

# USDA Sample Proposal

## Membrane-Based Process for Debittering Citrus Juice

(Figures and Tables are Unavailable on this Website.)

### I IDENTIFICATION AND SIGNIFICANCE OF THE PROBLEM

Citriculture is an important segment of world food production and nutrition. Oranges account for 67% of total worldwide citrus production. Oranges are consumed, principally in the form of juice, at an annual rate of approximately 17 kilograms per person (The Almanac of the Canning, 1979).

A major problem in the citrus industry worldwide is the formation of bitterness in citrus juice and products within hours after extraction from the fruit. The problem occurs in certain varieties of oranges (including mandarins), grapefruits, and lemons. The problem is estimated to cause losses for California citriculture of \$6 million to \$8 million per year (anon., 1986a).

The primary cause of the "delayed bitterness" in oranges is the presence of an intensely bitter group of compounds called limonoids, principally limonin and nomilin (Figure 1). The extent of bitterness imparted by limonin has been studied by Levi and coworkers (Levi et al., 1974), who obtained the values shown in Table I.

Much research has been focused on preventing the formation of limonin precursors prior to harvest, as well as on finding means to remove limonin after harvesting and processing. An excellent review of the approaches is given by Hasegawa and Maier (Hasegawa and Maier, 1983), and a summary of recent R&D activities is given in Section V.A. of this proposal. However, existing methods have severe economic and technical limitations (Anon., 1985). Additionally, existing methods often impair the stability and quality of the juice by affecting components other than limonin. Thus, despite extensive research efforts, there is no acceptable commercial method for reducing levels of bitter citrus components. The only current option is to blend excessively bitter juice with non-bitter juice.

The proposed program is directed at demonstrating the feasibility of using a novel process for the removal of limonin and nomilin from bitter navel orange juice. The process is based on a membrane that selectively allows the passage of limonin, limonoic acid, nomilin, and nomiloic acid, while retaining desirable flavor and nutritional components. The proposed process is designed so that the juice or concentrate contacts only materials that are accepted for food use or

have been shown to be generally recognized as safe. Furthermore, the proposed process promises to be economical on the basis of our preliminary analysis, as is discussed in Section II.C.

## **II BACKGROUND, TECHNICAL APPROACH AND ANTICIPATED BENEFITS**

### **II.A. SOLUTION-DIFFUSION MEMBRANES OFFER A MEANS TO DEBITTER ORANGE JUICE**

An attractive approach to the removal of off-flavors (a solute) in fruit juices involves the use of a synthetic membrane that allows the off-flavor to pass through but retains the desired components in the juice. Membranes can be conveniently categorized into two groups (Figure 2): 1) filtration membranes, and 2) solution-diffusion membranes. The more conventional filtration membranes have been studied extensively for food-processing applications, and their limitations are well known. Those limitations include severe problems with membrane fouling in the application of interest here (Matthiasson, E., 1985). Solution-diffusion membranes, on the other hand, show substantial promise in this type of application.

Filtration membranes contain pores. When a solution is forced through a filtration membrane (convective flow), solute molecules smaller than the pores pass easily; solute molecules larger than the pores are retained. Consequently, the selectivity of this type of membrane is dictated by molecular size. Moreover, a phenomenon known as “concentration polarization” – i.e., the buildup of solutes on the membrane surface—leads to membrane fouling and drastically reduced performance.

Solution-diffusion membranes do not have pores, and thus there is no convective flow through the membrane. Instead, solute molecules dissolve in the membrane phase and permeate the membrane by molecular diffusion. Molecular solutes that exhibit high solubilities and/or diffusivities in the membrane phase and/or that have low diffusivities are retained. Thus, the selectivity in this type of membrane is closely correlated with solute solubility, and an analysis of this type of membrane parallels liquid-liquid extraction rather than filtration. The key distinction is that, relative to filtration membrane processes, solution-diffusion membrane processes exhibit minimal concentration polarization and consequently resist fouling. This is because solute transport occurs via dissolution in the membrane phase, rather than by convective flow through pores.

In our proposed process, we will use solution-diffusion membranes. Specifically, the membrane consists of a thin layer of a hydrophobic liquid, about 25  $\mu\text{m}$  thick, that separates two aqueous solutions. The hydrophobic liquid is supported and

stabilized within the pores of a microporous, hydrophobic polymer film. Such supported-liquid membranes have been shown in our laboratory to be stable for up to a year, even when separating aqueous solutions that have acid concentrations that differ by ten or more pH units. That degree of chemical stability is critical in the proposed application.

The operation of this type of membrane for the removal of limonin and limonoic acid (*\*Because the solubility and chemical properties of limonin and nomilin are extremely similar, we believe that the membrane process will operate equally well for nomilin and nomiloic acid. We will therefore use limonin and limonoic acid as generic terms for all four types of liminoids of interest here.*) is illustrated in Figure 3. A feed solution containing orange juice at pH 3.2 flows on the left side of the membrane, and a stripping solution containing aqueous sodium hydroxide at pH 12 to 13 flows on the right side. Limonin from the feed solution dissolves in the hydrophobic supported liquid of the membrane and is transported across the membrane to the strip side by diffusion.

Limonoic acid, produced by the hydrolysis of limonin, is also present in the feed solution. Since the pKa's of limonoic acid are 2.7 and 4.7, at a pH of 3.2—the pH of the juice—one carboxyl group of limonoic acid and a significant fraction of the other carboxyl group are protonated. Thus, limonoic acid, bearing no charges, also dissolves in the hydrophobic supported liquid of the membrane and is transported to the strip side. At the membrane/strip-side solution interface, limonin and limonoic acid dissolve in the strip solution and are rapidly and irreversibly hydrolyzed and deprotonated to limonate under the basic conditions of the strip solution. Since anionic limonate, bearing charges, is insoluble in the supported liquid of the membrane, it cannot back-diffuse therefore, limonin and limonoic acid are irreversibly transported from the feed solution to the strip solution.

Because limonate is confined to the strip stream, it can be concentrated by using a strip-stream volume that is smaller than the feed-stream volume that. The strip-stream volume is reduced by setting the strip-stream flow rate lower than the feed-stream flow rate. From material balance considerations,

$$\text{Limonin Conc in Strip Stream} = \text{Limonin Conc. In Feed Stream} \times \left( \frac{\text{Feed-Stream Flow Rate}}{\text{Strip-Stream Flow Rate}} \right)$$

Hence, the proposed supported-liquid membrane process makes possible the removal and concentration of limonin from orange juice.

## II.B. PRELIMINARY EXPERIMENTS SUPPORT THE PROPOSED APPROACH

We have conducted preliminary experiments that indicate that the proposed supported-liquid membrane process efficiently transports limonin and limonoic acid. In a typical experiment, a supported-liquid membrane consisting of Shell Sol 71 (*\*Shell Sol is a mixture of aliphatic solvents manufactured by Shell Chemical Company; it is approved for contact with food products.*) supported in the pores of a flat-sheet microporous polypropylene membrane (Celgard 2400 manufactured by Celanese Separations, Inc., Charlotte, NC) was clamped between the two compartments of the membrane-permeability apparatus illustrated in Figure 4. The feed compartment was filled with limonin (60 ppm) dissolved in 20 vol% acetic acid (pH3.2); the strip compartment was filled with 0.01M aqueous sodium hydroxide (pH12). (*\*\*Control experiments indicated that the solubility of limonin in water was raised from about 6 to 8 ppm at pH 3.2 to more than 200 ppm at pH 12, presumably due to the base-catalyzed hydrolysis and ionization of limonin.*) The aqueous solutions in the two compartments were stirred and their temperatures maintained at 25 degrees C. The concentration of limonin in the feed compartment was monitored as a function of time by removing aliquots from the feed compartment and assaying the limonin concentration by means of HPLC and UV detection. (*+Limonin was separated from acetic acid on a C18 reverse-phase HPLC column using a 10 vol% to 50 vol% acetonitrile/water gradient and was detected on a diode-array UV detector set at 207 nm. Concentrations were determined from detector response curves obtained using limonin samples of known concentration.*) We determined an initial limonin flux (*++Flux is defined as the amount of material that permeates a given area of membrane in a given time.*) of 2.5 ug/cm squared-min from the slope of a plot showing limonin concentration in the feed versus time. Dividing the flux by the initial limonin concentration gave a concentration-normalized flux (permeability) of 1.0 cm/hr.

Since limonin in juice exists as a mixture of forms that include limonin and limonoic acid in three possible states of ionization (Chandler and Robertson, 1983), a major concern was whether the membrane could remove all forms of limonin. To address this question we conducted a membrane-based separation experiment on a sample of hydrolyzed limonin. Specifically, limonin (100 ml/L) was suspended in 20 vol% acetic acid and the pH of the suspension was raised to 12 by the addition of sodium hydroxide. Mild heating of the mixture (to 30 degrees C) caused all the limonin to dissolve. The solution was then heated to 65 degrees C to hydrolyze the limonin to limonate. After heating for 30 min, the pH of the solution was adjusted to 3.2 by the addition of concentrated sulfuric acid. The resulting solution (50ml) was then added to the feed compartment of a membrane-permeability apparatus containing a supported-liquid membrane composed of 30 vol% isohexadecyl alcohol and 70 vol% Shell Sol 71 and a strip solution (168 ml) of pH 12 aqueous sodium hydroxide. The experiment was

conducted and analyzed as described previously. The results are shown in Figure 5.

The results shown in Figure 5 make three important statements. One, the membrane process effectively reduces limonin in the feed from about 55 ppm to 11 ppm. Two, the membrane process is effective at removing all forms of limonin, as prior hydrolysis of limonin in the feed has no adverse effect on total limonin removal. And three, the membrane process follows the expected exponential loss of limonin in the feed with a permeability coefficient of 1.1 cm/hr.

The initial results obtained at Bend Research strongly support the validity of the proposed approach. However, the ultimate feasibility on actual orange juice and the favorable economics must be verified via a thorough R&D program designed to identify the optimum membrane materials and operating conditions. The elements of such a program are described in detail in later sections of the proposal.

## **II.C. PRELIMINARY COST ANALYSIS SUGGESTS THAT THE PROPOSED PROCESS IS ECONOMICAL**

### **II.C.1. Anticipated Technical Results**

In Phase I we will develop a membrane-based process that selectively removes and concentrates limonin. We will incorporate this membrane into a test module and use it to demonstrate the removal of limonin from samples of clarified, very bitter navel orange juice. We will carry out studies to measure the effect of operating parameters on limonin removal, including feed composition, temperature, pH, and feed-and strip-stream flow rates. The results of these studies will be used to make engineering calculations to establish the technical and economic feasibility of the membrane-based limonin-removal process.

### **II.C.2. Economic Impact of Proposed Debittering Process**

The economic impact of “delayed bitterness” in citrus can be illustrated by examining the commercial production of orange juice concentrate in California and Arizona. In a typical year, approximately 40 million pounds of navel orange solids are processed as juice concentrate. Of this amount, approximately 80% would benefit from a debittering process. (*\*\*Dr. Denny Nelson, Sunkist Research Center, Ontario, California, personal communication.*) Juice concentrate that is not bitter sells for approximately \$1.30 per pound of solids. Bitter juice, on the other hand, is discounted a minimum of \$0.20 per pound of solids. Consequently, “delayed bitterness” in navel oranges alone results in an economic loss of at least \$6.4 million in California and Arizona.

The technical objective in Phase I of the proposed program is to develop a process that reduces limonin concentration in orange juice from 40 ppm (a typical value for early-season navel oranges) to 8 ppm. The resulting debittered juice can be mixed with a late-season juice to produce a blend of marketable quality containing less than 6 ppm limonin. A preliminary analysis of the economics of the proposed process is given below.

Given an average concentration gradient across the membrane of 16 ppm limonin, the analysis uses an average limonin flux of 0.29 lb per ft squared of membrane per year. This value is based on the permeability values obtained in the preliminary studies reported in Section II.A. We assume that freshly pressed juice contains 11% solids. Equipment and operating costs are based on previously reported metal-recovery studies (Babcock et al., 1983) employing liquid membranes. A list of the assumptions is given in Table II.

The results of our preliminary analysis are shown in Table II. For debittering 32 million pounds of navel orange solids, the total process cost is \$605,940/yr, or 1.9 cents/lb of orange solids. The projected cost compares favorably with the minimum \$0.20-per-lb discount incurred with bitter juice and represents a \$6.1 million potential gain for the citrus industry in California and Arizona alone. Furthermore, it is important to note that in the above analysis the limonin flux used in the calculation is a lower limit that was achieved during very preliminary investigations. Process costs can be further reduced by using thinner membranes or optimized operating conditions to increase limonin flux.

### II.C.3. Advantages of the Proposed Debittering Process

The proposed membrane process offers a number of important advantages over existing processes for the removal of limonin:

- The process can be carried out at low temperature without phase change, thus minimizing deterioration of temperature-sensitive nutritional components in orange juice (e.g. ascorbic acid).
- The process is modular and thus can be operated at any desired scale by simply increasing or decreasing the number of membrane modules used.
- The process can remove limonin from dilute solution and produce it in concentrated form.
- The process can be operated in a continuous mode, thereby minimizing processing time while maximizing process reliability.
- The process is relatively immune to fouling problems that are common when more conventional membrane processes are used in food processing.

Other advantages that we expect to derive from the proposed membrane-based limonin removal process are listed below:

- The process is simple, requiring a minimum of operator control and judgment.
- The process is readily adaptable to sanitary operations.
- The process is designed for high throughput—a condition necessary for large-scale utilization.
- The process will not alter desirable flavor and nutritional components in orange juice or significantly remove them. *(Although some flavor components are hydrophobic and might permeate the membrane, they are not expected to be concentrated in the strip stream. Recall that limonin is hydrolyzed to limonate dianion in the strip stream and that the net charge on limonate is what prevents its back-diffusion and allows it to be concentrated. Using a ratio of (feed-stream flow rate)/(strip-stream flow rate) = 20/1, there would be—in the worst case—a 5% loss of those flavor components that rapidly equilibrate across the membrane.)*

## **II.D. STRUCTURE OF THE PHASED PROGRAM**

Phase I is directed at demonstrating the feasibility of using a membrane process to debitter early-season orange juice. Once proof of concept has been accomplished in Phase I, the phase II effort will focus on 1) optimization of the membrane separation, 2) development of more efficient membranes in hollow-fiber form, and 3) fabrication of prototype hollow-fiber membrane modules. During Phase II, we will do long-term testing of membrane modules under realistic field conditions. The goal is to establish that any adverse effects on module performance caused by sustained operation on actual juice can be rectified in a way that is consistent with large-scale plant operation. It should be noted that the field tests will form the basis for a comprehensive technical and economic evaluation.

If Phase II is successful, we anticipate entering into an agreement with a commercial sponsor for Phase III of the program. Phase III would involve construction of a 1,000-gal/day field-test unit and approximately 12 months (elapsed time) for field-testing and evaluation before full-scale commercialization would be initiated. We anticipate that the membrane modules necessary for Phase III will be fabricated by Consep Membranes of Bend, Oregon, a manufacturing subsidiary of Bend Research, Inc.

### **III. PHASE I TECHNICAL OBJECTIVES**

The overall goal of this program is to demonstrate the feasibility of using a membrane process to remove and concentrate bitter-tasting limonin from orange juice. We aim to reduce the concentration of limonin in early-season juice from 40 ppm down to 8 ppm so that the purified juice can be mixed with non-bitter, late-season juice to produce a blend of marketable quality (6 ppm limonin and acceptable flavor).

In pursuit of this goal, we will address the following technical questions:

- What type of solution-diffusion membrane offers high limonin fluxes and selectivities?
- How do operating parameters (e.g., flow rate, pH, temperature) affect membrane performance (selectivity and flux)?
- What is the most effective way to concentrate limonate on the strip side—e.g., high pH, anion-exchange resins, and charcoal absorbers?
- What is the projected lifetime of the membrane?
- Does the membrane process alter the flavor or nutritional value of the juice by removing beneficial components?
- Does the proposed membrane process release materials into the juice that are not accepted for food use or are not generally recognized as being safe?
- What are the projected economics of the process?

The tasks necessary to answer the above questions are detailed in the next section.

### **IV. PHASE I RESEARCH PLAN**

#### **IV.A. TASKS 1: SELECTION OF SUPPORTED-LIQUID MEMBRANE**

The objective of this task is to identify candidate membranes that transport limonin and limonoic acid but reject limonate. The best candidate membranes will be fabricated and evaluated as described in Tasks 2 through 5.

In this task we will investigate two types of supported-liquid membranes: immobilized-liquid membranes, and liquid-swollen polymer membranes (Figure



6). Immobilized-liquid membranes consist of a hydrophobic liquid held in the pores of a microporous support. Liquid-swollen polymer membranes consist of dense polymer membranes that have been swollen by hydrophobic liquids.

Our approach to selecting candidate-supported liquids is guided by the principle that high limonin and limonoic acid transport is associated with high limonin and limonoic acid solubility in the supported liquid of the membrane. Thus, by employing solubility and distribution-coefficient data, we aim to identify supported liquids that exhibit high limonin and limonoic acid solubilities but low solubilities to feasible flavor and nutritional components. We will use ascorbic acid as a representative desirable nutritional component, linalyl anthranilate (essence of orange) as a representative desirable flavor component, and a 0.1M (pH 3.2) citric acid solution containing 12 wt% sucrose as a synthetic orange juice base. We will then measure the distribution coefficient of limonin, ascorbic acid, and linalyl anthranilate between the synthetic orange juice base and a number of hydrophobic liquids. Candidate liquids include high-molecular-weight even-numbered straight-chain alcohols. (*\*We have chosen even-numbered alcohols because they are approved for some food-separation processes.*) For example, 1-decanol has low water miscibility and is essentially nonvolatile. Liquids will be ranked on the basis of their tendencies to preferentially partition limonin and limonoic acid.

Limonin and limonate concentrations will be determined by HPLC analysis as described in our summary of preliminary experiments (Section II.A.) and as reported by Shaw and Wilson (Shaw and Wilson, 1984). Ascorbic acid concentrations will be determined by the reduction of Fe(III) by the ascorbic acid and subsequent measurement of the absorbance of Fe(II)-ferrozine chelate at 562 nm as described by Taselskis and Nelapaty (Taselskis and Nelapaty, 1972). Linalyl anthranilate concentrations will be determined by HPLC analysis.

#### **IV.B. Task 2: MEMBRANE FABRICATION AND TESTING**

During the proposed Phase I feasibility study, we will study only flat-sheet membranes, as they are easy to fabricate and they can be readily evaluated in our membrane-permeability apparatus (Figure 4). However, we plan to use hollow-fiber membranes in Phase II development work because of their higher surface-area-to-volume ratio. It is our experience that developments obtained with flat-sheet membranes are readily transferable to hollow-fiber membranes.

Immobilized-liquid membranes will be prepared by absorbing the solvents selected in Task 1 into the pores of a microporous membrane. We intend to examine the feasibility of using Goretex Type S 11003 (polytetrafluoroethylene), Celgard (microporous polyethylene), and BRI's microporous polysulfone and microporous polyvinylidene difluoride as supports for the liquid membranes. The immobilized-liquid membranes will be prepared by immersing the microporous support in the solvent and removing the air bubbles remaining in the pores by

repeatedly drawing and releasing a vacuum above the solvent. The organic liquid is retained in the pores by capillarity.

Liquid-swollen polymer membranes are prepared by immersing the polymer membrane in the selected liquid with gentle warming. Polymer membranes will be obtained as commercial membranes or prepared as films supported on porous backings by using one of the following method: 1) casting a solution of the polymer dissolved in an organic solvent onto a preformed porous support, such as polysulfone, and letting the membrane air-dry to form a thin, nonporous film on the support; 2) forming a supported-polymer membrane by casting the polymer solution onto a glass plate and then precipitating the polymer in water; or 3) laminating a precast polymer membrane onto a preformed porous support by heating, such that the polymer membrane melts just enough to be "heat sealed" onto the support. These membrane-fabrication techniques have been successfully used at Bend Research for a variety of membranes, and thus we expect the probability of success in this task to be very high.

The supported-liquid membranes will be tested to ascertain that they are free of leaks by measuring initial fluxes of ascorbic acid in a membrane-permeability apparatus of the type illustrated in Figure 4. Defect-free supported membranes are expected to display high resistance to ascorbic acid transport. We will also measure initial fluxes of limonin and limonate. Initial fluxes will be determined by imposing a concentration gradient across the membrane and periodically removing and analyzing samples of the solution on the permeate side of the test cell as described in Section II.A. Permeabilities will be calculated using the relationship:

Permeability = (Permeate Flux)/(Concentration Difference).

Selectivities will be calculated relative to ascorbic acid permeability using the relationship: Selectivity = (Limonin Permeability/Ascorbic Acid Permeability).

#### **IV.C. TASK 3: OPTIMIZING STRIPPING CONDITIONS**

Limonin fluxes are governed, in part, by the limonin-concentration gradient across the membrane. Thus, effective limonin removal hinges on maintaining low concentrations of membrane-permeable forms of limonin in the strip side. This can be accomplished by transforming all limonin forms to limonate, or adsorption of limonin forms onto absorbents. In this task, we will measure the solubility of limonin as a function of strip-solution pH (in the range of 10 to 13) and temperature (in the range of 25 degrees to 65 degrees C). Additionally, we will study the use of commercially available, strong anion-exchange resins (e.g., Darco) as a means to absorb and concentrate limonin forms in the strip solutions.

#### **IV.D. TASK 4: MEMBRANE PERFORMANCE WITH CLARIFIED ORANGE JUICE**

On the basis of limonin flux and selectivity, we will select the two best supported-liquid membranes prepared in Task 2 and the best stripping conditions determined in Task 3 for evaluation on actual orange juice. A test module that holds a 1-ft section of flat-sheet membrane will be fabricated for this task. To eliminate problems associated with handling orange juice pulp, we will carry out our Phase I membrane-performance studies on clarified orange juice. During Phase II we would design a system that would treat all components of orange juice concentrate.

To aid us in this task, we have established a collaboration with Dr. Denny Nelson of the Sunkist Research Center in Ontario, California. Dr. Nelson has provided us with authentic samples of limonin and will provide us with clarified early-season navel orange juice containing 30 to 40 ppm limonin. Furthermore, he has offered to test the purified juice for bitterness removal, as well as nutrient and flavor loss. Additionally, we will test the purified juice for the presence of materials released from the membrane. If any major difference in membrane performance is evident when actual clarified juice is used as compared with performance when a synthetic mixture of limonin, ascorbic acid and linalyl anthranilate is used, an attempt will be made to determine the cause.

#### **IV.E. TASK 5: EFFECT OF OPERATING CONDITIONS ON LIMONIN REMOVAL**

The objective of this task is to measure the effect of operating conditions on the efficacy of limonin removal from clarified orange juice. Operating parameters to be considered include temperature, feed- and strip-stream velocity across the membrane, pH of the strip stream, and composition of the feed stream.

Liquid membranes similar to those to be used in the program but applied to inorganic-salt separations are known to perform adequately for 6 months without requiring reloading with fresh organic solution. Liquid-swollen membranes are known to perform adequately for up to 2 years. However, such membranes have not been evaluated for limonin removal from citrus juice. Hence, the additional purpose of this task is to run limited (about 1 month) lifetime studies using clarified orange juice to be certain that there are no short-term adverse effects on membrane life.

#### **IV.F. TASK 6: PRELIMINARY TECHNICAL AND ECONOMIC ANALYSIS AND PREPARATION OF FINAL REPORT**

In this task we will make use of the data obtained in Tasks 4 and 5 to perform a technical and economic evaluation. These evaluations will form the basis of the

decision to proceed into the Phase II program. The results will appear in our final report.

## **V. RELATED RESEARCH AND DEVELOPMENT**

### **V.A. R&D ACTIVITIES RELATED TO PROPOSED EFFORT**

Previous approaches to bitterness reduction in citrus products fall into three categories: 1) preharvest treatments that inhibit the formation of liminoids in citrus fruits, 2) biotransformation of bitter liminoids into non-bitter metabolites, and 3) liminoid removal by adsorption on polymer resins. However, none of these approaches has been put into commercial practice. A brief discussion of recent R&D activities in these three categories follows.

Shin Hasegawa from the Fruit and Vegetable Chemistry laboratory of the Department of Agriculture's Agricultural Research Service in Pasadena, California has recently reported a preharvest treatment that claims to inhibit the formation of liminoids in citrus fruit (Anon., 1986b). The treatment consists of applying synthetic auxins (plant-growth regulators) that are potent inhibitors of liminoid biosynthesis. However, this approach has not been demonstrated to be cost-effective.

Several investigators have reported studies directed at using biotransformations as a means to avert bitterness by converting bitter liminoids in citrus juice to non-bitter metabolites. Approaches include the use of immobilized cells (Hasegawa et al. 1983; Hasegawa and Pelton, 1983) and the use of enzymes (Hasegawa, 1975a; Hasegawa, 1975b). A drawback of these approaches is the deterioration of the flavor and color of treated juice.

Most R&D activities have been directed at removing bitter limonin from juice by adsorption or complexation on polymer adsorbents. Approaches include the use of ion-exchange resins (Coca-Cola Co., 1987; Mitchell et al. 1985; Johnson and Chandler, 1985; Purl, 1984), cyclodextrin polymers (Shaw et al., 1984), and cellulose gels (Johnson and Chandler, 1981a; Johnson and Chandler, 1981b, and Chandler and Johnson, 1979). These approaches, however, have a number of shortcomings, including unfavorable process economics, excessive process complexity requiring extensive operator control, the need for organic solvents to strip limonin from the adsorbent, and production of difficult-to-manage waste streams.

### **V.B. BEND RESEARCH ACTIVITIES RELATED TO THE PROPOSED EFFORT**

Bend Research is currently involved in several separate but related membrane-based separation projects. Dr. Paul van Eikeren, the principal investigator, is currently directing an NSF SBIR Phase II project entitled, "Optical Resolution of

D,L-Phenylalanine in a Membrane Reactor: that is focused on using supported-liquid membranes to selectively remove the product of an enzyme-catalyzed reaction. Additionally, he is directing several proprietary projects for private Bend Research clients directed at using membrane separations to recover valuable food additives and flavoring agents.

## **VI. KEY PERSONNEL AND BIBLIOGRAPHY**

It is anticipated that Dr. Paul van Eikeren will serve as principal investigator, with key contributions being made by Dr. Harold Lonsdale. Dr. van Eikeren has extensive R&D experience in areas directly related to the proposed work. He is now directing several Phase I and Phase II SBIR programs. Dr. Lonsdale has 25 years of experience in the field of membrane technology and is recognized internationally as a leader in the field. He is the founding and current editor of the Journal of Membrane Science. Abbreviated resumes for these individuals follow.

## **VII. FACILITIES AND EQUIPMENT**

Bend Research is a 10,000 square ft. laboratory and office complex; an additional 5,000 square ft. is under construction. The firm employs a technical staff of 45 and has 70 employees. Work is devoted exclusively to the development of membranes and membrane-based processes. In-house material and equipment relevant to the performance of the proposed program include the following: a) atomic absorption, UV-visible, and FT-IR spectrophotometers; b) multiple HPLC and GC instruments; c) scanning electron microscope; d) organic-synthesis laboratory and capability; e) continuous-production equipment for flat-sheet and hollow-fiber support membranes; and f) membrane-permeation apparatus.

## **VIII. CONSULTANTS**

Dr. Denny Nelson, Director of R&D at Sunkist Research Center, Ontario, California, is an expert in the field of debittering navel orange juice. He has agreed to consult with Bend Research on this project without compensation.

## **IX. POTENTIAL COMMERCIAL APPLICATIONS**

Successful development of a membrane system for the removal of limonin offers a practical procedure for the removal of bitter limonoids from all citrus juices. Furthermore, successful development would provide the basis for fabricating other supported-liquid membranes for the selective removal of off-flavors and off-colors in fruit-juice concentrates. For example, supported-liquid membranes could offer a means of removing polyphenol off-colors in natural sweeteners produced from apple or pear concentrates.

## **X. CURRENT AND PENDING SUPPORT**

No work substantially similar to that proposed here is being conducted at this time, nor is any pending.

# NASA SAMPLE PROPOSAL

(FIGURE AND TABLES ARE UNAVAILABLE)

TPL-P-3314  
SBIR 93-1 SOLICITATION  
FORM 9.B – PROJECT SUMMARY

PROPOSAL NUMBER 93-1 SUBTOPIC NUMBER – 12.07 AMOUNT REQUESTED \$70,000

TITLE OF PROJECT

## Miniature Solid State Sensors for Chemical Contaminants in Liquids

### TECHNICAL ASBTRACT (LIMIT 200 WORDS)

NASA has a serious unmet need for microminiature sensors capable of in situ, real-time analysis of contaminant levels in regenerative life support systems. Surface derivatized piezoelectric sensors can detect less than 10<sup>-11</sup>g of analyte using detectors weighing only 0.02 g with power consumption of 1 to 2 mW per sensor [1,2]. However, piezoelectric sensor technology has not resulted in the development of the ultra-high sensitivity, microminiature sensors needed by NASA for regenerative life support systems. The reasons include unsatisfactory sensor selectivity, poor sensor baseline recovery, degradation of sensor performance with time, and in the case of the bulk mode devices needed for liquid phase sensors, difficulties in signal processing due to the complexity of the output signal which leads to effects such as mode hopping.

TPL proposes to develop innovative sensor architectures, surface chemistries, electronics and software techniques to solve the problems that limit piezoelectric sensor performance. This will lead to miniature, low power, self-calibrating, high selectivity piezoelectric sensor systems suitable for detecting trace contaminants in the liquid phase suitable for space-based systems.

### POTENTIAL COMMERCIAL APPLICATIONS

The new, high performance sensor technology would be applicable to a wide range of sensors for chemicals, corrosion and other properties. Environmental monitoring, oil refining, chemical manufacturing, automotive control, and industrial process control are among the potential uses.

**KEY WORDS** (LIMIT 8): Piezoelectric, Sensor, Shear Horizontal, Acoustic Plate Mode, Contaminant

**NAME AND ADDRESS OF OFFEROR** (Firm Name, Mailing Address, City/State/Zip):

TPL, Inc.  
3768 A/B Hawkins NE  
Albuquerque, NM 87109

**PRINCIPAL INVESTIGATOR**

Timothy C. Tiernan

**TABLE OF CONTENTS**

SECTION

PROPOSAL COVER  
PROJECT SUMMARY

1. IDENTIFICATION AND SIGNIFICANCE OF THE INNOVATION
2. PHASE I TECHNICAL OBJECTIVES
3. PHASE I WORK PLAN
4. RELATED R/R&D
5. RELATIONSHIP WITH PHASE II OR OTHER FUTURE R/R&D
6. COMMERCIAL APPLICATIONS POTENTIAL
7. COMPANY INFORMATION
8. KEY PERSONNEL
9. CONSULTANTS AND SUBCONTRACTS
10. SIMILAR GRANT APPLICATIONS, PROPOSALS, OR AWARDS
11. PREVIOUS NASA SBIR AWARDS RECEIVED

SBIR PROPOSAL SUMMARY BUDGET

**1.0 IDENTIFICATION AND SIGNIFICANCE OF THE INNOVATION**

Surface derivatized piezoelectric sensors can detect less than 10 exp. (-11)g of analyte using detectors weighing only 0.02 g with power consumption of 1 to 2 mW per sensor [1,2]. However, piezoelectric sensor technology, has not resulted in the development of the ultra-high sensitivity, microminiature sensors needed by NASA for regenerative life support systems. The reasons include unsatisfactory sensor selectivity, poor sensor baseline recovery, degradation of sensor performance with time, and in the case of the bulk mode devices needed for liquid phase sensors, difficulties in signal processing due to the complexity of the output signal which leads to effects such as mode hopping. TPL proposes to develop innovative sensor architectures, surface chemistries, electronics and software techniques to solve the problems that limit piezoelectric sensor performance. This will lead to a miniature, low power, self-calibrating,



high selectivity piezoelectric sensor system suitable for detecting liquid phase analytes in either ground based or space-based systems.

Chemical derivatization of the piezoelectric device surface with a well-bonded, thin film that is highly selective to species such as organic contaminants in water, gives the theoretical capability for rapid measurements with an accuracy of parts per billion. This is due to changes in the oscillation frequency of the crystal in response to increased surface mass resulting from binding of the analyte to the derivatized crystal surface. The superiority of bulk mode devices in the liquid phase compared to the better characterized SAW mode devices arises from the difference in orientation of the acoustic oscillations through the crystal. The SHAPM waves move parallel to the crystal surface which prevents them from being damped at the interface between the crystal surface and the surrounding liquid.

During Phase I, new electronic and software techniques will be developed for exciting the sensor and monitoring its output. The new substrate will allow sensor refresh techniques to be developed that allow the sensor to be self-calibrating thus preventing problems associated with baseline drift. New methodologies will be developed for analyzing the sensor response that allow major improvements in sensor system selectivity. New fabrication techniques will be developed that make the sensors more durable increasing long-term performance in the field. The new concepts will be used to fabricate prototype SHAPM sensors for detection of organic contaminants such as urea in water samples. This approach will show the feasibility of using APM based sensors for regenerative life support systems.

## 1.1 BACKGROUND

### 1.1.1 Piezoelectric Devices

A piezoelectric sensor has a pair of interdigital finger transducers (IDT) on Piezoelectric substrate [3,4]. The IDT's form an acoustic antenna array which launch and receive surface and bulk waves through an interaction region where wave velocity is altered by surface mass loading (Figure 1). The mass induced change in velocity is then measured either as a change in the transit time of a pulse, a change in phase with respect to a reference frequency, or a change in frequency of an oscillator in which the sensor provides the feedback path.

In order to produce constructive wave generation the finger spacing between the polarity elements must be an integral multiple of the wavelength. For single finger elements the fingers are typically  $\frac{1}{4}$  wide spaced  $\frac{1}{4}$  apart with alternate fingers connected in common. To reduce reflections from the underside of the fingers and to reduce mechanical stiffening due to metalization, fingers  $\frac{1}{8}$  wide space  $\frac{1}{8}$  apart connected in alternating pairs are frequently used. The bandwidth of the resurfacing transducer  $BW = f/N$  where  $f$  is the center frequency corresponding to the element pitch and  $N$  is the number of element pairs. The passband shape is the Fourier transform of the finger overlap with uniform overlap resulting in a  $(\sin x)/x$  band shape being the most common.

The gain of the transducer array is given by,  $G = 4(rA(e))$ , where  $a$  is the effective aperture measured in wavelengths. For rectangular arrays,  $G$  is a maximum for a square IDT pattern. The insertion loss of the array reaches a minimum below a certain bandwidth,  $BW(\max)$ . The minimum number of IDT pairs,  $N(\min)$  required to achieve that bandwidth are shown in Table I.

In an infinity thick substrate only the surface Rayleigh wave (SAW) will be generated. For a finite thickness, three other main bulk modes may be generated, the shear horizontal acoustic plate mode (SHAPM), the antisymmetric shear vertical (A), and the symmetric longitudinal (S) waves (Figures 2). The number of allowed modes, their spacing and velocity are determined from the wave equations and mechanical properties. The electromechanical coupling efficiency of the modes is estimated from the fractional change in velocity  $dV/V$  due to surface metalization.

The amplitude of each type of wave depends on a number of factors including type of piezoelectric material, cut, wave propagation direction in relation to the axis of the crystal and coupling efficiency between the electrodes and the crystal. Figure 3 illustrates the presence of the different wave types at different frequencies.

Analysis of the frequency response of a piezoelectric substrate provides several insights into the problems encountered with sensors based on these devices. For a given device the speed of the various acoustic waves, and the IDT spacing are both fixed. The frequency relationships for the acoustic waves are therefore also fixed. In quartz, if the SAW mode is given a frequency of 1 then the SHAPM mode will have a nominal frequency of 1.12, the asymmetric shear mode will be 1.6 and the longitudinal shear mode will be 1.8

The amplitude of these waves is a measure of the efficiency of the energy transfer of the wave through the crystal. Most sensor research has been conducted using oscillator circuitry to excite the sensor. As analyte accumulates on the sensor surface the frequency response of the device is changed and the oscillation frequency of circuit goes down. Oscillator circuits are simple and inexpensive to build but have serious limitations. They tend to lock onto a frequency the value of which is determined by a fixed tuning of their impedance. However, since the piezoelectric sensors have many frequencies at which they can efficiently transfer energy (i.e. SAW, SHAPM, etc.), it can be difficult to make the oscillator lock on to the desired mode. This is not usually a problem with SAW mode because it has a far higher amplitude than its close neighbor the SHAPM mode. When sensors using the APM modes are attempted, problems with oscillator circuitry become even more difficult to solve. This is one of the reasons why SAW based sensors are more advanced than APM mode devices.

The major problem encountered with APM based sensors is mode hopping [5,6]. Acoustic plate modes are actually a set of waves that cause the crystal to oscillate at a number of slightly different frequencies simultaneously (Figure 4). These frequencies are called modes. As the mass loading is increased the modes will all shift to a lower frequency. A resonator circuit tuned to one mode will track that frequency peak until mass loading causes the next higher mode to become close enough to the tuned frequency of the resonator circuit. At this point the resonator will lock onto the next higher mode and the frequency output by the circuit in response to increased mass will appear to jump to a higher frequency. This is known as "mode hopping". Problems associated with mode hopping have seriously limited the performance of sensors made based on bulk modes.

### 1.1.2 Piezoelectric Sensor Sensitivity

The relative mass sensitivity for piezoelectric devices with thin surface coatings is given by the relation  $S(m) = df/(dm f)$ . In the case of SAW sensors,  $S(m) = Kf$  where  $K$  is a material constant. In the case of zero order bulk waves,  $S(m) = -1/(2M)$  where  $M$  is the substrate mass per unit area. Thus SAW sensitivity increases with increasing frequency while bulk mode sensitivity increases with decreasing substrate mass. In the case of the SHAPM, decreasing mass by decreasing substrate thickness also increases mode spacing. For the antisymmetric acoustic plate mode ( $A(o)$ ) decreasing thickness decreases phase velocity and the operating frequency for the substrate. Decreasing the thickness of APM devices below approximately  $\frac{1}{2}$  wavelength results in poor coupling between the IDT and the acoustic waves.

### 1.1.3 Commercialization of Piezoelectric Sensors

Saw based organic chemical sensors for gas phase detection have been studied by a number of groups including those at Sandia National Laboratories, the Naval Research Laboratory [7,8]. These sensors have proved very sensitive to a wide range of organic vapors. The lack of selectivity, characterized by response to a range of molecules with similar chemistries, was one factor that prevented the majority of the sensors from becoming commercial successes. A second problem encountered during development was poor recovery to baseline when the analyte was removed for the sensor environment.

To date, the only actual commercial product based on piezoelectric, mass sensor technology is a SAW microbalance developed for Langley Research Center by Femtometrics of Costa Mesa, CA. This device actually uses a SAW resonator, a specialty designed substrate that enhances the SAW mode amplitude and refines its frequency response. The device does not use a chemically derivatized surface and is not susceptible to baseline drift due to residual analyte.

Although a significant amount of research has been conducted for the development of APM based sensors, no APM sensor based products are currently on the market. In addition to the drift and long term stability problems

associated with basic SAW devices, APM's have serious additional problems including mode hopping, complexity of the output waveform, amplitude degradation and shift with mass loading and acoustoelectric coupling when used with ionic solutions [9]. The result of this coupling is a reduction in oscillation amplitude to unusable levels. These and other effects make the development of APM based liquid sensors a difficult but potentially highly rewarding prospect.

## **2.0 PHASE I TECHNICAL OBJECTIVES**

The primary objective of Phase I is to demonstrate the feasibility of detecting trace organic contaminants in water by making major advancements in piezoelectric based sensors. Questions concerning the design and operation of the sensor substrate, mechanisms for exciting and reading the sensor, methods of analyzing the data, chemistry of the derivatized surface, priming and binding of the derivatized layer to the piezoelectric, and response of prototype sensors to known concentrations of organic materials in water will be examined and quantified. To answer these questions, the Phase I research will focus on the following specific objectives:

1. Design and fabrication of prototype sensor substrates with the characteristics need for improved performance.
2. Development of new methods for exciting the sensors and monitoring their response.
3. Fabrication of prototype sensors for testing performance enhancement concepts.
4. Testing the response of the sensors to trace organic materials water.
5. Development of a preliminary design for the Phase II field prototype instrument system.
6. Preparation of the Phase I final report.

## **3.0 PHASE I WORK PLAN**

### **3.1 TASK 1 – APM SUBSTRATE DESIGN AND FABRICATOIN**

The first step in developing an extremely high performance sensor system based on piezoelectric sensor technology is the design and fabrication of a piezoelectric substrate incorporating innovative techniques that lead to the required performance capabilities. By analyzing the characteristics responsible for piezoelectric substrate performance it is possible to design a substrate with maximum sensitivity, high signal amplitudes, immunity to mode hopping, and acoustoelectric coupling when used in ion containing liquids.

For effective sensing of gas phase analytes, SAW mode devices have already proven to have most of the required characteristics. The major limitations are involved with inadequate selectivity and baseline drift. APM devices for use in the liquid phase have more serious limitations involving poor signal strength,

difficulty in sensor readout, mode hopping and others. The work to improve sensor response will be applicable to both APM and SAW devices.

In piezoelectric devices, the shear horizontal mode exhibits a cutoff frequency independent of plate thickness given by  $F_c = \frac{C(a)}{l(o)} \sqrt{\frac{C(66)}{\rho}}$  where  $C(a) \exp 2 = \frac{C(55)}{C(66)} - \frac{C(56)}{C(66)} \exp 2$ ,  $C(a)$  is the anisotropic factor,  $l(o)$  is the wavelength,  $\rho$  is the density and  $C(ij)$  are stiffness. For the higher order modes  $F_m = F_c [1 + \frac{m l(o)}{2 C(a) h}] \exp \frac{1}{2}$ , where  $m$  is the integer mode number and  $h$  is the plate thickness. Constructive interference from the IDT requires the bulk mode wavelength  $l(b)$  be related to the emission angle  $\theta$  by  $n l(b) = l(o) \cos \theta$ , where  $n$  is an integer. The velocity of the wave  $v(b) = \frac{f(b)}{l(b)}$ , thus the bulk mode frequency is  $f(b) = n v(b) / l(o) \cos \theta$ , where  $n = 1$  for the fundamental mode. The horizontally polarized wave does not change polarization upon reflection from the surface boundary thus mode conversions do not occur. The bounce length  $L(b) = 2h / \tan \theta$  and the spacing between IDT's is an integral multiple  $nL(b)$ .

The antisymmetric (A) and symmetric (S) waves for certain materials and cuts may support low pass modes where the zero order antisymmetric wave  $A(o)$  phase velocity tends to zero with decreasing thickness while  $S(o)$  approaches a constant. As the plate thickness increases the phase velocity of all modes  $A(n)$  and  $S(n)$  must asymptotically approach the SAW velocity. The vertical shear antisymmetric waves and the longitudinal symmetric waves have displacements in the plane of reflection thus a portion of the energy undergoes mode conversion resulting in vertical shear and longitudinal waves resulting at each reflection. The coupling factor for higher order modes is generally small, thus the zero order modes are of primary interest. For a plate thickness more than a few wavelengths the  $A(o)$  and  $S(o)$  modes are generated almost equally and have velocities very near the SAW velocity. As the thickness decreases the coupling of one or the other may be strongly dominant.

In the case of the piezoelectric crystal  $\text{LiNbO}_3$ , the SHAPM mode is most strongly generated in the Z-cut X-propagating substrate with thickness  $h = 3l(o)$  with angle  $\theta = 21.8$  degrees and  $L(b) = 15l(o)$ . The antisymmetric mode dominates the Y-cut Z-propagating substrate for  $h = l(o)/2$  with a coupling efficiency of 5.6%. The symmetric mode with  $h = l(o)/2$  dominates the X-cut Y-propagating substrate with a coupling efficiency of 15%, as well as the Y-cut X-propagating substrate with a coupling efficiency of 13.5%. Based on the above analysis, a piezoelectric substrate will be designed and fabricated that takes advantage of the effects of materials and physical characteristics on acoustic wave propagation. The device will be of Z cut, X propagating  $\text{LiNbO}_3$ . Its nominal oscillation frequency will be selected such that the pseudo SAW mode enhances the SHAPM providing good SHAPM signal amplitude. The substrate will be thin and low mass to enhance SHAPM mode separation and mass sensitivity. The number of IDT's will be selected to maximize the bandwidth

without causing excess bounce length. The IDT pattern will be square for high gain and use split fingers to minimize spurious reflections (Figure 5).

Another problem encountered with APM liquid phase sensors is acoustoelectric coupling. If there are ions in the liquid under test, the conductive nature of the solution allows the APM to dissipate its energy to the liquid resulting in reduced oscillation amplitude and unacceptable signal to noise ratio for the sensor. TPL has recently examined a solution to this problem first developed at Sandia that appears to have great promise. A very thin layer (20 angstroms) of conductive metal is deposited on the APM surface before the analyte sensitive polymer film is applied. The layer of metal has sufficiently low mass to pose no significant reduction in oscillation frequency and amplitude yet it effectively shields against acoustoelectric coupling when properly grounded.

### 3.2 TASK 2 – SENSOR EXCITATION AND DATA ANALYSIS

The second aspect of APM sensor technology that has prevented high performance is the inability to accurately monitor the response of the device to mass loading. To enhance sensor accuracy and prevent deleterious effects such as mode hopping, TPL will investigate and develop several new approaches for sensor excitation and response monitoring.

#### 3.2.1 – NEW METHODS OF DATA GENERATION AND ANALYSIS

A promising technique for monitoring piezoelectric sensor response involves a circuit which sends a short (approximately 5 us) pulse of high frequency sine waves into the crystal and monitors the time required for the pulse to appear at the output transducer. The frequency of the sine wave will be the nominal frequency of the shear horizontal APM mode for the crystal. The time required for the signal to reach the output transducer is a measure of the velocity of the wave in the crystal. Mathematical analysis shows that mode velocity is directly related to device frequency and mass loading. The uncertainty of the arrival of the signal will determine the degree of accuracy for the mass loading measurement. A number of techniques including a precision voltage comparator, and degree of correlation circuitry between the input and output waves will be investigated in the determination of the accuracy possible with this method.

Recent advances in the speed, and reductions in power consumption and price of microprocessor electronics make possible the use of digital signal processing (DSP) for the determination of APM sensor response. Digital signal processing is a method of refining desired signal characteristics using high speed analog to digital converter circuitry (ADC) and sophisticated, real time, software analysis. DSP can emulate any analog process in addition to providing a nearly unlimited array of linear/nonlinear processing techniques that are difficult or impossible to implement using analog signal processing. The DSP approach involves three areas; stimulation of the sensor to provide information about the resonance peaks, detection of the desired information in the sensor response, and

compensation for spurious sensor responses. These following techniques will be used:

1. Exciting the sensor with an rf pulse and measuring the delay in propagation due to mass loading. When this technique is used with analog circuitry it suffers from the pulse dispersion and subsequent pulse arrival time ambiguity. Transmission line theory provides for the existence of an rf pulse shape that will be relatively unaffected by dispersion. The effects of alternative rf pulse techniques will be examined in order to isolate the correct non-dispersive rf pulse shape. When isolated this pulse shape will eliminate ambiguities in pulse delay by allowing more effective pulse detection techniques.
2. A more effective time pulse detector based on "matched filter" DSP techniques. Given a known pulse shape with unknown delay and amplitude, an optimal pulse detector can be designed providing for very accurate determination of actual pulse arrival time.
3. Using DSP concepts, the sensor can be considered a frequency-filtering element with a response controlled by chemical loading. If a known input signal is used, the effects of sensor filtering can be determined. Auto-regression and resonance peak analysis algorithms will be developed to provide detailed information on the sensor response. Using this information, tracking of many individual sensor resonance peaks will be performed instead of the single resonance peak tracked with standard resonance circuitry that leads to mode hopping.
4. A separate detection of environmental temperature, pressure and humidity factors will be conducted and regression analysis performed on the results. Trends associated with these factors can be compensated for with software once their formats are understood.

### 3.2.2. PATTERN RECOGNITION

Substantial improvements in overall sensor flexibility and reliability can be achieved by relating measurements from several different sensors. Use of multiple sensors can both sharpen selectivity and broaden the range of discernible chemicals. Outputs from the sensor array form a "pattern" which can be compared to other known patterns to deduce the actual concentration of the various contaminants in the environment [10].

Two approaches to this pattern recognition problem will be considered: non-parametric decision theoretic methods and neural networks. These approaches are complementary, the decision theoretic approach tends to decompose patterns by chemical and neural networks evaluate patterns for all chemicals simultaneously without an implied decomposition, Development of high performance pattern recognition is an iterative process with the results of each iteration suggesting methods of improving performance such as the need for new

sensors, the removal of redundant sensors, the need for improved training sets, etc.

1. Decision theoretic pattern recognition assumes that environmental information can be effectively represented by a pattern vector and that given suitable evaluation criteria the pattern can be assigned to a cluster of related patterns. The approach used will be non-parametric in that the distribution of pattern cluster members is not considered to be consistent and will not be used in characterizations. The following efforts will be performed: calculation of pattern normalization, test for redundant sensors, training of discriminant functions, evaluation of sensor importance to overall performance.
2. Neural networks attempt to imitate human pattern matching capabilities. This approach has proven very effective in recognizing complex patterns such as the ones produced by sensor arrays in actual environmental conditions. The following efforts will be performed: selection of network structure and training method, training of the network, evaluation of network to determine the importance of each sensor to overall performance.

### 3.2.3 SELF-CALIBRATION

A major factor in baseline drift not related to environmental effects on the sensor substrate is caused by the accumulation of residual analyte molecules on the derivatized surface of the sensor. A solution to this source of drift is the incorporation of a sensor refresh cycle for the sensor. A cycle would involve refreshing the sensor to a known baseline by actively driving off the residual analyte followed by reading the sensor response to a known, calibrated baseline.

Two methods for refreshing the sensor will be investigated. The first will involve heating the sensor. Since sensitivity is a function of mass per unit area a small sensor can have the same sensitivity as a large one. The amount of energy required to heat a 0.02g sensor would therefore be extremely small and quick to apply. A simple, miniature resistive device would be pulsed by the microprocessor to heat the surface providing the energy needed to liberate residual bound analyte.

A second approach to the refresh would involve the use of conductive polymer films as the surface derivatization. Conductivity in these materials is known to be affected by the degree of oxidation of the polymer. The conductive polymer could be made selective for organics by developing an anionic substituent specific for the contaminant. The advantages of a conductive polymer are twofold. First, transition between the oxidative state and neutral forms of the polymer can be accomplished by the application of a suitable electric potential. This allows the sensor to be actively driven to a known oxidative state where analytes would be unbound from the sensor surface. The polymer film could then be conveniently returned to a known oxidative with known sensitivity free of



residual analytes, thus significantly increasing sensitivity and reproducibility of the sensor. Second, because of the conductive nature of the material, the substrate could be coated by electro polymerization. This allows the film to be actively engineered with respect to both morphology and thickness yielding an extremely thin but porous coating that improves sensor sensitivity, response rate, and recovery time.

#### 3.2.4. ELECTRONIC TEST INSTRUMENTATION

The electronics TPL will use for the evaluation of sensor response will be composed of a network analyzer coupled through an GPIB interface to a high performance frequency counter and a personal computer. The network analyzer is able to excite the input electrodes and sense the amplitude of the output signal over a frequency range of .001 Hz to 500 Mhz.

A personal computer will be used to control the network analyzer and collect the data generated. Parameters such as excitation frequency, voltage and bandwidth will be selected. The output of the network analyzer will be transferred to the PC in both tabular and spectral form for detailed analysis. As the sensors are developed the PC will be able to perform rapid, automated analysis of the data using DSP and other techniques. This will provide the needed information for the calculation of the performance potential made possible with the proposed methods for improved sensors.

### 3.3 TASK – 3 FABRICATOIN OF THE PROTOTYPE SENSORS

Ultimately, the advanced sensor substrates and data analysis techniques will be applicable to sensors for a wide range of analytes. During Phase I, TPL will limit the coating materials use to conductive polymers and the analytes sensed to trace organics such as urea in water. The rationale for this approach is to study the potential for sensor performance based on the improvements outline in this proposal. A suite of refreshable sensors whose outputs are read using sophisticated DSP, pattern recognition, and neural network techniques could form the basis for a synthetic “nose” capable of monitoring a wide range of analytes with extremely high sensitivity and stable long term performance.

#### 3.3.1. – PRIMING THE SENSOR SUBSTRATES

One of the major problems that has limited piezoelectric sensor performance is the lack of long-term stability. Adhesion between the analyte coating material and the piezoelectric substrate surface is critical for high durability. The strongest method for anchoring the sensitive film is to form a covalent chemical bond between the surface and the film. There are several methods that can be used to anchor materials such as polymers or ceramics to the APM device surface. A well-established technology exists for binding materials by derivatizing with silane coupling agents [11, 12], proper choice of silane functionality allows a variety of materials to be chemically attached to glass-like surfaces. Glow discharge plasmas can be used to create the proper surface for chemically binding a variety of materials. TPL has the experience and equipment

to perform these priming techniques. The strength of adhesion will then be determined using standard ASTM mechanical testing procedures.

### 3.3.2. COATING THE PROTOTYPE SENSORS

The sensor coatings must form a reversible bond to the analytes for repeatable long-term performance. Three conductive polymers will form the basis for the substrate surface derivatizations, polypyrrole, polyaniline and polythiophene. Self-doping, organic contaminant attractive side chains will be incorporated to enhance analyte sensitivity without compromising the conductivity of the films.

Polyaniline films will be prepared in 50 ml of 2 M sulfuric acid solution containing 0.1 M aniline. The applied voltage will range from  $-0.1$  to  $+0.90$  volts with scan rates in the 50 Mv/sec range. By varying the duration of the electroplating process it will be possible to adjust the morphology and thickness of the coating to obtain enhanced sensor performance characteristics. Polypyrrole films will be deposited in a 0.2 M potassium chloride solution containing 10 Mm pyrrole. A plating potential of 0.9 volts will be applied for different periods and the results observed and quantified. Other conductive polymers will be electro polymerized using techniques similar to those described. The films produced will be examined by obtaining voltammograms and performing scanning electron microscopy (SEM).

### 3.4 TASK 4 – LABORATORY TESTING OF THE PROTOTYPE APM SENSORS

The test apparatus will allow the prototype sensors to be exposed to a selected level of analyte under controlled temperature and humidity. A glass test cell, approximately 2 cc internal volume, will sensor under test. An aperture at the top of the housing will provide a good glass to sensor seal. Teflon tape will be wrapped around the sensor and glass aperture to produce a gas tight seal. The glass test cell will have Teflon fittings for 1/8 inch diameter tubing which connect it to a precision analyte stream generation system. Separate precision flow controllers deliver a precise amount of diluting material (water) to the mixing system. The sensors will be tested inside a temperature and humidity controlled environmental chamber. Temperature, humidity and pressure will be monitored by computer to determine correlations between these factors and sensor performance. Prototype sensors will be tested by exposure to the selected organics such as urea, at the 20 ppb to 200 ppm levels in water.

### 3.5 TASK 5 – PRELIMINARY SENSOR SYSTEM DESIGN

A sensor system design that incorporates all of the features described above will be formulated with a twofold purpose. 1) To determine the feasibility of the proposed instrument and predict its performance capabilities under actual field conditions. 2) To determine the technical difficulties and costs associated with full development and fabrication so that detailed and accurate projections can be made concerning the fabrication of the Phase II functional prototype of the instrument.

### 3.6 PERFORMANCE SCHEDULE

Task 1 will be completed two months after the beginning of work.

Task 2 will be completed three months after the beginning of work.

Task 3 will be completed four months after the beginning of work.

Task 4 will be completed five months after the beginning of work.

Task 5 will be completed six months after the beginning of work.

Task 6 will be completed six months after the beginning of work.

TPL will provide a final report containing the data, analysis, and conclusions based on the research conducted in tasks 1 through 5.

## 4.0 RELATED R/R&D

### 4.1 RELATED RESEARCH

The proposal research represents an extension of the efforts of TPL in the areas of piezoelectric sensor technology, specialty coatings, surface chemical modification processes, chemical synthesis, and surface chemical characterization techniques. It is also a direct extension of R&D work conducted at TPL and Sandia National Laboratories on acoustic wave devices. TPL has interacted quite extensively with the personnel of Sandia in the development of piezoelectric devices.

In 1991 TPL conducted a Phase I program for NASA with informal collaboration from personnel at Sandia National Laboratories. The focus of that program was the development of an organic contaminant sensor for the drinking water system in space station freedom based on APM piezoelectric sensors. The results were promising in that the prototype sensor was able to detect a number of analytes at ppb levels. However, Phase II was not funded. This was due to a number of factors including unsatisfactory sensor selectivity and poor sensor baseline recovery. The proposed solution to those problems was to incorporate a chromatography unit into the system to separate and concentrate the analytes prior to sensing. That approach was deemed too large, heavy, complex and expensive to be practical for the space station.

Since that program, TPL has made significant progress in the development of theoretical models and realistic approaches to the solution of the limitations of APM based sensor for liquid based measurements. The solutions proposed in this proposal are an outgrowth of that new and innovative thinking. The proposed new APM architecture with enhanced signal characteristics; new methods for self-calibration of the sensor, and advanced techniques for data analysis should make possible the simple, miniature sensor system needed by NASA.

TPL has recently been awarded a Phase II program from NASA to develop a SAW based sensor for hydrazine vapor in air. The goal of that program is a highly specific sensor for use in an environmentally controlled area. The Phase I

program was successful in the development of a surface chemistry with sensitivity to hydrazine.

TPL was awarded a Phase I contract by the NSF to develop a SAW based sensor for monitoring CO(2) concentrations in seawater. A sensor based on the solubility of CO(2) in polyalkoxphosphazene polymers was fabricated and tested and showed significant promise. A Phase II program is anticipated for the development of a field prototype sensor system.

Some of the technology developed during these research programs is applicable to the proposed program and should improve the probability for success. However, the goals of the two programs are fundamentally different since the previous research is based on SAW sensors rather than SHAPM sensors. As previously discussed there are fundamental differences between the two device types. In general APM sensors have far more challenging obstacles impeding high performance but have the potential for use in the liquid phase, something SAW mode devices cannot do.

In addition to chemical sensor research, the Principal Investigator, Mr. Timothy Tiernan, has been involved in a wide range of research for the development of sophisticated instrumentation for automated sensing, and data acquisition. Prior to his work at TPL, Mr. Tiernan was employed at Radiation Monitoring Devices Inc. as the Manager of Biomedical Engineering. While there, he was responsible for research programs aimed at the development of a wide range of instrumentation for a number of applications including non-destructive analysis of fiberglass reinforced composites, analysis of bulk grain supplies using genetic engineering techniques, and development of a complex dosimetry system for flight personnel in low Earth orbit.

## 4.2 REFERENCES

## **5.0 RELATIONSHIP WITH PHASE II OR OTHER FUTURE R/R&D**

### 5.1 ANTICIPATED PHASE I RESULTS

The result of a successful project will be the demonstration of the feasibility of major enhancements to piezoelectric based sensors that will allow them to be used for extremely rapid and accurate analysis of contaminants in liquids. Development of the sensor fabrication and data analysis methodologies for the system during the Phase I program will form the basis for the development and fabrication of a field prototype monitoring instrument during Phase II.

### 5.2 SIGNIFICANCE OF PHASE I TO PHASE II

The phase I program will demonstrate the feasibility of using APM technology to analyze for trace organic contaminants in water. During Phase I, research will focus on performance enhancements for the sensor substrate, new electronics and software techniques for exciting and monitoring the sensor that result in

improved data analysis capabilities, new concept for maintaining sensor baseline stability and long term performance, surface derivatizations based on conductive polymers, and preliminary specifications for pattern recognition algorithms for data analysis. Prototype sensors will be fabricated and examined for their ability to perform the desired measurements in the laboratory.

During Phase II, the design of actual field prototype will begin. The phase I effort will provide the knowledge required to determine realistic performance specifications for the system and these will be fully developed. Sensors that were found to be lacking in certain performance characteristics will be improved. The required electronics will be designed and fabricated so that a complete instrument for automated measurements can be fabricated for field-testing.

## **6.0 COMMERCIAL APPLICATIONS POTENTIAL**

### **6.1 FEDERAL GOVERNMENT APPLICATIONS**

In addition to NASA's need for regenerative life support, a simple yet accurate instrument for detection of organic contaminants in water that could be operated in the field or automatically at remote locations and provide real time data would have widespread application for the U.S. environmental program. It could provide critical information on the status of groundwater, aid in the demarcation of pollution sites, monitor the progress of cleanup efforts and provide data for correlation of water quality and biological activity. The proposed device would be simple and inexpensive enough for widespread use. The concept for the sensor is very flexible and could be applied to a wide variety of contaminants so that the basic sensor system could be used to monitor most of the pollutants found in the environment. It could also be used to evaluate antipollution programs that are being developed to prevent contaminants from entering the groundwater environment.

### **6.2 COMMERCIAL APPLICATIONS**

Piezoelectric based sensors have numerous potential applications. The technology that will be developed with respect to surface treatment, packaging, data collection and analysis and overall performance would be applicable to a wide range of sensors for chemicals, corrosion and other properties. Oil refineries, nuclear reactors, and chemical plants have a large number of situations where sensor arrays capable of monitoring critical parameters would be invaluable. The potential accuracy and sensitivity of the proposed sensor technology suggest that it has the potential for application in many industrial and manufacturing processes.

The number of U.S. companies with interest sensors is extremely broad and includes major oil companies, water districts, automakers, chemical and glass manufacturers and many others. Because the APM sensor provides more potential sensitivity to mass changes than virtually any other chemical sensing technique, and because the surface modification schemes proposed here could

impart these devices with specificity for a large number of materials the potential market is very large.

Follow-on Phase III funding is expected to be obtained from a number of industrial concerns, including the limited partners of the venture capital fund, AMT Venture Partners, Ltd. Of Dallas, TX, that has an equity investment in TPL, Inc. The limited partners of AMT are some of the largest international companies concerned with sensor technology including DuPont – chemical sensors for industry, Showa Shell (Japan) – petrochemical industry, and Lubrizol - lubricant additives. This relationship provides TPL with direct access for probable strategic alliances that will provide the funding for additional development of sensors for specific applications. Under this scenario, TPL is prepared to utilize the technology in-house to manufacture sensors for commercial applications.

## **7.0 COMPANY INFORMATION**

### **7.1 TPL, Inc.**

TPL was established in late 1989 by H.M. Stoller, its President and Chief Executive Officer. It has two major business areas; advanced materials and sensors R&D, and applications of energetic materials. The former is technically directed by Dr. Richard Brotzman, Director of Research, and includes programs in sol-gel ceramics, high technology polymers, chemical and radiation sensors, and reactive chemistry for adhesive applications, the latter is directed by Mr. Stoller. TPL currently has 19 employees and anticipates FY93 revenues in excess of \$2.4 million.

TPL's primary long-term objective is developing commercial products from its research and development efforts. To this end, a financial investment was obtained, in May 1991, from AMT Venture Partners, Ltd, Dallas, TX and its co-investor, the John Hancock Advanced Materials Fund. These venture capital firms and AMT's limited partners (11 international materials related companies, DuPont, Toray, St. Gebain, etc.) provide both the financial backing and strategic business relationships that will help us attain our objective.

TPL intends to remain a highly diversified materials technology company and commercialize its technologies, either through developing a manufacturing capability or licensing, depending on the particular business strategy adopted. A major advance occurred in June, 1992 when TPL was awarded a \$1.5 million contract to continue development of a high energy density storage dielectric polymer. This contract, an outgrowth of an SBIR program, is being accompanied by a TPL-funded business plan development which is formulating a commercialization strategy based on capacitor products.

TPL is pursuing the development of sensors and imaging systems based on novel technologies. Its research in the areas of new radiation detection materials

is expected to play a major role in the commercialization of the instrumentation concepts detailed in this proposal.

## 7.2 FACILITY/EQUIPMENT

TPL occupies over 10,000 square feet of office and laboratory space. Facilities of importance to the proposed program include:

1. Electronics Testing Laboratory containing an HP network analyzer model 4195 A with test kits, HP multi-input data acquisition system, computerized LCR meter, 350 Mhz and 100 Mhz digital oscilloscopes, capacitance meter, signal generator, plotter, impedance bridge, digital multimeters, computerized frequency counters, low and high voltage power supplies with ramp generator, a large selection of passive and active components, a variety of computational, analysis, plotting and database software, thinkjet printer, BP plotter, strip chart recorders, temperature and humidity controlled test chambers, BP microprocessor development system, a variety of data acquisition and control boards for PC computers, PC/AT and Hewlett Packard computer systems.
2. Synthetic Chemistry Laboratory containing hoods, glassware, heaters, balances, and inert atmosphere chambers, which provides the capability to do complete chemical synthesis of advanced polymers and sol-gel ceramics.
3. Analytical Diagnostics laboratory containing a nuclear magnetic resonance (NMR) facility, gas chromatograph, Fourier Transform Infrared Analysis Spectrometer, UV-visible spectrometer, fluorescence spectrometer, Cahn Wet-Tek Surface Energy Measurement System, BloSym Corporation's molecular modeling of materials software and a Silicon Graphics Workstation which provides the capability to perform significant materials analysis.
4. General high bay laboratory space which includes: United Mechanical Test Machine with 1200 degree F temperature capability; 12" X 12" hot press, 30 ton force and 600 degree F; metallography table, chemical hoods furnaces; storage cabinets; electronics laboratory; and sample preparation areas.

TPL is an industrial member of the NSF-sponsored Center for Micro-Engineered Ceramics, University of New Mexico. TPL presently has access to two laboratories at CMEC. The first is a fully equipped analytical chemistry lab which we use for both sol-gel ceramics and polymer synthesis work. The second laboratory contains an ultra high vacuum apparatus for the measurement of diffusion properties in ceramic coatings and optical equipment to conduct strain birefringence measurements in gels and polymers. As an industrial member of CMEC, TPL has direct access to all of their analytical equipment. A summary of this equipment follows: High field liquid FT-NMR spectrometers; GE NT-360, JEOL GX-400, Bruker AC-250P; Low field pulse NMR spectrometers; 10, 20, 4-60 Mhz Hitachi S-800 field emission SEM with low Z x-ray analysis; UNM

Electron Beam Microanalysis Facility, with JEOL 2000FX; TEM with TN5500 EDS, and a JEOL superprobe with 5 spectrometers; UNM Powders and Granular Materials Laboratory, with porosimeters, image analyzer, nitrogen sorption analyzer, particle size analyzers, adsorption instruments, gas permeation apparatus, TGA, DTA, DSC, dilatometer, single-crystal and powder x-ra diffractometers; Temperature-programmed desorption/Auger apparatus; Aerosol reactors for powder generation and gas-phase particle-size distribution analyzers.

The facilities and equipment used in this program will comply with environmental laws and regulations of the federal government, the State of New Mexico and local governments.

## **8.0 KEY PERSONNEL**

### **8.1 TIMOTHY C. TIERNAN – PRINCIPAL INVESTIGATOR**

Mr. Tiernan will be the principal investigator. Mr. Tiernan joined TPL in January, 1991 as a Senior Scientist. He played a major role in the conduct and analysis of the experiments that resulted in the development of SAW based sensors for hydrazine and CO<sub>2</sub>. While at TPL, Mr. Tiernan has also been involved in the development of neutron activation analysis instrumentation for industrial process control, and large pixel arrays made with hydrogenated, amorphous silicon. Mr. Tiernan's extensive experience in the engineering and development of commercial sensor systems and radiation detector products provides the necessary qualifications to direct the proposed program.

Previously, Mr. Tiernan was employed at Radiation Monitoring Devices Inc. as Instrumentation Manager. He was responsible for the development of a range of radiation detection and nuclear medical instrumentation. Under an Air Force contract, Mr. Tiernan led a team of scientists in the development of a complex radiation environment composed of alpha and beta particles, gamma rays and neutrons and provide separate dose information for each type of radiation. A prototype of the instrument was designed, fabricated, tested and delivered to the Air Force for their evaluation.

Mr. Tiernan has also been responsible for the development of instrumentation for commercial products. An example of an industrial device based on radiation detection techniques was the development of a system for analysis of bulk grain supplies. Under contracts with the NIH, instrumentation was developed for a number of nuclear medical applications. Two examples are: instrumentation for the analysis of cerebral blood flow in the intensive care situations and during surgical procedures in the operating room; a small, computerized, battery powered, hand-held probe for the location of radiolabeled tumors during surgery.



Mr. Tiernan has also been involved in the development of a number of radiation detection systems for industry including stack monitors for nuclear power plants, on line controls for nuclear waste storage facilities and coal mining operations.

Mr. Tiernan has also been involved in the development of a number of radiation detection systems for industry including stack monitors for nuclear power plants, on line controls for nuclear waste storage facilities and coal mining operations.

Mr. Tiernan earned his B.S. in biochemistry from the University of Maine in 1979 with a focus on biomedical engineering and instrumentation.

Some of his publications pertinent to the current work include:

1. T.C. Tiernan, K.B. Kidd, R.W. Brotzman, "CO<sub>2</sub> Sensor System for Long-Term Ocean Monitoring," Final Report submitted to NSF, TPL, Inc. Contract No. ISI-9160100, November 1992.
2. T.C. Tiernan, R.W. Brotzman, H.M. Stoller, "High Sensitivity Hydrazine/N<sub>2</sub>O<sub>4</sub> Detector System," Final Report submitted to NASA, TPL, Inc. Contract No. NAS9-18675, September 1992.
3. P. Waer, G. Entine, T. Hazlett, and T. Tiernan, "Small, Remote Cadmium Telluride Radiation Monitor," presented at the Health Physics Society Meeting Boston, MA, June 1988.
4. T. Tiernan, V. Nagarkar, G. Entine, J.G. Hardy, et al., "Portable Solid State, Real-Time Instrument for Space Dosimetry," presented at the Health Physics Society Meeting, Boston, MA, June 1988.
5. T. Tiernan, G. Entine, D.A. Stump, D.S. Prough, "Portable Real Time Analysis Systems for Regional Cerebral Blood Flow," IEEE Proc. Of Nucl. Sci., NS-35, No. 1, February 1988, pp. 698-702.
6. T. Tiernan, G. Entine, D.A. Stump, D.S. Prough, "Intra-Operative Regional Myocardial Blood Flow Monitor," Abstract, Soc. Of Nuc. Med. Symp., San Francisco 1988.

## 8.2 DR. RICHARD O'BRIEN –STAFF SCIENTIST

Dr. O'Brien will perform the chemical synthesis and polymer side chain modifications required to develop the surface chemistries needed for high sensitivity and selectivity to trace organics. Dr. O'Brien has extensive experience in synthetic chemistry with major emphasis on the development of new approaches to polymer modification. His current research involves the development of new types of polyalkoxyphosphazene polymers. He is also participating in the development of new pathways to cubanes.

Dr. O'Brien earned his Ph.D. in Chemistry from the University of Nebraska at Lincoln. He has extensive experience in the synthesis and characterization of organic, organometallic, and polymer compounds as well as significant academic training in these areas. He also holds an M.S. in Organic Chemistry from the

University of North Dakota and a B.S. in Professional Chemistry from South Dakota State University.

Before joining TPL, Dr. O'Brien was a Senior Research Scientist at Rieke Metals, Inc. His research included the preparation and characterization of functionalized organic molecules, organometallic reagents, and a wide variety of conducting polymers such as polythiophenes, poly 3-alkyl thiophenes, poly-para-phenylenes, and poly phenyl ketones.

1. R.A. O'Brien, R.D. Rieke, "Direct Metalation of p-Bromopolystyrene Using Highly Reactive Copper and the Preparation and Reaction of Highly Reactive Copper Bound to an Insoluble Polymer," J. Org. Chem. 55,788 (1990).
2. R.A. O'Brien, T. Chen, R.D. Rieke, "Chemical Modification of Halogenated Polystyrene Resins Utilizing Highly Reactive Calcium," J. Inorg. And Organomet. Polym. 2(3), 345 (1992).
3. R.A. O'Brien, T. Chen, R.D. Rieke, "Chemical Modification of Halogenated Polystyrene Resins Utilizing Highly Reactive Calcium and Formation of Calcium Cuprates in the Preparation of Highly Functionalized Polymers," J. Org. Chem. 57,2667 (1992).

### 8.3 DAVID W. CUTLER – SENIOR ENGINEER

Mr. Cutler will participate in the design of the SHAPM sensor substrate, electronics and software needed for the development of the prototype piezoelectric sensors. Mr. Cutler has extensive experience with mathematical modeling of complex systems, digital signal processing techniques, and the development of sophisticated real time analysis methodologies based on neural networks. Mr. Cutler is currently engaged in the development of chemical sensors for hydrazine and software based image enhancement techniques for silicon pixel arrays.

Prior to joining TPL, Mr. Cutler was employed at E-Systems, Inc. During his 15-year term of employment, Mr. Cutler has held a number of positions covering the hardware, software, and systems designs. Mr. Cutler designed a number of digital control related instruments including a receiver interface for a Watkins-Johnson wideband receiver system, a control unit for a video crossbar switch, computer keyboards, a format convert for a "T1" like TDM multichannel digital audio system, and an embedded controller for a multichannel steerable beam antenna. He was the task leader for the 7-person hardware and software design team on a high integration card tester. This tester provided both debug and production test capability for a set of 13 cards averaging over 100 VLSI and other ICs per card.

Mr. Cutler was a senior team member of a 10-person team that implemented a multifunction receiver/modem. He provided leadership in the creation of a real-time, multiprocessing/multitasking operating system for this modem, implemented the receiver and modem functions, was a technical resource for the

coding of the data stream manipulation and EDAC functions, and provided an interface to other design and systems groups. He was responsible for the design of the "next generation" receiver/modem being designed at his leaving E-Systems.

Mr. Cutler has an M.S. in Electronics Engineering with concentration in Digital Signal Processing from Southern Methodist University, an M.S. in Systems Management from the University of Southern California, and a B.S. in Electronics Engineering from Louisiana Tech University.

## **9.0 CONSULTANTS AND SUBCONTRACTS**

No consultants or subcontracts are proposed.

## **10.0 SIMILAR GRANT APPLICATIONS, PROPOSALS OR AWARDS**

As mentioned previously, NASA has funded a Phase II program for the development of a hydrazine detector and NSF has funded a Phase I proposal for monitoring CO<sub>2</sub> in seawater. Both of these programs are based on SAW mode devices which are significantly different from APM mode sensors. In addition, the focus of those programs is on different types of measurement problems, a different detection medium (gas rather than liquid) and a different emphasis for the resulting instruments which makes that research significantly different from the proposed program for an APM based sensor.

## **11.0 PREVIOUS NASA AWARDS**

NAS 10-11654, "A Repair Coating for Cryogenic Transfer Lines," 1990, Phase I, Kennedy Space Center

NAS8-38909, "Aerogel Processing of Ceramic Composite Membranes," 1991, Phase I, Marshall Space Flight Center

NAS8-38891, "Organic Contaminant Monitor," 1991, Phase I, Marshall Space Flight Center

NAS9-18675, "High Sensitivity Hydrazine/N<sub>2</sub>O<sub>4</sub> Detector System," 1992, Phase I, Johnson Space Center

# **SUPERADHERENT HARD COATINGS BY ION BEAM ENHANCED DEPOSITION**

(FIGURES AND TABLES ARE UNAVAILABLE)

## **2. IDENTIFICATION & SIGNIFICANCE OF THE OPPORTUNITY**

The objective of this proposal is to demonstrate the feasibility of producing superadherent protective coatings at low processing temperatures using energetic ion beams in conjunction with conventional deposition techniques. This process, coined Ion Beam Enhanced Deposition (IBED), is depicted in Figure 1 and promises a new generation of exotic coatings with superior adhesion, near theoretical densities, very high hardness, and, at the same time, capable of being deposited at low temperature. The effect of the ion beam (e.g., N) is to initially "intermix" the deposited atoms (e.g., Ti) with the substrate for superior adhesion as well as to provide energy to the grown layer for effectively "high temperature" processing at low substrate temperatures. Highly adherent coatings of "TiN" with low friction (Figure 2) have already been demonstrated by Kant et al (1) at Naval Research Laboratory by N-bombardment of deposited Ti. This proposal is to extend the range of protective coatings produced by IBED to include HfN, Al<sub>2</sub>O<sub>3</sub> and to characterize such films for mechanical and chemical properties as well as microstructural analyses. Evaluation of mechanical properties will include adhesion tests and wear tests. Initially laboratory pin-on-disc tests will be used for screening purposes with in-situ component tests planned for later. Microstructural analyses deemed necessary include: 1) sputter Auger electron spectroscopy for compositional analysis, 2) sputter ESCA for composition and chemical bonding information, 3) glancing x-ray analysis for lattice structure, 4) ion backscattering for nondestructive composition vs. depth information, and 5) SEM and TEM for grain structure and lattice microstructure information.

### **2.1 BACKGROUND**

There is an acute need for development of high quality, low temperature thin film deposition techniques that can achieve thin film qualities found in high temperature processes. Present low temperature thin film deposition techniques sometimes result in inferior microstructural features within the film such as columnar growth and not the preferred equiaxed grain structure ordinarily found in high temperature processes. Conventional methods of laying down films result in a greater or lesser degree of departure from bulk material properties (density, grain structure, etc.) depending, among other things, on the energy of the atoms as they arrive at and arrange themselves on the substrate surface.

Table I shows the typical energy ranges associated with various physical vapor deposition and ion beam based techniques.

The three PVD processes in the table above, namely evaporation, sputtering, and ion plating are discussed here briefly since eventually any coating produced by a new method, such as IBED, will have to be compared with those in common usage. (2)

Evaporation can be done directly in a high vacuum to provide an extreme range of deposition rates with extreme versatility in the coating composition obtainable.

Sputter deposition, in general, has lower deposition rates than either evaporation or ion plating; however, high throughput production units utilizing magnetron type sputtering are being used industrially. In general the adherence of films deposited by sputtering are better than by simple evaporation because of their higher energy. The wide variety of geometrics employed for various applications by sputter deposition has been recently reviewed by Thornton. (3)

Ion plating is a process largely developed and recently reviewed by Mattox (4) in which the substrate and/or the deposited film is bombarded by energetic (10-100eV) particles. This particle bombardment can significantly affect film characteristics such as: adhesion, morphology, stress and surface coverage. The process is typically carried out in an inert gas plasma discharge with a potential applied to the substrate, although many other variations of the technique have been developed including reactive ion plating. One early benefit recognized for this process is that the atoms in the plasma often undergo considerable scattering and are able therefore to reach surfaces not accessible to line-of-sight processes such as high vacuum evaporation as well as an enhancement of diffusion and chemical reactions without the need for high bulk temperatures. It is interesting to note that the origin of these benefits was at first poorly understood and somewhat controversial, although in intervening years, the importance of the kinetic energy of the bombarding particles and the degree of ionization has been recognized.

#### 2.1.1. ION BEAM ENHANCED DEPOSITION – EFFECTS OF ION BEAMS ON FILM GROWTH

The lack of control as well as understanding of the role particle energy and ionization played in these various PVD processes just mentioned was motivation for at least some workers to conduct deposition experiments where one has independent control of the ion energy and ion type as well as the rate of bombardment (5-11). Several aspects of film growth that have been influenced by ion bombardment during deposition are listed in Table 2.

TABLE 2. Film Growth Characteristics Affected By Ion Bombardment During Deposition

1. Super Adhesion
2. More Uniform Nucleation and Growth Kinetics
3. Lowered Tensile Internal Stresses

4. Improved morphology
5. Controllable Composition

Green and Barnett (12) have recently reviewed the area of ion surface interactions during crystal growth from the vapor phase. Most of the work done in this area thus far has been associated with semiconductors using low energy ions (1keV), to avoid lattice damage. One common goal is to promote lower temperature epitaxial growth of semiconductor films and to incorporate desired impurities for doping purposes. Optical coatings, as mentioned previously, are another current application area for ion beam assisted deposition of these films. Here one objective is to increase the packing density (13) and thereby make the films more stable since they pick up less water from the atmosphere. The following examples of ion bombardment effects on film growth are directed towards non-semiconductor applications, which is the thrust of the present proposal.

Pranevicius (6) demonstrated the effect of ion bombardment on nucleation during A1 deposition, done both with and without simultaneous 5 keV Ar<sup>+</sup> bombardment. Electron microscopy measurements showed that ion bombardment increased the density of nucleation sites by 2X-4X and that the size of the A1 island structures were 3X-15X less in the case of bombarded films.

Adhesion measurements, taken on the A1 films discussed above, showed that improved adhesion results from both surface cleaning and interfacial mixing. Others have seen significant improvements in film adhesion and stress using concurrent ion bombardment. In one such study, Franks et al., (14) used 5 keV Ar<sup>+</sup> ions before and during the first stages of film evaporation of Au on a number of substrates including Si, Ge and Cr, with improvements of adhesion seen in all cases. With regard to stress, Hoffman and Gaertner (15) found that simultaneous irradiation of evaporated Cr with 11.5 keV Xe<sup>+</sup> ions caused a sharp transition from tensile to compressive stress for relative concentrations of Xe exceeding 0.3 at %. At about 1 at % concentration the stress is maximum, and on the order of the yield strength. This stress reversal was accompanied by an increase in the optical reflectance of this Cr film.

Ion bombardment during deposition has also been shown to produce quite drastic changes in structure. For example, Bunshah (16) has reported that ion bombardment changes a normally columnar morphology of metals into a denser, isotropic structure.

Perhaps the most striking change in structure has been the deposition of carbon films with "diamond-like" properties observed either after ion bombardment of carbon films or the deposition of energetic ionized hydrocarbons. It was first seen in 1971 by Aisenberg and Chabot (17) and later by many other groups. The carbonaceous films produced by these methods (termed I-C denoting the role of ions) appear transparent with a high refractive index, quasi-amorphous,

very hard and have high electrical resistivity. Weissmantel et al. (9) have reviewed this area of producing hard coatings by ion beam techniques, including the production of I-BN<sub>x</sub> in attempts to produce cubic-BN, another extremely hard material second only to diamond in hardness. Weissmantel et al. (9, 18) evaporated pure boron in a residential atmosphere of nitrogen, and subsequently ionized and accelerated the resultant species at 0.5-3.0 keV onto various substrates. IR absorption spectra confirmed that B-N bonding states predominate, while transmission electron microscopy and selected area electron diffraction patterns indicate a quasi-amorphous structure; however, high energy deposits contained small crystallites of about 100 Å diameter which had a lattice constant corresponding to cubic BN.

Shanfield and Wolfson (19) present hardness, x-ray, and Auger analysis data supporting the production of dispersed cubic BN by using an ion beam extracted from a borazine (B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>) plasma. Satou and Fijimoto (20) have also reported similar results by using simultaneous boron evaporation and (40 keV N<sub>2</sub><sup>+</sup>) nitrogen bombardment. Using electron diffraction, they have identified microcrystallites of CBN after using specific boron to nitrogen ion fluxes.

Figure 3 shows the hardness of these I-C and I-BN coatings. Although very hard and adherent, the i-C coatings have very high compressive stress which gives rise to crackling and lift-off. Weissmantel (21) suggests using laser glazing or use of graded metal/i-C composite coatings to alleviate this. Such i-C composites, produced by RF discharge, are being tested for both tribological applications (wear resistant coating on video recorder heads) and corrosion protection (electrochemical electrodes).

Studies of the i-BN<sub>x</sub> system are by comparison in a much earlier stage and appear particularly amenable to the use of ion beams. Coatings of I-BN<sub>x</sub> have not yet shown a maximum in hardness when using increasing bias voltages in an ion plating system (22). Hence, energetic ion beams offer a promising way to further explore and develop i-BN<sub>x</sub> and composite i-BN<sub>x</sub> coatings optimal composition and structure.

The roles of ions in thin film growth has been recently reviewed by Takagi. (23) He concludes that the presence of ions produces a remarkable effect on chemical activity, particularly on the critical parameters of the condensation process.

### 2.1.2 CHOICE OF COATING SYSTEMS

The choice of what protective coating to be used for a particular application depends on a number of factors including in part: i) relative coating/substrate thermal expansion; ii) chemical stability of coating, iii) coating hardness, iv) required deposition temperature. The following systems have been chosen to cover a wide variety of anti-wear applications in actual practice.

One principal reason for initially studying TiN is that it serves as a benchmark for any new process, since it is being deposited by a variety of other PVD (physical vapor) and CVD (chemical vapor deposition) techniques for a variety of applications. Secondly, even though such TiN coatings are improving in adherence at lower processing temperatures, there still remain many critical applications where current temperature or adherence criteria are not satisfied.

HfN has a significantly higher hot hardness (i.e. 800-900 kgf mm<sup>-1</sup>) at 1000 degrees C) than does TiN (200 kgf mm<sup>-2</sup>) and is of interest for high temperature cutting application. Its preparation should be a natural succession to TiN because of similar chemical reactivities.

A principal reason for studying Al<sub>2</sub>O<sub>3</sub> is because of the tremendous difference in its theoretical and actual performance. Kramer (24) points out that Al<sub>2</sub>O<sub>3</sub> coatings falls short of achieving theoretically expected lifetimes, as a high temperature cutting tool coating, by three orders of magnitude, whereas other coating lifetimes (TiN, TiC) are in reasonable agreement with theory. Another reason for studying Al<sub>2</sub>O<sub>3</sub> involves its relatively poor adherence to substrates, like many other oxides. The adherence of ceramic coating; are definitely expected to be improved by ion beams, (25) and any improvement in microstructure is expected to help its deficiency in lifetime. (24) Al<sub>2</sub>O<sub>3</sub> has also been prepared by the ARE technique, however, high substrate temperatures (1000 degrees C) are required (2) to avoid growth defects that adversely effect microhardness. It is possible, because of higher surface diffusion during bombardment that significantly lower temperatures will be required to produce dense Al<sub>2</sub>O<sub>3</sub> coatings by the IBED technique.

### **3. PHASE I TECHNICAL OBJECTIVES**

The overall objective of the proposal is to develop the energetically enhanced deposition process and to investigate the quality of the coatings synthesized by this process. The specific objectives of the program can be enumerated as follows:

1. Modify and adapt a commercial electron beam evaporation source to fit inside Spires' metal ion implanter.
2. Operate the simultaneous thin film deposition – ion implantation system and obtain the optimum process parameters for the deposition of hard coatings.
3. Characterize the morphology and microstructure of selected coatings as a function of process parameters.
4. Investigate the mechanical properties of the coatings as a function of process parameters. These include hardness and adhesion properties as well as friction and wear behavior.
5. Compare their tribological properties and their microstructures to coatings produced by other (higher temperature) processes like CVD and PVD.



## 4. PHASE I – WORK PLAN

Phase I research will be restricted to showing feasibility of producing TiN and HfN. Investigation of Al<sub>2</sub>O<sub>3</sub> will be undertaken in Phase II.

The Phase I work plan will include the following tasks for achieving the stated objectives:

### 4.1 TASK 1 – ELECTRON BEAM EVAPORATION SOURCE INSTALLATION AND TEST

In this task, a commercial electron beam evaporation source will be modified as necessary to allow for incorporating it into the vacuum workstation of Spire's Metal Ion Implanter.

After the new source is reassembled inside the workstation, the components of the system will be tested and operated simultaneously. This task is expected to take one month after receipt of the evaporation source.

### 4.2 TASK 2 – TiN and HfN PREPARATION

Initially TiN will be studied but since TiN and HfN are chemically similar, it is planned that the HfN work will start two months after the TiN commences. These anticipated tasks for HfN are the same as for TiN, hence the outline below pertains to both.

First the optimal N ion bombardment conditions and Ti (Hf) deposition parameters to achieve stoichiometric TiN (HfN) will be determined. This will include taking into account the following:

1. Sputtering (ion energy, target geometry, substrate composition)
2. Substrate reactivity (substrate temperatures, incorporation of background vacuum constituents such as N<sub>2</sub> and hydrocarbon contaminants).
3. Film growth processes (grain size, nucleation, internal stresses)

The following measurements will be made in the efforts to produce TiN (HfN): Ti (Hf) will be evaporated at various rates (Å/sec) with respect to the arrival rate of nitrogen ions. It will be necessary to increase the Ti (Hf) deposition rate to compensate for the sputtered particles. The sputtering rate will also depend on geometry (approximately as  $1/\cos(\theta)$  where  $\theta$  is the angle of incidence with respect to the normal).

The variables to be studied for TiN include:

1. Effect of substrate temperature on grain size and on microhardness
2. Effect on geometry on grain size (if any)
3. Effect on ion energy on grain size, adhesion, and composition

X-ray diffraction and TEM will be used to study the microstructure of the coatings produced. Sputter ESCA profiling will also be available on a service basis.

Coatings to be examined by Rutherford backscattering for stoichiometry will be deposited on pyrolytic graphite to allow low background in the spectra.

The mechanical properties (density, morphology, hardness, adhesion, wear resistance, scratch resistance) of the thin films developed in Task 2 will be measured at the Tribology Laboratory of Spire's Surface Modification Center. The optimum process parameters will be identified. A flow chart like the one shown in Figure 4 will be used for this purpose.

#### **4.3 REPORTING**

In addition to day-to-day informal contacts with the program monitor, monthly technical progress reports will be submitted with a complete Technical Progress Report being submitted at the end of each program year, as requested.

### **5.0 RELATED WORK**

The principal Investigator has been involved in pursuing ion beam enhanced deposition for the past two years. At his previous place of employment he was responsible for the conceptual design of a commercial IBED machine and ran a prototype machine for R&D activities on hard coatings (TiN) as well as for commercial service. The PI is in close contact with other researchers exploring the IBED technique for hard coatings for example (21,22).

### **6.0 RELATIONSHIP WITH FUTURE RESEARCH OR RESEARCH AND DEVELOPMENT**

Anticipated improvements in coating adhesion and morphology will be of immediate use where conventional (PVD) coating techniques currently have limitations at lower temperatures. The proposed Phase I work will determine the fundamental IBED parameters to produce adherent, low stress hard coatings in production line lots during the Phase II effort.

### **7.0 COMMERCIALIZATION STRATEGY**

The use of hard productive coatings produced by both PVD and CVD processes is steadily growing in the cutting tool industry as well as for decorative purposes. The trend is towards lower temperature PVD processing generally with an accompanying loss of adherence or desirable structure of the coating. Successful application of IBED processing will eliminate both of these concerns and open up new applications especially for dimensional and temperature sensitive applications such as for precision aerospace bearings.

### **8.0 KEY PERSONNEL**

JAMES K. HIRVONEN

Senior Scientist

EDUCATION:

Ph.D., Physics, Rutgers University, NJ 1971

M.S., Physics, Rutgers University, NJ 1968

B.S., Physics, Syracuse University, 1964

#### CURRENT POSITION AND RESEARCH:

Dr. James Hirvonen is a Senior Scientist within the Materials Modification division of Spire Corporation. He is responsible for overseeing government R&D contracts relating to aerospace applications of ion beam modification of materials and for monitoring process development and control for commercial implantation services. He has more than 18 years of experience involving ion implantation in materials.

#### RELEVANT EXPERIENCE:

Prior to joining Spire Corporation, J.K. Hirvonen was a founder, V.P. and Director of Research for Zymet, a start-up company dedicated to the production of ion implantation equipment for metals. There he was responsible for process control in the service laboratory and was responsible for the conceptual design of the companies first ion beam enhanced deposition machine. In 1971-1982, Dr. Hirvonen was a technical staff member at the Naval Research Laboratory where he headed a seven member technical group (1976-1982) conducting basic and applied R&D on the application of ion implantation for beneficially modifying chemical and mechanical surface sensitive properties of materials.

He has co-written over fifty papers in this area and has edited two books on ion implantation. He organized topical symposia and taught several short courses on this topic as well as speaking at numerous national and international conferences.

## **9.0 FACILITIES/EQUIPMENT**

To support its position as a leader in surface modification technologies, Spire maintains extensive laboratory facilities dedicated to the production and characterization of novel thin films and thin film techniques.

### 9.1 ION BEAM ENHANCED DEPOSITION FACILITY

Drawing upon its extensive background in surface modification technology, Spire has designed a powerful, highly versatile IBED system. The facility consists of a modified EATON NV 10-160 high current (10mA) implanter mated to a Spire designed high volume end station, along with a customized ion beam control system resulting in a highly versatile unit capable of forming nearly any simple compound. The customized end station houses an Airco 4-pocket electron beam turret source (8kW capacity) and an Inficon deposition rate controller.

Evaporation deposition rates range from 3-300 A/sec. The end station with its 27 cubic ft volume can accommodate virtually any part less than 3 feet long, yet can still attain a background pressure of  $10^{-7}$  torr. Ion beams of up to 10 mA intensity from 10-160KeV energy can be generated for a variety of elements and provide versatility in the choice of IBED parameters. Handling of all parts to be coated is done in a Class 10,000 clean area, ensuring cleanliness and quality control (see Figure 6). Temperature control and feedback are implemented via a Williamson 8200 dual wavelength IR pyrometer.

### 9.2 THIN FILM DEPOSITION FACILITIES

In addition to the IBED facility, Spire operates a variety of tin film deposition equipment. Boron nitride has previously been deposited via Spire's MRC Model 8620J RF Sputter facility. In addition, Spire has designed plasma and ion beam deposition systems for in house and service work. For simple evaporated films, Spire has three Sloan electron beam evaporators and one Edwards thermal evaporator. Spire also operates an ion beam sputter deposition facility designed around the needs of its surface modification service area. For additional support, Spire presently operates 6 ion implanters dedicated to a variety of applications primarily in the metals implantation areas. Finally, Spire offers services and equipment sales for application of coating via chemical vapor deposition (CVD, MOCVD, LPCVD).

### **9.3 MATERIALS CHARACTERIZATION**

Spire is well equipped to handle material characterization by photometry, ellipsometry and optical analysis, with elemental and crystallographic analysis being provided by local services and universities. The Spire tribology laboratory is equipped to characterize the mechanical properties of the hard coatings. For hardness measurements, either Tukon microhardness tester or Mhos scratch tests can be used. To measure wear resistance and mechanical integrity, several pin-on-disc testers are available. A Dectak surface profile plotter is available to analyze resultant wear and decohesion areas. Cornell University will be used to provide Rutherford Backscattering analysis and the services of SUNY/at Stony Brook will be used to provide ESM, TEM and x-ray measurements.

### **10.0 CONSULTANTS**

No consultants are presently foreseen for the Phase I program. If a need should arise, Spire has several well-known consultants available from the facilities of M.I.T. Harvard, Boston University and other local universities.

### **11.0 PRIOR, CURRENT, PENDING SUPPORT**

Spire has no prior, current or pending support for a similar proposal.

### **12.0 COST PROPOSAL**

See Attached.

### **13.0 REFERENCES**

# **Sample SBIR Abstracts**

## **ABSTRACT**

Hypoglycemia represents a dangerous acute condition for neonates and for diabetics of all ages. For neonates, careful monitoring of plasma glucose concentrations in at-risk newborns over the first few hours of life has become standard medical practice throughout the nation to guard against hypoglycemia. However, today's state-of-the-art techniques for accurately detecting hypoglycemia do not adequately address the needs of neonates nor of their care providers. In fact, manufacturers are careful to publish the testing ranges for which their systems have been "validated"—which do not include the key hypoglycemic ranges—and some *specifically warn care providers in writing that the systems are not to be used for neonate testing.*

The overall goal of this multi-phase SBIR project is to develop a specialized, economical, hand-held glucose-senor technology that will overcome the limitations of current glucose tests for neonates. We expect to primarily address the 10- to 50-mg/dL range, with a secondary goal of addressing the entire relevant neonate range (perhaps 10 to 90 mg/dL). Our approach for Phase I will be to investigate the feasibility of combining a novel electrochemical sensor technology with a new generation of a proprietary, prototype hand-held point-of-care monitor that has already been developed by our firm. We have assembled a highly qualified interdisciplinary team to carry out this work—which experts in diabetes and neonatal care—and the principal investigator is recognized as a leading researcher in the area of electrochemical devices.

A successful Phase I will lead to a Phase II prototype-development program designed to validate our approach through initial clinical trials and to prepare for follow-on Phase III development, FDA approvals, and ultimate commercialization. The resulting product would serve a significant neonate population in the U.S. (4 million annual births) and a larger international market. Moreover, the technical success achieved would likely lead directly to production of an improved point-of-care glucose-monitoring product for all Type I diabetics who require extremely accurate, reliable, low-cost home-testing capabilities for aggressive diabetic monitoring.

## **ABSTRACT**

A child dies of malaria every twelve seconds. Hundreds of millions of all ages are infected annually. If carried out aggressively, new initiatives for preventing and treating malaria could soon save the lives of one-fourth of those children and could reduce the suffering of millions—and could also eliminate the threat of renewed outbreaks in temperate regions (*including the United States*). In support of those initiatives, we have assembled a highly experienced R&D team that is capable of successfully carrying out an expanded (12-month) SBIR-AT-NIAID Phase I project to develop and apply an innovative, highly sensitive electrochemical sensor-array technology for high-throughput screening for drugs to treat human malaras. As envisioned, this technology will represent a significant advance in the state of the art. The two overall goals are 1) to develop

new sensors and sensor arrays in a microtiter-plate format for direct, quantitative measurement of malarial gene expression in multiple samples, and 2) to demonstrate the utility of the sensor arrays for high-throughput screening for drugs to treat human malarias. The main focus is on developing advanced molecular tools for diagnosis, prevention, and treatment of infectious diseases. Substantial Phase I work in this expanded SBIR project will address the need for high sensitivity, innovative plate and instrument design, and performance evaluation to establish system feasibility – with a focus on malaria as a model that illustrates the power and sensitivity of this new tool for drug discovery.

When scientists can identify drugs that are unique to a stage of growth of a particular microbe, drugs can then be targeted to specific growth stages. Success in this project will provide essential new tools for efficient, economical, high-throughput screening to make this process of drug discovery much more rapid and cost-effective. The market that this technology ultimately will address is clearly a segment representing tens of millions annually within a drug-discovery market that totals some \$5 billion.

## **ABSTRACT**

The Phase I SBIR project addresses the need for a body-powered voluntary-closing (VC) prosthetic prehensor offering variable mechanical advantage (VMA) and passive gripping assist. In this three-phase program, a unique VC design will be developed to potentially assist thousands of individuals for whom existing prehensor designs are unsuitable. VC prehensors have long been desired for their natural and intuitive operation, and their ability to promote proprioception. Unfortunately, engineering difficulties have prevented the creation of practical designs. Using a synergetic combination of VMA and holding assist mechanisms, the proposed device solves the problems of high control cable tension and grip-lock characteristics that have prevented widespread acceptance of VC prehension.

In Phase I, a prototype will be designed, fabricated, and tested with several human volunteers to show that it 1) changes mechanical advantage and locks appropriately, 2) requires less work to use than do existing voluntary opening (Vo) devices, and 3) performs reliably. Limited field-testing by amputees will provide key feasibility information needed for Phase II optimization and full-scale development and Phase III commercialization. We have assembled a highly qualified team of expert to carry out this work. The principal investigator has substantial experience in robotics and prehensor design, and he is teaming with nationally recognized experts in prosthetics research, manufacture, and fitting.

Creation of new opportunities to rehabilitate and restore key physical capabilities for thousands of individuals with upper-limb traumatic injuries, diseases, or birth defects is the primary goal of this R&D project. The proposed prehensor device addresses a clear unmet need for a practical body-powered, voluntary-closing gripping device. Between 30,000 and 50,000 individuals in the U.S. alone desire

restored gripping capability, but existing commercial devices do not work or are inadequate. Given the option of using a practical VC prehensor, many individuals would switch, and others who do not use grippers would start, expanding the market further.

## **ABSTRACT**

Thousands of adults and children suffer from upper-limb deficiencies and rely upon externally powered (myoelectric) prehensors to provide limited gripping capability. Current grippers employ lightweight, miniature drivetrain components to effect grasp, making them both fragile and expensive to repair. They are also expensive to buy. This Phase I SBIR project proposes to replace this traditional drivetrain with an innovative new “solid state” actuator fabricated from an “active” metal alloy. Active materials convert input electrical energy directly into physical work with an efficiency exceeding 90%. This robust actuator will effectively use only a single “moving” part.

The overall goal of this multi-phase project is to make a next-generation prehensor available to individuals of all ages—offering the benefits of lower weight, greater reliability, longer battery life, and substantially lower cost. Advances in material science have yielded new metal “actuator” alloys that have the potential to become powerful, lightweight, high-efficiency grippers. The principal investigator has assembled a team of experts in materials science and will combine their expertise with his own in mechanical engineering, robotics, and prosthetics to successfully demonstrate Phase I feasibility of this novel concept.

In Phase I, a prototype prehensor will be designed, fabricated, and tested extensively to demonstrate the feasibility of using active materials to power a class of grippers offering 1) small sizes specifically tailored for children’s grasping needs, and 2) the robust, reliable performance required by many adults with active lifestyles.

This new generation of externally powered prehensor is expected to meet the needs of thousands of individuals who will welcome the combined benefits of natural appearance, higher performance, and lower cost. While the existing marketplace for myoelectric hands is significant, this new device will likely expand the total marketplace to a number of first-time users who are attracted by the range of new benefits being offered—thus improving the lives of tens of thousands in the U.S. alone.