

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 30 APRIL 98	3. REPORT TYPE AND DATES COVERED Interim 26 APRIL 96-26 MARCH 98
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4. TITLE AND SUBTITLE PROPOSAL TO DEVELOP MULTI-FUNCTIONAL COMPOSITES FOR SENSOR AND ACTUATOR APPLICATIONS	5. FUNDING NUMBERS N00014-95-C-0426
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11. SUPPLEMENTARY NOTES Report prepared in cooperation with Rutgers University	
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12a. DISTRIBUTION/AVAILABILITY STATEMENT This report contains no proprietary information and may be made available publicly.	N/A
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13. ABSTRACT (Maximum 200 words) The intent of this research was to develop a procedure to produce piezoelectric fiber composites for use in ultrasound transducers, under water hydrophones and preliminary actuator designs. All facets of the proposed research were successfully addressed with performance results exceeding expectations. Ultrasound transducers have been built for a range of frequencies that are equal to the best "dice and fill" composite transducers but without any lateral wave interference providing clean signals up to 40 MHz. Recently a 20 MHz transducer was built which compared with the best results seen previously. Before the end of this STTR work was completed, products of this technical breakthrough were commercialized and are the subject of an exclusive supply agreement with the largest manufacturer of NDE equipment in the U.S. Hydrophones were constructed using ACI's PZT fiber composite transducers which compare favorably with the best commercial units and are an order of magnitude more sensitive than state of the art injection molded transducers. Discussions with Northrop-Grumman are underway for a Phase III effort to develop hydrophone/sonar transducers for the next generation submarine. The first test actuators were constructed using ACI's PZT fiber performance rivalling the best devices available	
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14. SUBJECT TERMS PZT, Transducers, Hydrophones	15. NUMBER OF PAGES 30
	16. PRICE CODE N/A

17. SECURITY CLASSIFICATION OF REPORT None	18. SECURITY CLASSIFICATION OF THIS PAGE None	19. SECURITY CLASSIFICATION OF ABSTRACT None	20. LIMITATION OF ABSTRACT UL
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DISTRIBUTION STATEMENT A
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19980430 036

ONR STTR Second Year Interim Report

Progress on Contract Number N00014-95-C-0246 is divided into 5 sections - Fiber Manufacturing Optimization, Composite Preform Manufacturing, Preform Sintering, Composite Coupon Evaluation, Prototype Devices, and Commercialization. A copy of the first year progress report is attached as an Appendix for reference purposes.

1. Fiber Manufacturing Optimization

1.1 Spinning Machine Modifications and Improvements

As noted in the first year progress report, a second set of washing stations significantly improved the purity of the fiber. In addition, a continuous hot water washing system (up-graded from a batch hot water system) also improved the fiber cleanliness. The installation of the in-line sizing bath also greatly improved the green fiber's handleability. The application of a proprietary sizing formulation to the green fiber is now standard procedure in VSSP fiber production. This sizing aids in the textile processing, despooling, weaving and braiding, and also helps to minimize the cross sintering between the individual filaments. All of these spinning machine improvements - the washing stations, continuous hot water washing, in-line sizing bath represent approximately \$15,000 from the contract in components and set-up labor.

1.2 Standard VSSP Filaments

The VSSP PZT filament diameter and tow size have been standardized for production, based on the spinnerettes available in-house. The following table describes the standard PZT filament diameters (green and fired), number of filaments per tow and the current production rates.

Fiber Designation	Spinnerette Hole Diam., μm	Green Filament Diam., μm	Fired Filament Diam., μm	Number of Filaments per Tow	Production Rate, kg/hr.	Production Rate, meters/hr.
1	100	25	15	790	0.63	1500
2	150	50	30	100	0.95	2000
3	225	90	70	44	1.62	2000
4	445	150	120	100	3.10	1200

The green fiber production rates for the four standard VSSP PZT fibers have been increased to 0.63 (1500), 0.95 (2000), 1.62 (2000), and 3.10 (1200) kg/hour (m/hour) for VSSP fibers 1, 2, 3 and 4 respectively. The majority of the data and testing has been done on the VSSP PZT #1 fiber, however the larger diameter filaments are beginning to become more important, particularly in the actuator applications.

VSSP PZT fiber is now available in PZT-5H type (DOD-Type VI), in which the majority of the work has been done. However, other materials (from other powder vendors) have been

spun and made into successful transducers including EC64, (DOD-Type I), BM740, EC65 (DOD-Type II) and EC76 (DOD-Type VI).

2. Composite Preform Manufacturing

The composite preform manufacturing methods discussed below - braided rope, woven carpet, plain weave and unidirectional - were designed by and are carried out at ACI. Section 2.4 describes the composite architectures designed and constructed in collaboration with Rutgers University's, Center for Ceramic Research.

2.1 Braided Rope Preforms (Ultrasonic Transducers)

The braided rope composite preform, as described in the first year-end report, is the method for producing 1-3 type composites with 30-40 vol% PZT for disc-shaped transducers. For Morgan Matroc PZT-5H (#1 fiber, 790 filaments/tow), 1200, 5000 and 10000 tow bundle preforms sinter to give 0.75", 1.25" and 2" diameter transducer blanks. These preforms are then potted, diced into wafers, electroded and poled. Target markets for these preforms are ultrasonic transducers for industrial and medical imaging, and hydrophone and sonar applications.

2.2 Woven Carpet Preform (Hydrophones)

The woven carpet (or pile fabric) composite preform generates a larger area 1-3 type composite. Woven carpets 4" x 4" green sinter to 3"x 3" transducer blanks. The carpets have lower PZT volume fractions, typically 10 - 15 vol% through the thickness. These lower volume fraction preforms are targeted for large-area hydrophone applications.

2.3 Unidirectional and Plain Weave Preforms (Actuators)

Unidirectional and plain weave preforms are also produced for 1-3 type and 3-3 type composites. The fiber tows are strung up on the loom and weft fiber (perpendicular to the unidirectional tows) is used at a predetermined spacing. For unidirectional preforms, the weft fiber is spaced about 5 inches apart (longer than the firing setters) to allow handling of the preforms prior to sintering. The weft fiber is then cut off after binder burnout and before sintering. Figure 1 illustrates the flexibility of the sintered VSSP PZT fiber (PZT-5H, #3 fiber, 70 micron filament diameter). These unidirectionals are targeted for planar actuator applications.

2.4 Composite Preform Architectures Produced at ACI and Rutgers University

The plain weave preform architecture was evaluated in two designs - spiral composite (1-3 type) and laminate (3-3 type). For the spiral composite, the plain weave fabric is rolled tightly and tied around the circumference. The preform is then treated similarly to the braided rope preform. The laminate is produced by stacking many layers of plain weave fabric on top of one another and sintering the stack.

3. Preform Sintering

ACI's lead-atmosphere-controlled furnace, with a 1.25 cu. ft. firing chamber, is fully

operational. This furnace was required to meet the growing demand for VSSP PZT fiber composites. Rutgers University was not equipped to handle the pre-production quantities needed to carry out the program. ACI allocated approximately \$12,500 from the contract for the kiln, controller, refractories and set-up labor. Having the sintering in-house ensures the consistency of the sintered product as commercialization is approached.

The 1.25 cu. ft. firing chamber allows for sintering of up to 18 rope preforms or 14 carpet preforms per firing run and the kiln cycle is 42 hours (three runs per week). Different firing procedures are used for the braided rope and woven carpet and unidirectional preforms, as discussed below. Kiln furniture and PbO-vapor containment methods are all in-house developments from both materials and component design stand-points, and appear to be innovations for processing PZT materials.

3.1 Binder Burnout

All composite preforms are first subjected to a binder burnout heat treatment, as excess carbon present during the sintering will reduce the PZT and reduce (or eliminate) the piezoelectric properties of the sintered composite preform. Binder burnout is performed by slow heating in air to 500 - 550 °C and hold for 2 - 8 hours to remove the cellulose binder and sizing compounds in the fiber. Burnout is performed in the same crucibles or firing setters as sintering, as direct handling of the burned-out preforms is not possible.

3.2 Braided Rope Transducer Preforms

Braided rope preforms are burned out and sintered, buried in a bed of coarse PZT sand (-20, +60 mesh). The sand is made using a proprietary granulation method developed in-house for this project. The firing crucibles are 99.5% alumina (ACI formulation) and drain-cast using existing tooling. The top lip and crucible lids are surface ground to provide a tight fit and prevent PbO vapor from leaking out of the crucible during sintering. So long as the crucibles do not crack during sintering, the sand is reusable. The coarse sand provides sufficient PbO over-pressure to ensure that the sintered fiber has the correct lead content and piezoelectric properties.

3.3 Woven Carpet, Plain Weave and Unidirectional Preforms

The carpets, plain weaves and unidirectional composite preforms are sintered slightly differently. For these preform architectures, the green preform is placed on a zirconia setter and burned out using a similar firing schedule as the one used for the braided rope preforms. The zirconia setters were developed and manufactured in-house specifically for sintering the VSSP PZT fiber. No setting sand is needed to keep the fiber preforms from sticking to the zirconia firing setters, as it is with the standard alumina setters. This development and use of zirconia firing setters is also an innovation in the processing of PZT materials. The setter is then transferred to a 99.5% alumina firing box. As with the crucibles for the braided rope preforms, the firing boxes have machined mating surfaces for a tight seal to prevent PbO vapor from leaking out of the firing box. Present tooling allows for firing up to 4.5 x 4.5 inch preforms which sinter to about 3.25 x 3.25 inch sintered composite blanks.

The source powder for this firing method is a mechanical mixture of PbO + ZrO₂ powders, with excess zirconia (above the stoichiometry of lead zirconate) to prevent the PbO

from running as it melts. The amount of source powder required for sufficient lead content in the sintered fiber composite preforms was determined experimentally and is dependent on the volume of the firing box. Each firing box (or crucible) is placed inside a second large refractory box (with diamond ground mating surfaces). This double-shelled firing system ensures the containment of the lead oxide vapor during sintering.

4. Composite Coupons

Coupon evaluation of VSSP PZT fiber composites was performed at Rutgers University's Center for Ceramic Research. These coupons were made from the VSSP PZT fiber composite preforms described in Section 2 of this report. The preforms are discussed individually below.

4.1. Braided Rope Preforms

After sintering, the preforms were potted in Spurr's epoxy (Earnest Fullman Co.), sliced into discs, electroded with an air-drying silver paint, and poled using the Corona poling technique at Rutgers University. Figure 2 are SEM micrographs of individual filaments (#1 fiber) of PZT-5H, EC64 and EC76 materials. Figure 3 is an SEM micrograph of a cross-section of the braided rope VSSP fiber composite transducer prior to electroding. Note the random array of PZT fibers in the cross-section. Table I illustrates the nominal properties of the braided rope VSSP PZT-5H (#1 fiber) and EC64 (#1 fiber) composites for ultrasonic transducers and sonar applications.

4.2. Woven Carpet

Similarly, after sintering, the preforms were potted in Spurr's epoxy, lapped flat and diced into transducers 1 cm on an edge, electroded and poled for evaluation. Figure 4 is an SEM micrograph of one of these carpet fiber composite preforms. Table II illustrates the nominal electromechanical properties of this composite preform architecture (PZT-5H, #1 fiber). Note the volume fraction is lower than the braided rope composite preform method. This lower volume fraction finds application in hydrophones, particularly for the ease at which large-area 1-3 composite devices can be produced.

4.3 Plain Weave (Spiral, Laminate)

Figure 4 also shows a cross-section of a spiral composite transducer. The nominal properties of the spiral and laminate composite architectures also appear in Table II. The anisotropic nature of the laminates, that is the relatively poor through-thickness properties relative to the properties in plane, is a result of the poor connectivity of the fiber through the thickness. This will be overcome by decreasing the thickness of the composite and reduce the number of layers of fiber. The spiral architecture was not chosen for development at this time due to the extra processing steps presently required (hand weaving) to produce viable candidate structures. Once automated textile machinery is in use, this method will be revisited. The laminate architecture and the unidirectional architecture are the basic designs for the planar actuators. This portion of the program was put off onto another (separately funded) research program due to the amount of effort required to bring the technology to the prototype level.

5. Prototype Devices

5.1 Ultrasonic Transducers - Krautkramer Branson

ACI has been working with Krautkramer Branson (Lewistown, PA) to commercialize ACI VSSP PZT fiber composites for ultrasonic transducers. Figures 5 and 6 are typical pulse-echo and impedance spectrum responses for a braided rope preform (VSSP PZT-5H, #1 fiber), at 1 MHz. The fiber composite transducer had the same sensitivity and bandwidth as their current "dice-and-fill" transducers. However, the VSSP PZT fiber composite transducer has no lateral wave interference up to 40 MHz. This significantly increases the design flexibility of the VSSP PZT fiber composite transducer over the current state-of-the-art "dice-and-fill" transducers. For higher frequency operation, such as 3.5 and 5 MHz, other PZT formulations (EC64 and BM740) were spun and made into braided rope preforms, also yielding the same sensitivity and bandwidth as their "dice-and-fill" counterparts, again with no lateral wave interference. Transducers have been built and tested for operation at 20 MHz with encouraging sensitivity and bandwidth. The cost of the VSSP PZT fiber composite preforms is dramatically lower than the "dice-and-fill" composites, providing significant cost savings on transducer manufacture. The finer feature size of the VSSP PZT #1 fiber also is an advantage over the "dice-and-fill" technique.

5.2 Hydrophones - Wilcoxon Research

ACI contracted Wilcoxon Research Inc. (Gaithersburg, MD) to test the braided rope fiber composite preforms in their standard H505L internally amplified hydrophone device. ACI produced a drop-in replacement composite preform (VSSP PZT-5H, #1 fiber) for their standard monolithic PZT core (thick-walled tube geometry). Without design optimization (impedance matching, prestress level and PZT volume fraction) the sensitivity of the H505L hydrophone with the VSSP fiber composite core had a sensitivity of -170 dB re 1V/ μ Pa (with a 10 dB internal amplifier) comparable to their current technology. ACI contracted Wilcoxon to manufacture two H505L hydrophones, one of which accompanies this report.

5.3 Hydrophones - Northrop Grumman

ACI and Northrop Grumman (Annapolis, MD) have a MOU to develop ACI's woven carpet VSSP PZT fiber composite preform for hydrophone applications after the completion of this STTR. ACI will deliver a double-face composite hydrophone blank for Northrop Grumman evaluation in their testing tank.

6. Commercialization (Ultrasonic Transducers)

Presently ACI is in the final qualification for the sale for its braided rope preforms for ultrasonic transducers with Krautkramer Branson (KB), the largest supplier of NDT equipment in the U.S. KB also is the leader in composite transducers manufacture using the "dice-and-fill" method. ACI's braided rope composite preform (#1 fiber, in specified material formulations) provides Krautkramer Branson with significant cost-savings over their current manufacturing

route. ACI will sell two standard braided rope fiber composite preform sizes (50 feet/year for each material initially) to KB starting in the next 2-4 months.

Hydrophones (Northrop Grumman and Wilcoxon Research) sonar and medical transducers are later down the development scale (6-12 months) and require additional funding to implement.

7. Summary

ACI's VSSP PZT fiber is approaching commercialization. The nearest term market is transducers for nondestructive evaluation. Sales of VSSP PZT fiber composite will begin in 2-3 months to Krautkramer Branson. Development of transducers for the medical market are approximately 4-6 months away from first prototypes. Hydrophones and sonar device prototypes are 6-12 months away and are expected to be the subject of a Phase III effort. Naval applications are the first target market, with civilian markets later. The VSSP patent has been granted. A number of the processing innovations developed under this program, such as the materials used in the processing of PZT, may be patentable. ACI will investigate the patentability of the production of VSSP PZT fiber composites.

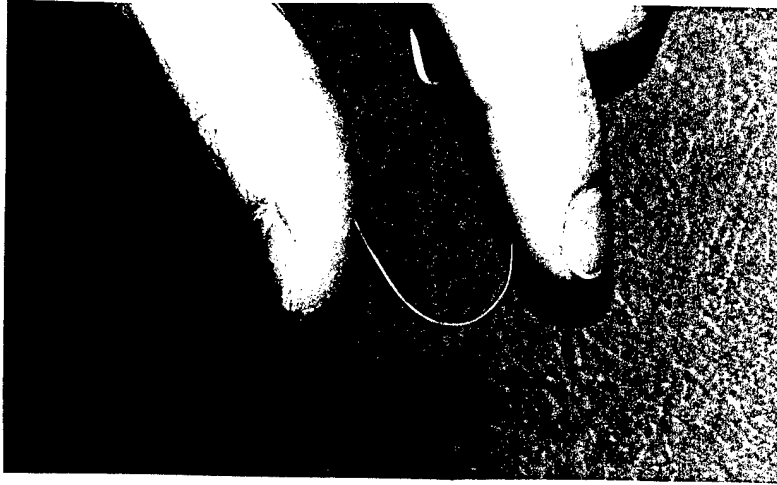


Figure 1. Demonstration of the flexibility of a single sintered VSSP PZT filament (PZT-5H, #3 fiber, 70 micron filament diameter).

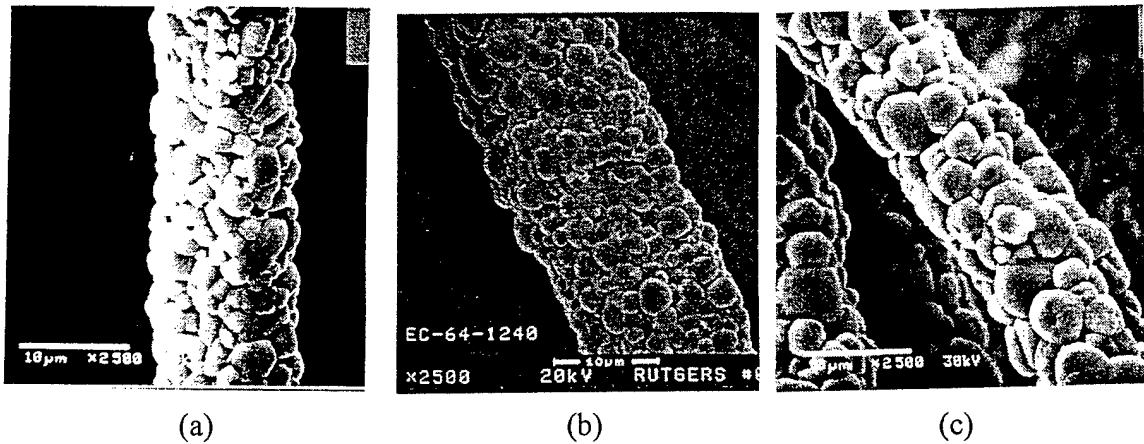


Figure 2. SEM micrographs of sintered filaments. (a) PZT-5H, (b) EC64, (c) EC76

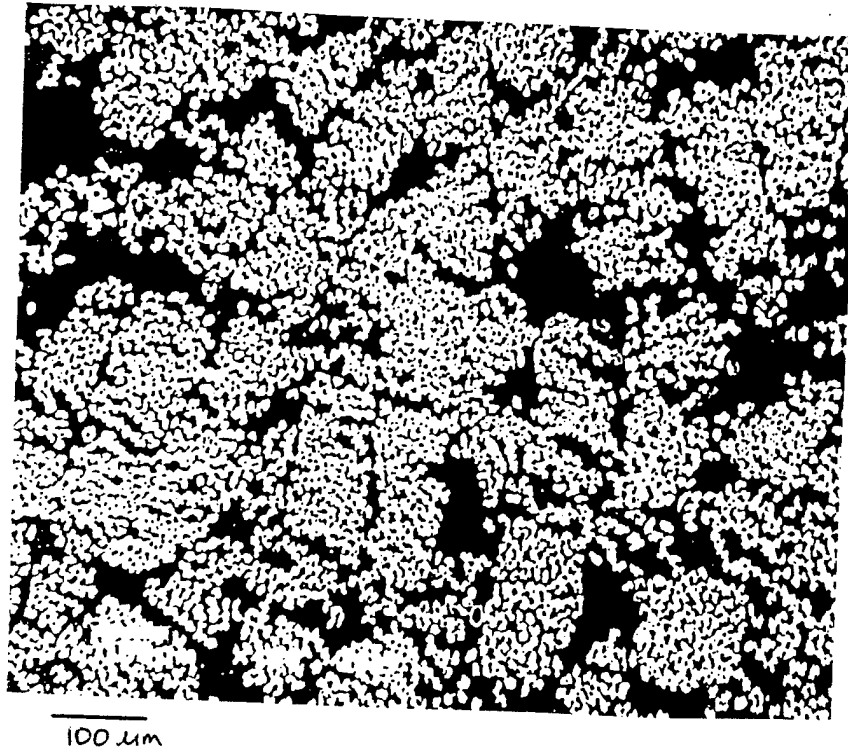


Figure 3. SEM micrograph of the cross-section of a typical braided rope preform. Spurred epoxy filled, PZT-5H, #1 fiber.

Table I. Nominal electromechanical performance of VSSP PZT fiber composites made from the braided rope manufacturing method. VSSP #1 fiber, PZT-5H, EC64 and BM740 materials.

Property	PZT-5H	EC64	BM740
Vol% PZT	35	40	35
Dielec. Constant	700	332	70
loss, %	2.14	0.68	0.52
d_{33} , pC/N	375	125	60
g_{33} , mVm/N	67	42	97
k_t	0.61	0.38	0.36
k_p	0.29	0.24	0.23
Z, Mrayls	9.7	11.0	5.2

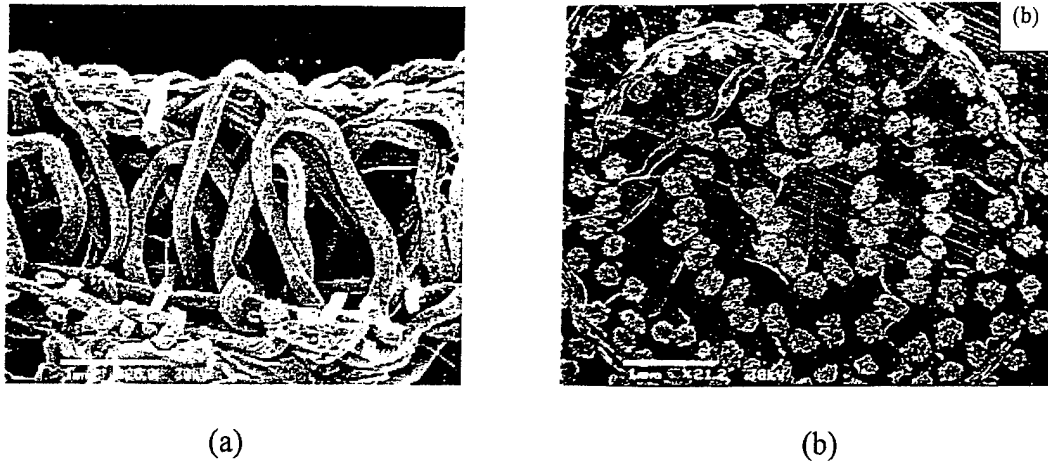


Figure 4. SEM micrograph of (a) sintered woven carpet preform, and (b) potted spiral composite

Table II. Nominal electromechanical performance of spiral, woven carpet, and laminate made at Rutgers University and ACI using VSSP PZT #1 fiber (PZT-5H).

Property	Spiral	Woven Carpet	Laminate, poled through thickness	Laminate, poled parallel to weft fiber direction
Vol% PZT	32	12	37	43
Dielec. Constant	400	100	130	495
d_{33} , pC/N	280	150	80	250
g_{33} , mVm/N	70	160	70	57
loss, %	3.3	3.1	1.9	4.5

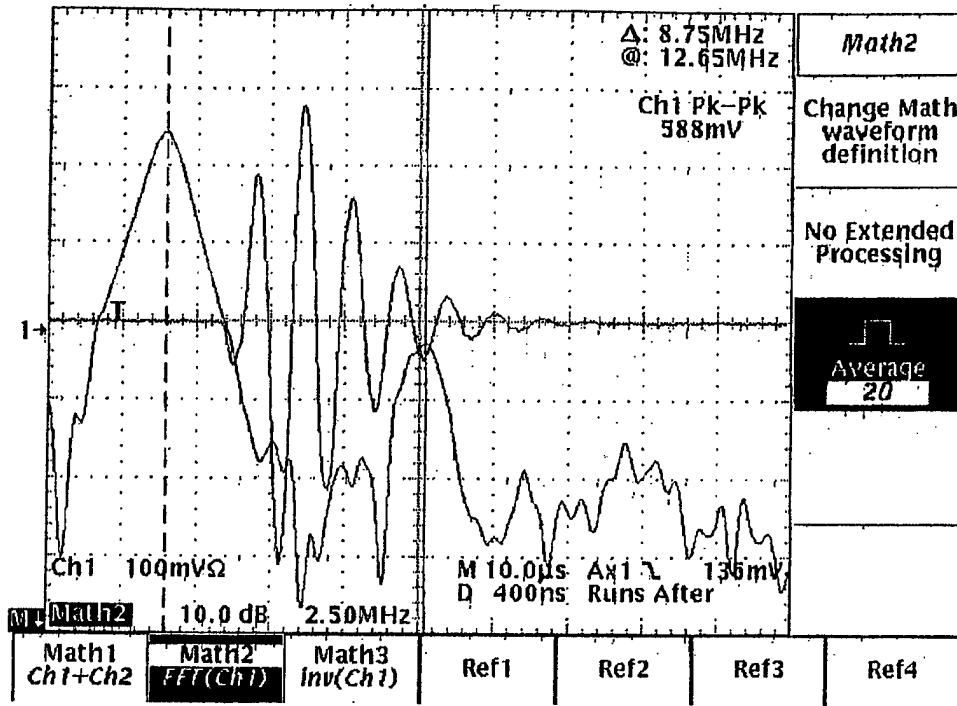


Figure 5. Typical pulse-echo response of transducers made from VSSP EC64 fiber composites. 1 inch water path to a steel block. Frequency was 2.5 MHz.

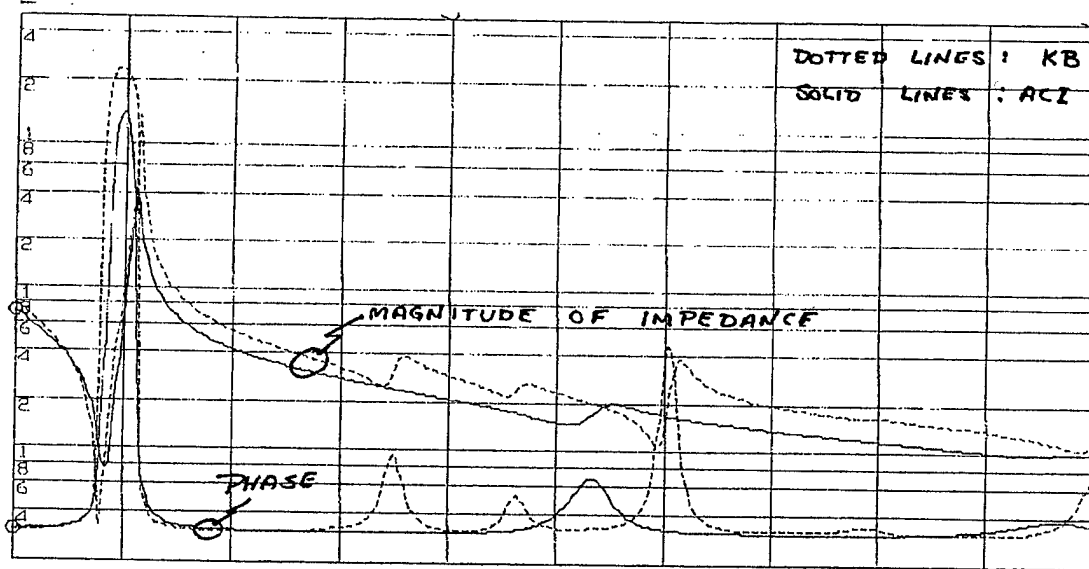


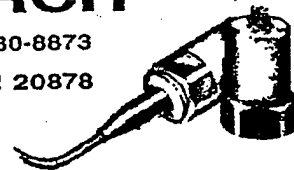
Figure 6. Typical electrical impedance comparison of transducers made from VSSP EC64 fiber composites (solid lines) to “dice-and-fill” transducers (dotted lines). The test was run up to 40 MHz with no lateral wave interference in the VSSP fiber composite transducer.



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PIEZOELECTRIC VIBRATION INSTRUMENTATION

January 5, 1998

Dr. Jonathan D. French
Director of Research
Advanced Cerametrics, Inc.
245 N. Main Street
Lambertville, NJ 08530

Dear JD:

I am pleased to report that the H505L hydrophones, employing your piezoelectric materials, have recorded a sensitivity on the order of -170 dB re $1\text{V}/\mu\text{Pa}$. This is quite encouraging, given the fact that these results are comparable to those sensors utilizing bulk piezoelectric materials. When the other attributes of your material are included, I think the potential exists for making an impact in this industry. Wilcoxon Research, Inc. is interested in participating in your continued work.

To assess the hydrophone completely, it will be necessary to conduct more tests. A hydrophone is only as good as its signal to noise ratio. Electrical testing and measurement of circuit noise needs to be conducted. Furthermore, we observed and measured a very low capacitance on your material. This too needs to be investigated, along with other mechanical properties since it will have ramifications on the overall noise.

Fax Ref. #: 98-0302-1

Date Sent : _____

Time Sent : _____

**Krautkramer****Facsimile Transmission**

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ATTN: J. D. French
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FROM: Paul A. Meyer

(717)242-0320, Ext. 237

DATE : March 2, 1998

Page 1 of 7

SUBJECT: Fiber piezocomposites

Hi J.D.,

Attached are performance characterizations of finished transducers utilizing fiber piezocomposites. Performance is very similar to the "dice-and-fill" unit. We consistently measure capacitance values lower than expected. I believe that the higher area-to-volume ratio of the fiber results in altered dielectric properties. This is not necessarily bad so long as it is repeatable. We will have a better measure of repeatability when we test Batch 2.

Also, it appears that the larger diameter (> 1 inch) has a lower volume fraction than the smaller samples. Is it more difficult to compress the larger diameter samples?

I've made a 20 MHz disk which performs well (I have nothing to compare it to). It should be in a transducer by Wednesday. The impedance spectrum is attached.

Will you be attending the ONR review this Spring? That might be a good time to get together and review the program status. Let me know.

Thanks,
Paul

EXHIBIT 2

ONR Phase II STTR first year progress report

ACI's first year effort on the Phase II STTR for production of piezoelectric fibers and devices can be broken down into 3 major areas: 1) fiber spinning production, 2) firing, 3) prototype device production and testing.

1. Fiber Spinning Production

1.1. Pilot Production Machine Upgrades

ACI's pilot-scale production spinning machine is now fully operational (see Figure 1). Production rates are presently 1-1.5 pounds of green PZT fiber per day (3 - 5 pound/week). The introduction of in-line sizing has improved the fiber quality and handleability significantly. In addition, an extra set of wash drums, hot water heater and stripper guides for better fiber washing has improved the green fiber cleanliness, strength and handleability. The current winder for fiber take-up uses 6" diameter tubes, which is an inconvenient size. A second winder is being rebuilt to take 3" diameter tubes, a composite industry standard size. This rebuilt winder also will have a better take-up speed control and will be incorporated into the spinning line in the next quarter of the program. A spool of the standard PZT fiber (790-filament, ~1500 meters in length) is shown in Figure 2.

1.2. Green Fiber Characterization

Green fiber characterization (breaking load, elongation, denier, sizing content) tests are performed at North American Fibers Inc. Typical breaking strengths are 400 - 800 grams for the standard 790 filament tow, with a 1 - 3% strain at failure (Table I). On unsized fiber, Table I illustrates the importance of the rayon additive amino-2 propanol in the spin mix. The 961024 fiber had the additive, whereas the other unsized fiber lot did not. The sized fiber lots did not have the additive, to isolate the strength enhancement of the sizing. The small measured sizing content on the unsized fiber is likely a result of residual spinning chemicals present. The added wash station and increased wash water capacity will reduce this. The PVA+PEG sizing gave the highest breaking strength, likely due to a high concentration of sizing relative to the other, commercial sizings. The PVA+PEG sizing did not give a lubricous fiber, however, whereas the Sonostat gave the most lubricous fiber. Future fiber lots will contain both the rayon additive and the Sonostat sizing. The green strength is sufficient for the hand weaving and braiding currently being used for preform fabrication but insufficient for commercial textile processing. Experiments are planned to increase the fiber strength (through ceramic solids loading, rayon additives and finish application chemistry) for textile machinery handleability. Minimum handleability, defined by breaking strength, breaking elongation and lubricity, will be specified by the particular textile machine of interest or textile fabricator (e.g. Fiber Materials Inc.). These experiments will go on during the next 2 quarters of the program.

1.3. Multiple Powder Vendors

Several vendors' PZT powder are presently being spun. Navy VI, 5H-type, materials, Morgan-Matroc, Edo and Sensor Technology Ltd. powders all perform well in our spinning production. Once sintered product from the various vendors meets acceptable piezoelectric performance standards, such as $d_{33} \geq 300$ for a 40 vol% PZT composite, multiple PZT powder vendors will be possible for PZT fiber production.

2. Firing

2.1. Sintering Schedule Optimization

At present, the sintering schedule for the PZT fiber is 1285° C for 10 minutes. This has given satisfactory piezoelectric properties, but likely at the cost of fiber strength. The average grain size achieved for this sintering regime is 8-15 microns (cf. the fired fiber diameter is in the range of 15-25 microns). Since the validation of the production technique has been achieved with over-firing the fiber, optimization of the firing schedule is now underway. By decreasing the temperature (and time), the grain size in the sintered product and the lead volatility during firing will decrease. The optimum grain size for high fiber strength and high piezoelectric properties will be determined (estimated at 2-3 microns). Sintering studies in the temperature range of 1100 - 1250° C for 5 - 30 minutes are underway to finalize the sintering for the fiber from Morgan Matroc PZT-5H powder.

Current issues to be addressed include a discrepancy in piezoelectric properties between bulk discs which were produced from fiber and discs produced from the raw powder (see Table II). The apparent decrease in properties (especially d_{33} and dielectric constant) would indicate a change in composition as a result of the spinning process or a lower firing temperature required for the fiber. Chemical analysis of the raw powder, green fiber and sintered fiber is currently underway to determine any changes in composition. Microstructural evaluation of the discs are also currently under investigation.

2.2. On-Site Sintering Capability

ACI's PZT controlled-atmosphere sintering furnace (elevator kiln type) has been installed and is on-line (Figure 3a). Precautions to handle lead oxide fume, in the event of a crucible leak or fracture, have been installed. The material will be fired in a double-shelled crucible system to minimize lead loss during firing (Figure 3b). Individual sealable crucibles with excess source powder will be used for firing the composite preforms. In addition, a vented hood with multiple filters for handling the PZT packing powder has been installed (Figure 4). On-site firing capability will occur early in the next quarter of the program.

3. Prototype Production Development

3.1. Fiber Preform Manufacturing

3.1.1. Braided Rope Method

Figure 5 illustrates this production route for 1:3-type composite devices. For traditional ultrasonic transducers and hydrophones, green PZT fiber is gathered into straight bundles and fiber is braided around the bundle to form a thick rope-like structure (0.875" and 1.5" diameter, 12" - 15" in length). For 0.875" diameter ~800 tows of 790 filaments/tow are bundled, and for 1.5" diameter, ~1200 tows are bundled for each braided rope fiber preform. The composite preforms are sliced into 2" lengths and sintered standing on end in a bed of sacrificial coarse PZT powder. After sintering, the preforms are embedded in epoxy, and sliced into transducer discs or ground into hydrophones. Conventional electroding and poling are used.

3.1.2. Plain Weave Method

Plain weave fabrics, for generating 3-3 type large-area composites, are being hand produced at ACI and Rutgers University. Figure 6 shows the hand loom at ACI. Coupons of 2"

x 4" for evaluation are currently the prototype size. Figure 7 shows examples of plain weave fabrics with different filling yarn thread densities. Piezoelectric performance as a function of filling yarn density is scheduled for next quarter.

3.1.3. Woven Carpet (Pile Fabric) Method

Prototype production of large-area PZT components for hydrophones also has begun at ACI. For large-area 1:3 composites, a woven pile fabric (shag carpet) of green PZT fiber is the device preform (Figure 8). The pile provides through-thickness fiber orientation needed for the large-area 1:3 composite architecture. Typical pile height is ~1 cm. 1.5" x 2" pile fabric preforms are now routinely produced, for test coupon size. Pile fabric preform sizes up to 3.5" x 4.5" have been produced (Figure 8). Potting and sectioning to determine the volume fraction of PZT fiber oriented in the thickness direction is underway. Presently, all of the textile processing is done by hand during the proof-of-concept stages. Tech-transfer to textile machinery for mass production is scheduled for late summer-early fall of '97 once textile machinery handleability issues have been addressed.

3.2. Prototype Device Testing

3.2.1. Coupon Testing

Some of the coupon production, and all of the sintering and coupon testing of composites for material certification, are conducted at Rutgers University. Standard 1-3 composites, by bundling and sizing ~500 filaments, and incorporating them into "pick-and-place" composites, show encouraging results (Table III). Data on the hydrophone figure of merit (d_{hg}) clearly illustrates the benefits of low-cost hydrophones produced from PZT fiber, compared to bulk PZT ceramic. Electromechanical results on discs sliced from the sintered braided rope preforms appear in Table IV. Further pulse-echo results on discs made by the braided rope method are presented in the next section.

Electromechanical test results of laminated plain weave composites appear in Table V. The through-thickness properties (first and second columns) illustrate the poor connectivity between the laminated plain-weave layers. The slightly higher properties achieved with the softer epoxy are a result of the lower elastic modulus. When the composite is turned edge-wise and poled in the direction of the filling fibers, the electromechanical properties are greatly improved, resulting from the greater connectivity of the ceramic. The "spiral" structure is a single fabric layer rolled up tightly and tied around the circumference. The spiral is then fired, potted and sliced into discs (much like the braided rope method for preform production).

3.2.2. Ultrasonic Transducers

The smaller piezo elements in the PZT fiber composites permit operation at higher frequencies than "dice-and-fill" composite transducers. Krautkramer-Branson (K-B) in Lewistown, PA is completing ultrasonic characterization of the fiber transducer discs including a wide range of frequencies and electrical impedance testing as well as producing prototype fiber transducers. Figure 9 is the pulse-echo response (1" water path to a stainless steel block) of a transducer disc produced from preforms made by the braided rope method. Initial testing (5 MHz) of the fiber composite transducer discs (three batches, three discs from each batch) yielded an average sensitivity of only -7 dB below K-B's standard "dice-and-fill" composite transducer discs. The sensitivity of the fiber transducers will improve as the production procedures and sintering schedules are improved. Better impedance matching to the fiber composite transducers

will also improve their sensitivity. More significantly, Figure 10 illustrates the absence of any lateral wave or third harmonic peaks in the fiber composite transducer response. The lateral wave resonance limits the range of usable frequencies for a given "dice-and-fill" composite transducer. Integration of fiber composites into ultrasonic transducer devices is underway.

Transducers made from PZT fiber offer the advantages of lower cost fabrication methods, a wider range of operating frequencies possible for a given transducer, as well as higher operating frequencies.

3.2.3. Hydrophones

Prototype hydrophone production will follow the same production route as for ultrasonic transducers. The first hydrophone for proof-of-concept will be Wilcoxon Research, Inc.'s H505L hydrophone. This device is a short tube (0.625" OD, 0.373 " ID and 0.250" thickness) poled in the thickness direction. A direct 1-for-1 replacement of the bulk PZT ceramic currently used with the PZT fiber composite is scheduled for the next quarter of the program. The braided rope method for composite preform production is applicable for manufacturing components for many of the Wilcoxon hydrophone device designs (tubes, discs or ring shapes). Prototype testing of the large-area woven carpet composite preform is also scheduled for the next quarter of the program.

Table I. Green Fiber Characterization

Fiber Lot	Sizing Type	Breaking Load, g	Breaking Strain, %	Rayon Denier	Tenacity, g/denier	% Sizing
961024	unsized	685.5	2.4	300	2.29	---
970124	Unsized	398	1.11	284	1.40	0.08
970220	Unsized	303.3	4.66	331	0.92	0.19
961108	PVA+PEG	863.6	2.1	300	2.88	---
970306	5% Emerlube	445	1.49	292	1.52	0.47
970307	Sonostat	555	1.44	299	1.86	1.03
970320	5% Sonostat	324	1.18	275	1.18	0.63

Rayon denier is calculated from the 15wt% cellulose present in the fiber.

Table II. Discrepancy in Piezoelectric performance of discs pressed from VSSP PZT fiber and discs pressed from the raw Morgan Matroc 5H powder.

Property	Pressed Disc of Fiber	Pressed Disc of raw PZT-5H
Density (g/cc)	7.2	7.3
% TD	91	92
Dielectric constant, K	1590	2820
tan δ	0.018	.025
d_{33} (pC/N)	360	620
g_{33} (mVm/N)	26	25

TD is theoretical density

Table III. Piezoelectric Data from Bundled, "Pick-and Place" Composites

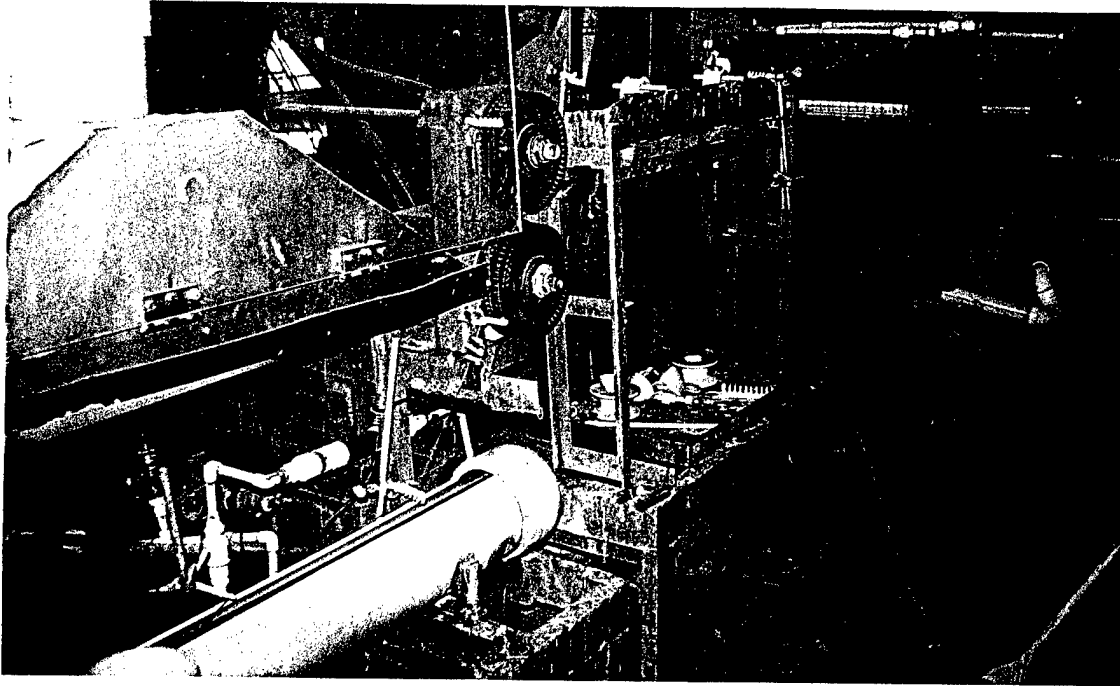
Property	1-3 Composite	PZT-5H
Density, g/cc	2.8	7.3
Vol% PZT	25	100
Dielectric Constant, K	470	2820
$\tan \delta$	0.047	0.043
d_{33} (pC/N)	340	520
g_{33} (mVm/N)	80	30
k_t	0.54	0.50
d_h (pC/N)	50.1	45
g_h (mVm/N)	13	1.5
Hydrophone Figure of Merit, $d_h g_h$	651.3	67.5

Table IV. Piezoelectric Data from Composites made from Braided Rope preforms.

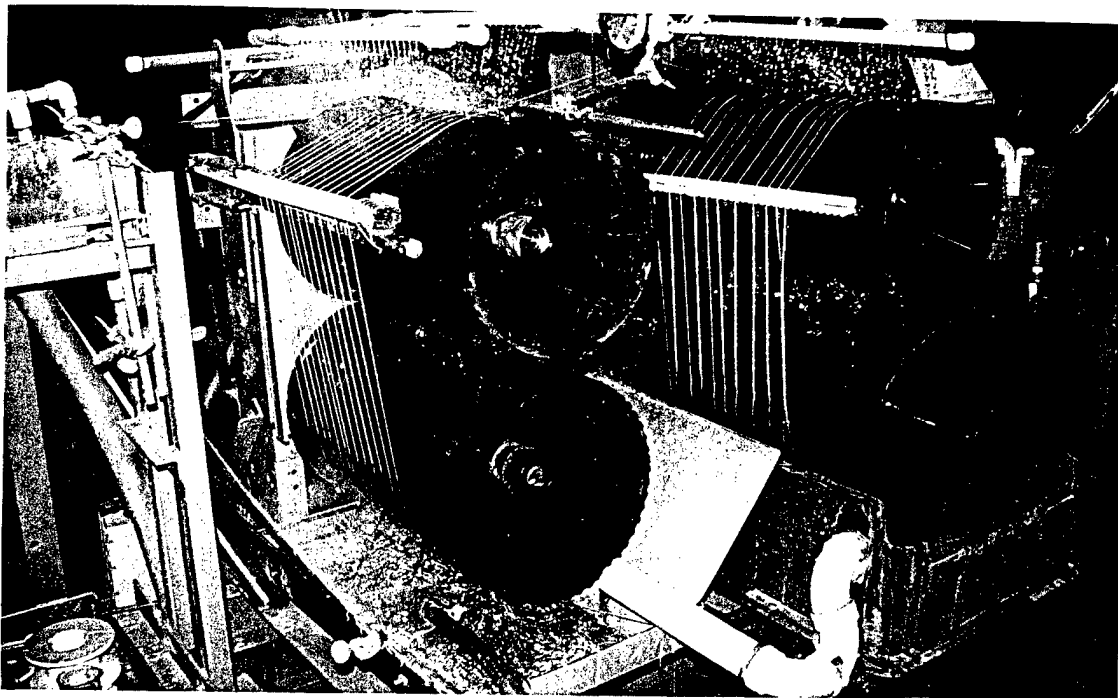
Property	1-3 Composite
Density (g/cc)	3.4
Vol% PZT	40
Dielectric Constant, K	655
d_{33} (pC/N)	295
k_t	0.53
k_p	0.27

Table V. Piezoelectric Data from Composites made from Plain Weave Fabrics

Property	Soft Epoxy, Poled through Thickness	Hard Epoxy, Poled through Thickness	Hard Epoxy, Poled Parallel to Filling Fibers	Hard Epoxy, Spiral
Density, g/cc	3.6	3.6	4.0	3.3
Vol% PZT	37	37	43	32
Dielectric Constant, K	206	130	495	400
d_{33} (pC/N)	180	80	250	280
g_{33} (mVm/N)	100	70	57	70
$\tan \delta$	0.0509	0.019	0.045	0.030

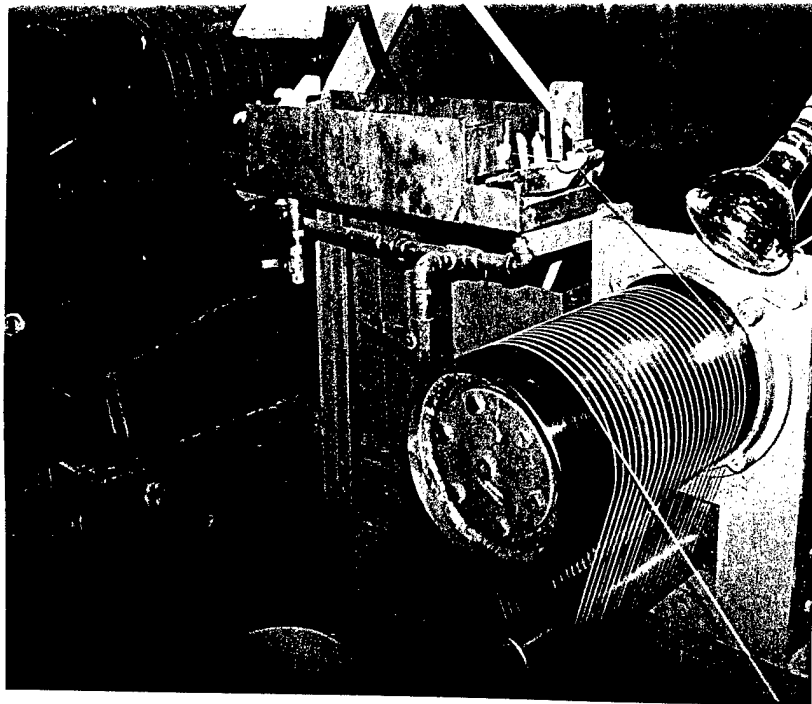


(a) Bottom left to top right: Spin bath, 1st godet, regeneration bath, 1st and 2nd wash stations.

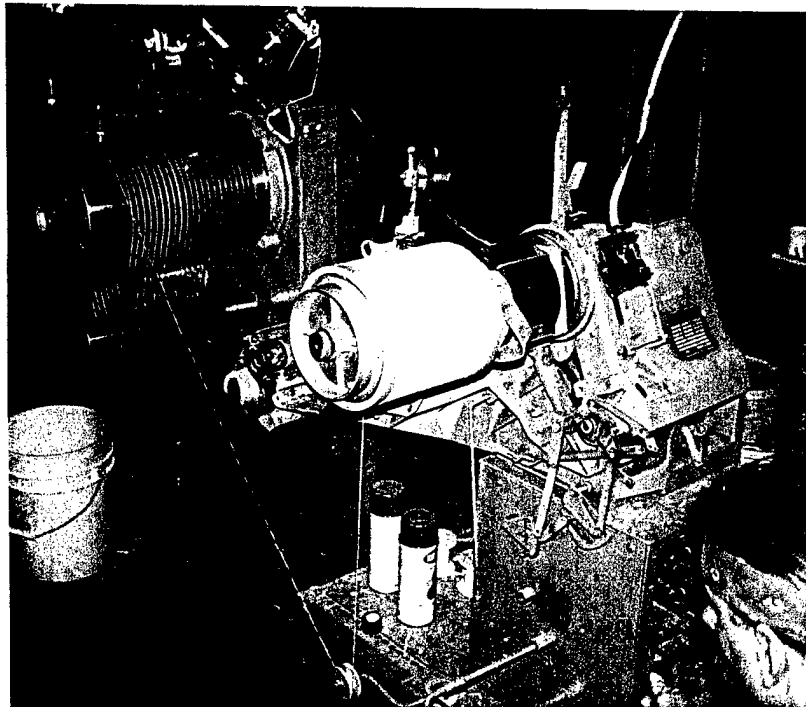


(b) Left to right: 1st and 2nd wash stations.

Figure 1. ACT's pilot-scale production spinning machine.



(c) Left to right: 2nd wash station, in-line finish bath and dryer drum.

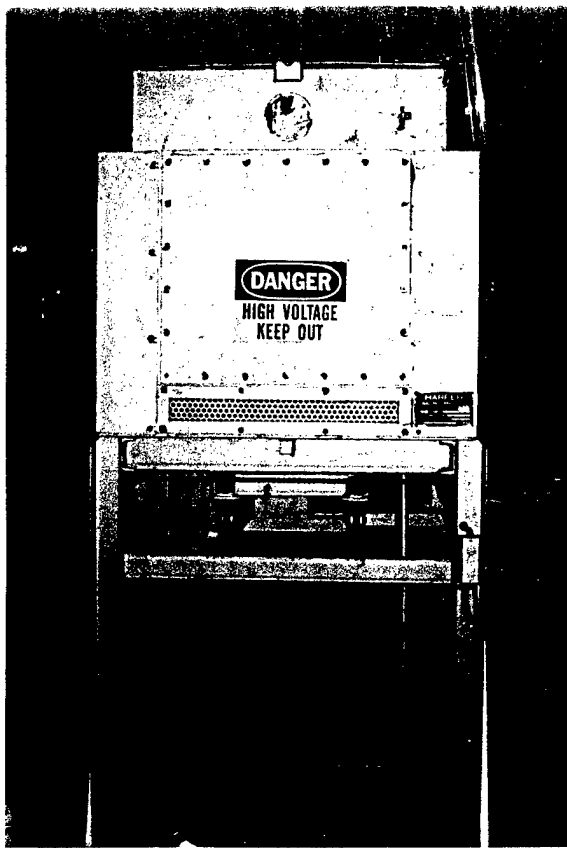


(d) Left to right: Dryer drum and take-up reel.

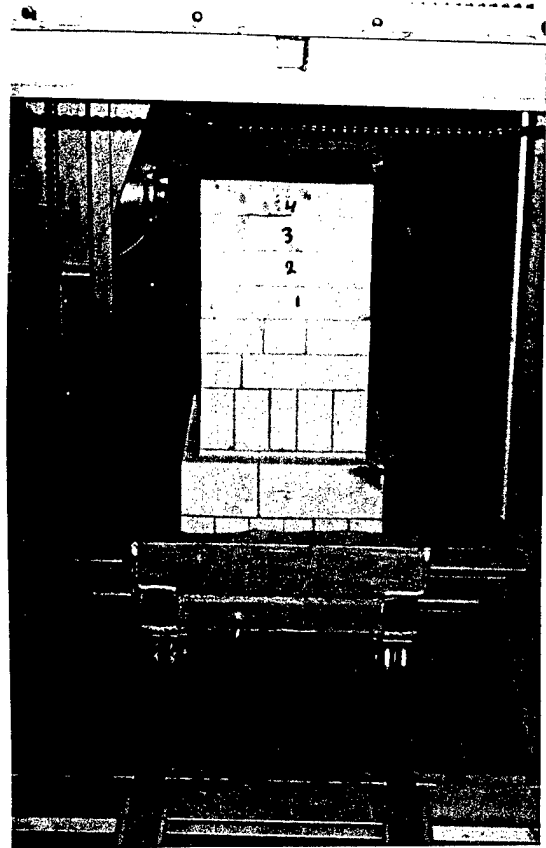
Figure 1. ACI's pilot-scale production spinning machine (continued)



Figure 2. A package of 790-end PZT fiber (~1500 meters in length). Scale is 6" long.



(a)



(b)

Figure 3. (a) ACI's controlled-atmosphere sintering furnace (elevator kiln type), with the car in the firing (up) position. (b) Car is shown in the loading position (lowered) showing the closed, outer shells of the double-shelled crucibles (labeld 1,2,3,4). The outer shell is 12" wide.

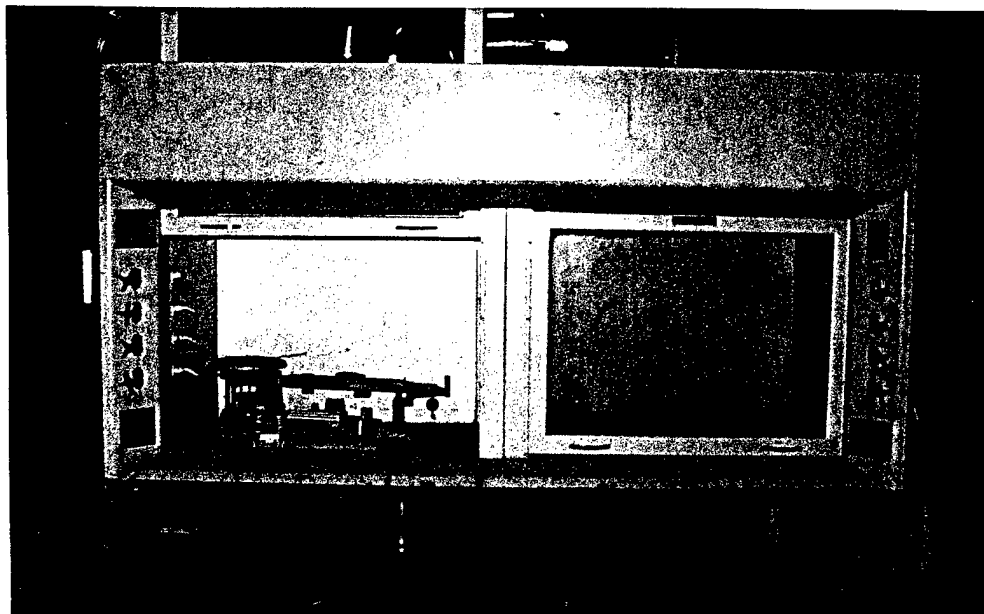
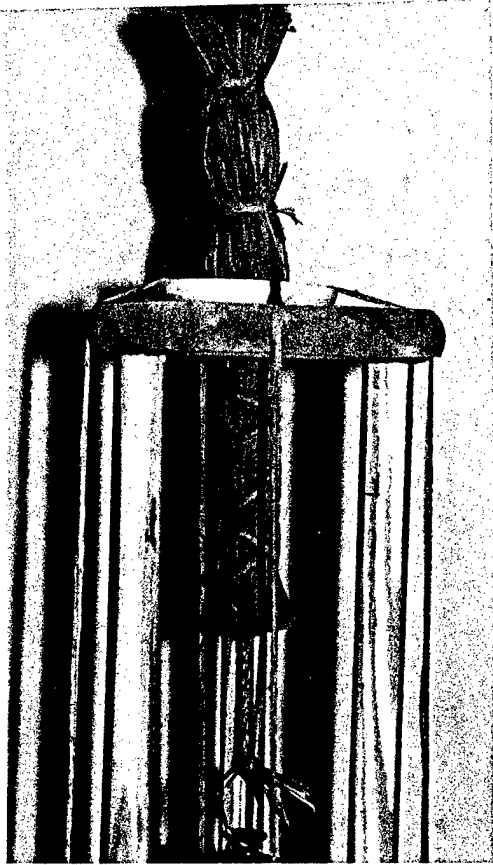
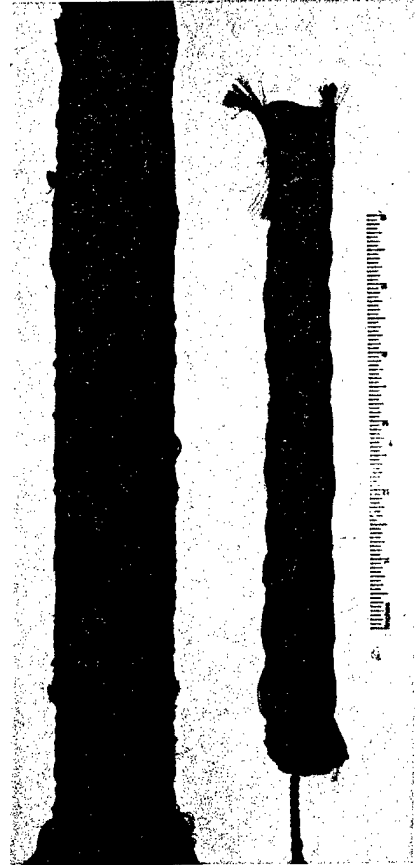


Figure 4. Fume hood installed for handling PZT powder.



(a) Bundle of fiber on ACI's hand-braiding stand



(b) Finished Braided ropes



(c) Ropes cut into 2" lengths

PROTOTYPE ULTRASONIC TRANSDUCER PRODUCTION
 Production blanks - "braided rope" - core of aligned PZT fiber

Green Blank Sintered Blank Infiltrated Blank Transducer disc
 (Standard Spurr's Epoxy)

TYPICAL PROPERTIES
 $d_{31} = 295 \text{ pC/N}$ $K = 655$ $k_t = 0.53, k_p = 0.27$

(d) Sinter, pot and electrode

Figure 5. Production steps for the braided rope method for 1-3 composite transducers.

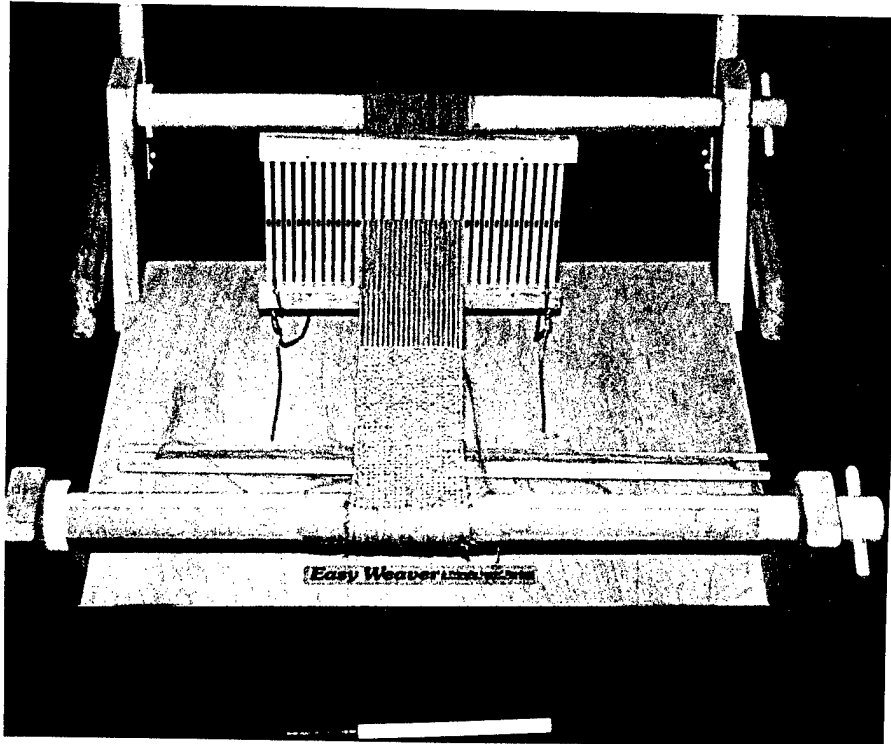


Figure 6. Hand loom at ACI for weave and pile fabrics for large-area devices.

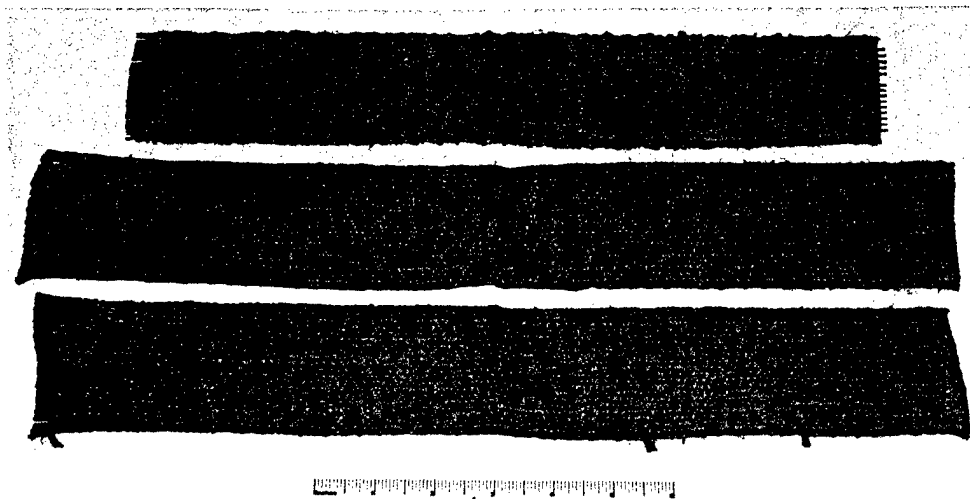


Figure 7. Plain weave fabrics. Increasing filling fiber density bottom to top.

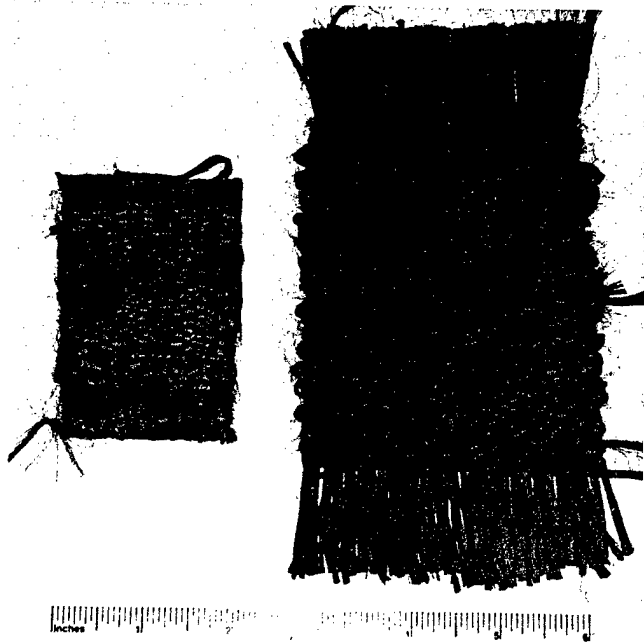
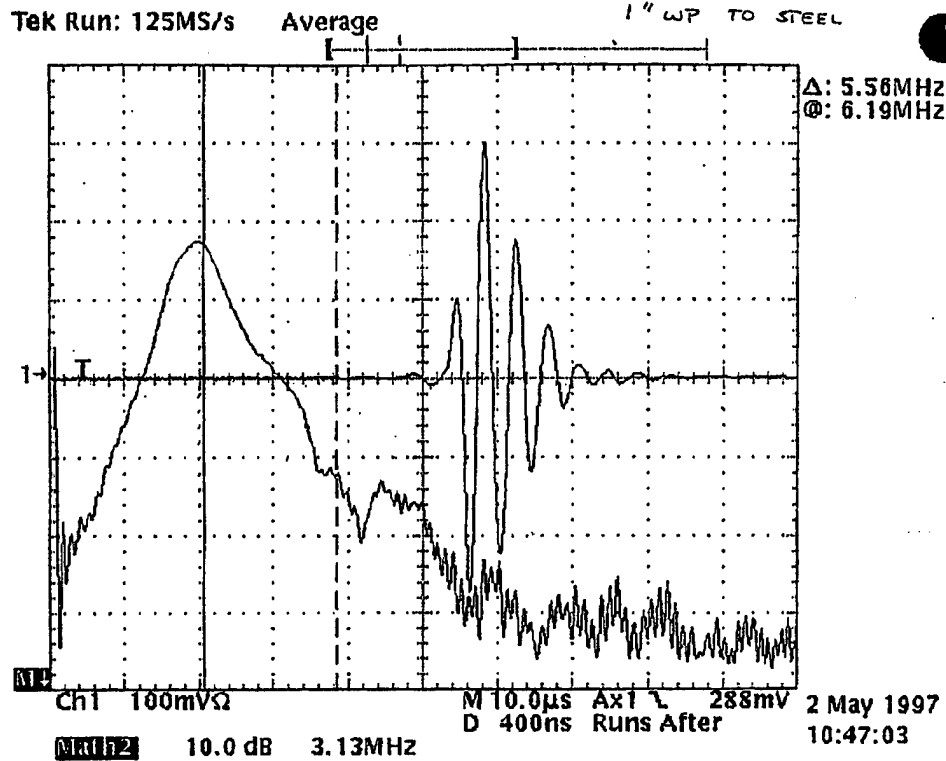
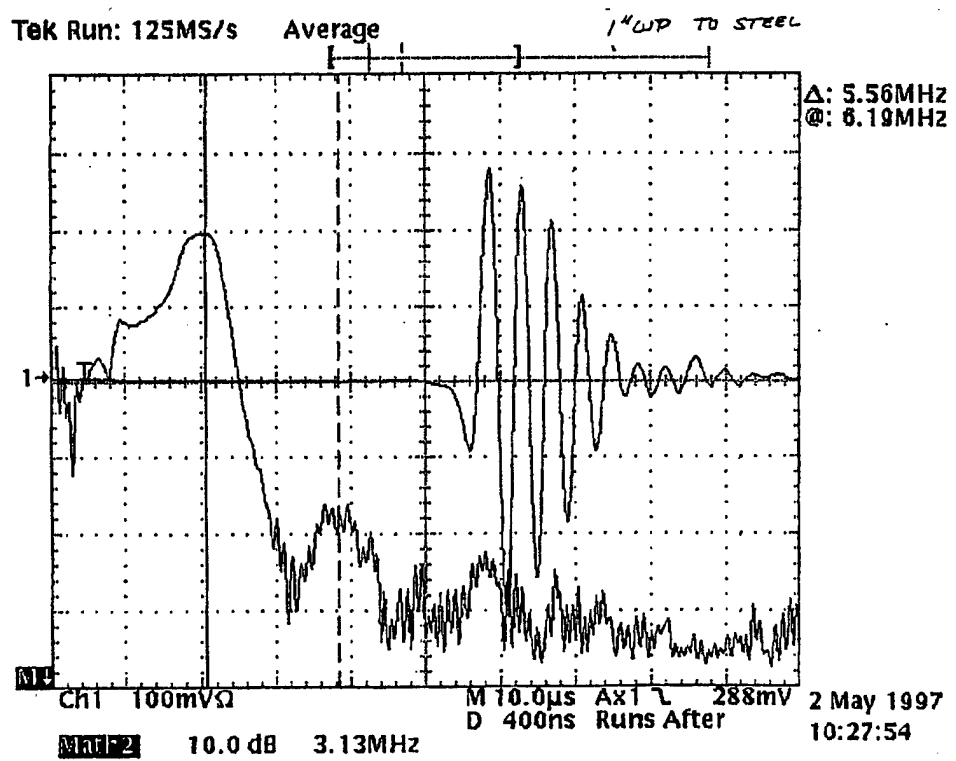


Figure 8. Coupons of green PZT fiber pile fabrics for large-area 1-3 composite hydrophones. Scale is 6" long.

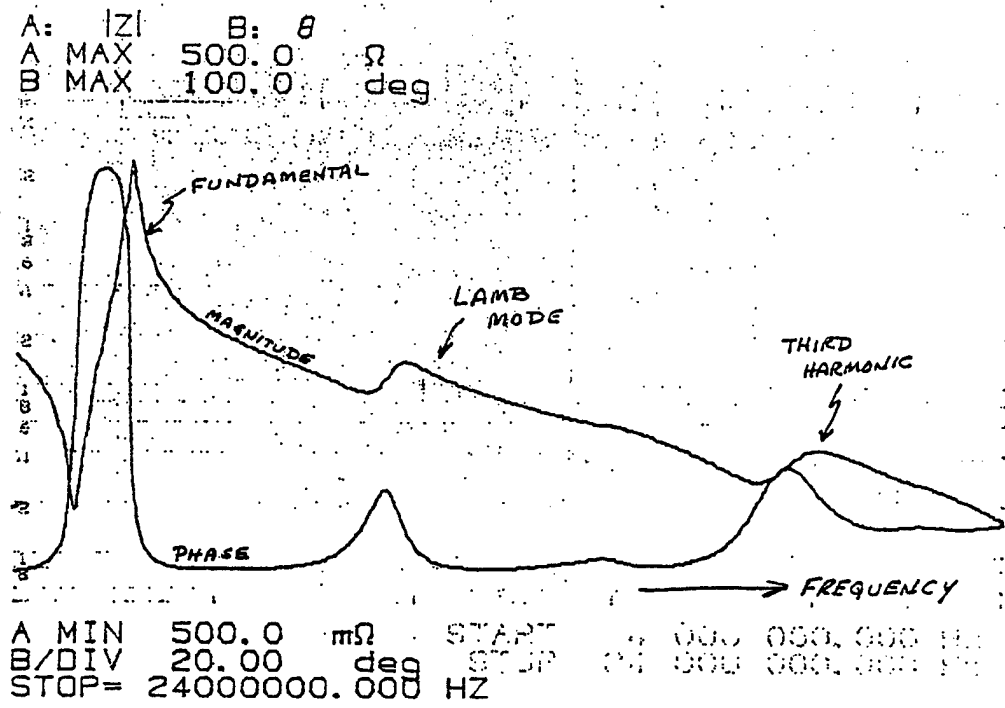


(a)

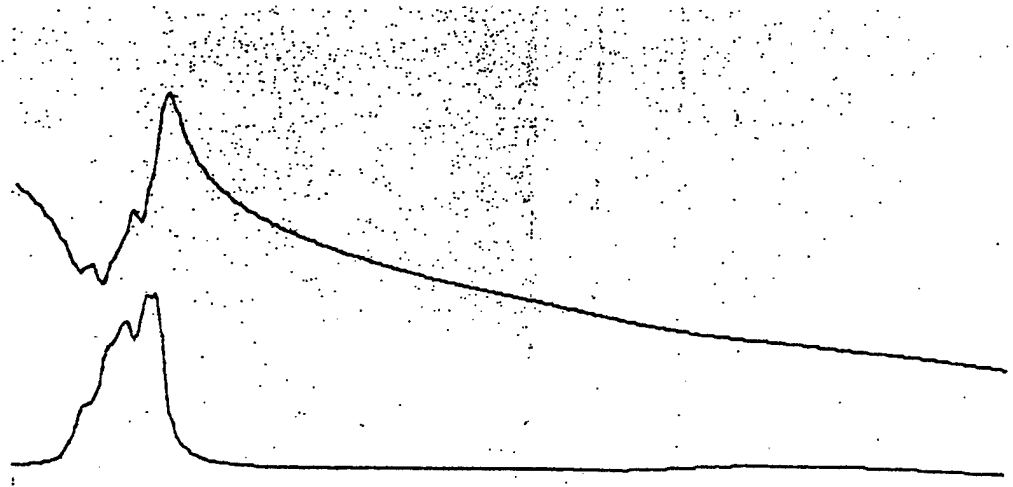


(b)

Figure 9. (a) Typical pulse-echo response from (a) K-B's standard "dice-and-fill" composite transducer disc and (b) ACI's piezoelectric fiber composite transducer discs.



(a)



(b)

Figure 10. Typical electrical impedance plots of (a) K-B's standard "dice-and-fill" composite transducer discs and (b) ACI's fiber composite transducer discs. Note the absence of any lateral wave (lamb mode) or third harmonic peaks in the fiber composite transducers.