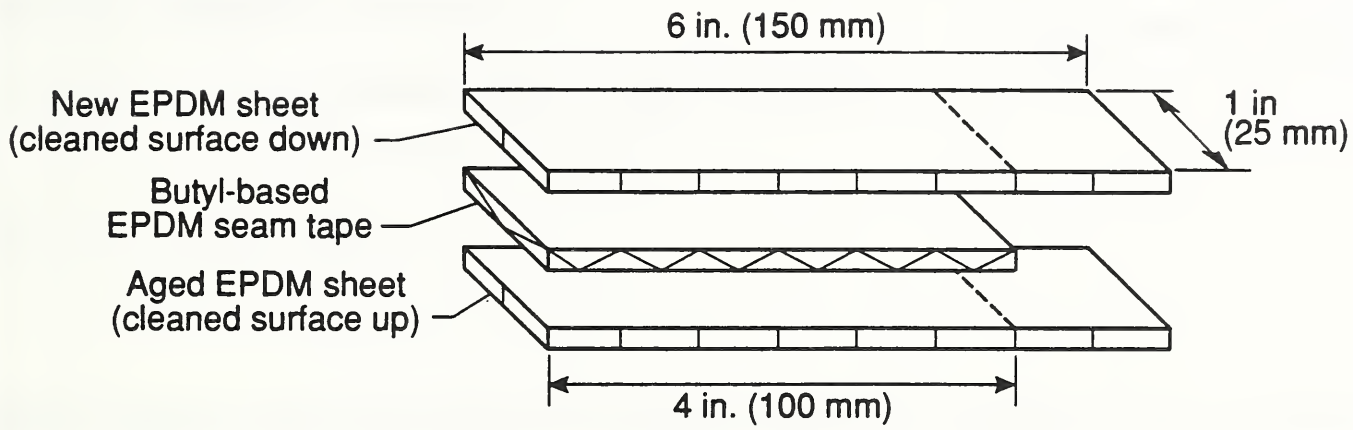


A. Exploded View of the Test Specimen

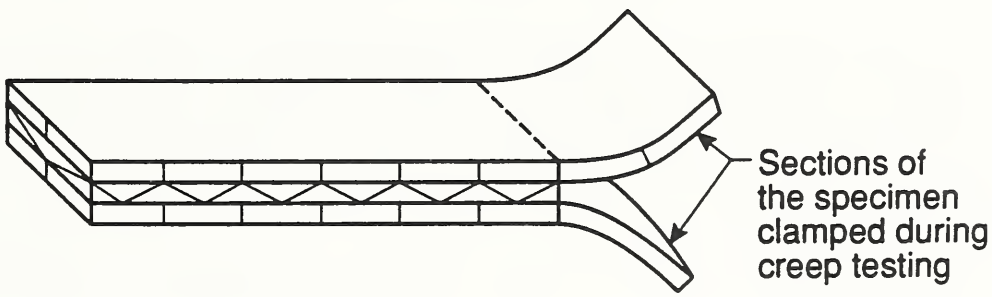


B. View of the Completed Test Specimen

Figure B1. Configuration of the test specimen used for the short-term T-peel strength measurements



A. Exploded View of the Test Specimen



B. View of the Completed Test Specimen

Figure B2. Configuration of the test specimen used for the long-term creep-rupture measurements

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This study assessed the relative effectiveness of different surface cleaning methods used for preparing the surface of aged EPDM membranes for patching, and recommends procedures for use in the field. The effectiveness of the methods was evaluated using tests of short-term strength and long-term creep rupture in peel, and surface analytical techniques, namely, scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and contact angle measurements. A section of an aged, ballasted EPDM membrane, sampled from a roof after 10 years in service, was used in the study. The majority of the cleaning methods evaluated was selected based on a review of procedures used in the field to prepare the surface of aged EPDM rubber before patching.

Cleaning the aged EPDM rubber surface removed the bulk of the contaminants and resulted in an increase of the exposed surface area of the EPDM rubber. This resulted in a decrease in the rubber's wettability by water, and a concomitant gain in the peel strengths of joints made with the cleaned rubber. All cleaning methods used in the study provided aged EPDM rubber surfaces that formed joints having peel strengths comparable to those of seams formed in the field between solvent-based adhesives and new EPDM rubber. Short-term strength and creep-rupture joints, prepared by tape-bonding the surface of heptane-cleaned aged EPDM to a surface of well-cleaned new EPDM, failed at the interface between the tape and the new rubber. But, no relationships between contact angle and cleaning method were found. In particular, the contact angles measured using methylene iodide varied only slightly as a function of cleaning method. The FTIR technique could distinguish the uncleaned surface of the aged EPDM from those which were well-cleaned and/or coated during cleaning. No major differences between the FTIR spectra of the specimens cleaned using the various methods were observed. SEM analysis was the only technique that distinguished particle-free surfaces from those which retained particles after cleaning. The rate of spreading of dimethyl formamide (DMF) droplets on the surface of the aged EPDM rubber was found to relate to the degree of surface cleanness.

Based on the results of this laboratory study on cleaning a section of an aged EPDM rubber membrane, it was concluded that such membrane materials may be suitably cleaned for patching. It was recommended that: (1) a number of cleaning methods may be used to prepare the surface of aged EPDM rubber membrane material before patching, and (2) the change in size over time of a droplet of DMF, placed on the aged EPDM rubber after cleaning, be used for preliminary assessment of the condition of the cleaned surface.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

aged EPDM membranes; cleaning methods; contact angle; creep rupture; FTIR; low-sloped roofs; peel strength; roofing; scanning electron microscopy; seams; surface analysis, surface preparation methods; wettability

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