MIDWEST RESEARCH INSTITUTE

REPORT

THE PRODUCTION OF ULTRATHIN POLYIMIDE FILMS FOR THE SOLAR SAIL PROGRAM AND LARGE SPACE STRUCTURES TECHNOLOGY (LSST)

A Feasibility Study

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FINAL REPORT

MRI Project No. 4437-N

JPL Contract No. ~~954489~~ 954849

For

JET PROPULSION LABORATORY
California Institute of Technology
4800 Oak Grove Drive
Pasadena, California 91103

MRI—NORTH STAR DIVISION 10701 Red Circle Drive, Minnetonka, Minnesota 55343 • 612 933-7880

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by

R. H. Forester

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PREFACE

MRI successfully carried out a program on JPL Contract No. ~~954489~~ 954849 to demonstate the feasibility of large scale, continuous production of ultrathin polyimide films using the MRI-developed technology of casting the film from solutions on a water surface. The facility was erected and several batches of continuous, two-feet-wide polyimide films about one μm thick were prepared and delivered to JPL. The solar sail also requires that one side be a good emitter of heat. Films impregnated with finely divided carbon black were also prepared. Because the facility can produce two films simultaneously and laminate them, the carbon black-filled polyimide films were laminated to clear polyimide films.

The films described in this report also have potential uses in the Large Space Structures Technology (LSST) programs.

This report also discusses the costs of full-scale production and metallizing of these films.

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Approved:

for Ronald Rengel
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INTRODUCTION

The objective of this program was to demonstrate the feasibility of the continuous production of thin polymer films with sufficient stability to high temperatures to satisfy the stringent operating requirements of a solar sail mission.

The polymer films would be metallized on the sun-facing surface to provide a high reflectance, thereby maximizing momentum transfer from the photon pressure to the sail. The background of solar sailing and the details of a system design are described in Reference 1. The critical technology for any solar sailing mission is an ultralight sail materials system. This system must be capable of sustained operation at high solar intensities (high temperature, high radiation) since the benefits accrued from the mode of propulsion are most favorable whenthe spacecraft gains increased momentum during near-sun encounter and then spins off towards its mission objective.

CONCLUSIONS AND RECOMMENDATIONS

MRI has successfully demonstrated the feasibility of large scale production of very thin polyimide membranes at reasonable costs; the cost of production is estimated at about 50¢ per m^2 (plus the cost of the polymer). While polyimide films were necessary for solar sailing, because of the high heat and radiation resistance requirements, there are probably other space applications for these thin films where high performance commercialized polymers, such as polysulfone, could be used. MRI suggests that the films described in this report could well be used in space missions requiring large collectors, antennas, screens, etc. The Large Space Structures Technology (LSST) program may well require such large structures.

There are two problems to be resolved for the use of the MRI thin films as a solar sail or in LSST. The first is adapting the film and paper composite so it can be carried through a vacuum metallizing system without excessive damage from overheating or from damage caused by running the film over rollers. The second problem is to develop assembly systems which involve development of adhesive and fastening techniques and the removal of the paper support. Finally, methods for manipulating large membrane devices and their packing and deployment would have to be developed. MRI considers none of these problems particularly difficult and bases this statement on MRI's extensive experience with ultrathin membranes.

In conclusion, MRI submits that ultrathin polymer films could have wide application in space programs. The MRI production method can prepare films using a variety of polymers and the films have a moderate cost per unit area. The large areas required for the solar sail or in LSST missions would weigh significantly less if MRI ultrathin films were used rather than conventional films.

THE ULTRATHIN FILM PROCESS

Ultrathin films have been investigated by the North Star Division of MRI for over ten years. A number of patents have been issued to MRI as a result of this work.(2-4) The preparation of such thin films is relatively simple. The polymer of interest is dissolved in a solvent which is soluble in water. The polymer solution (or casting solution) is allowed to flow down an inclined ramp onto a water surface where a pool of floating polymer solution develops. Solvent dissolves into the water lowering the surface tension of the water. Consequently, the contact angle of the polymer pool is very low and the edge of the pool is very thin. Solvent dissolves from this thin region too rapidly to be replenished from the bulk of the pool and a solid polymer film forms. Film formation is rapid and spontaneous and the film will spread out, unaided, many feet from the leading edge of the pool. The driving force for this process is the exothermic solution of the organic solvent from the polymer solution into the water.

The range of film thicknesses which can be achieved by this process varies from well under 0.01 μm to greater than 1 μm. Thickness is controlled using a combination of three factors: (1) the viscosity of the casting solution; (2) the rate of removal of the cast film; and (3) the temperature of the water on which the film is prepared. For example, thick films are prepared by using a high viscosity solution, a slow rate of film removal and a hot water bath.

Film formation can be inhibited by pre-existing surface films (e.g., films of oily contaminants or surface active agents) or an aqueous phase saturated with solvent. Films cannot be formed using solvents with little or no solubility in water. Neither can they be made if the aqueous-nonaqueous roles of the film-formers are reversed, i.e., using a water-soluble polymer in an aqueous solution and casting on a solvent bath using a solvent with limited water solubility. Solvents which are too soluble in water are not useful; the solution instantly gels on the water surface rather than forming a pool.

The cohesive strength of the polymer must be sufficient to maintain the integrity of the film. With certain low molecular weight resins, for example, the "film" becomes a surface dispersion of dust-like particles.

Thus, it can be seen that while the film formation system is relatively simple, the requirements for the polymer and its solvent are restrictive. Among the common, commercial solvents, there is one which is powerful, active and with the proper solubility in water--cyclohexanone.

In the past, these films have been subjected to a number of physical characterization studies. Thus, MRI has employed the transmission electron microscope to examine a wide variety of ultrathin films. No structure could be observed at the highest magnification available (about 40,000 X). In fact, the films were so perfect that a considerable area had to be examined under the microscope until a bit of dirt could be found with which the microscope could then be focused.

The water content of a freshly-formed film varies considerably with the polymer used. For example, the polyimide polymers used in this project formed films with so much water that they were hazy. The addition of a few weight percent of a solvent with little or no water solubility renders the as-formed film much more hydrophobic and clear films can be formed. Two hydrophobic solvents were investigated: toluene and methylene dichloride. These were added to the casting solution at the level of 5 and 10 weight percent of the solvent weight in the solution. Methylene dichloride is a solvent for the polymer and toluene is not. However, toluene is tolerated when added at sufficiently low levels. The films prepared with toluene were judged superior to those prepared with methylene dichloride and much better than the films prepared from solutions without the hydrophobic additives. The films containing toluene displayed a highly reflective surface and interference colors which were clear and sharp.

EXPERIMENTAL RESULTS

Thin Film Production Facility

MRI has had considerable experience in the development of thin film production facilities, both bench and pilot scale. The thin film production facility for this project was a modification of other such devices MRI has previously assembled. This facility can continuously retrieve one or two films from a water surface as they are formed. A sketch of the facility is shown in Figure 1. In operation, a roll of paper is mounted on the unwind stand and the web of paper is fed through the device to the windup roll. The type of paper is not critical but MRI has selected papers with two criteria. The first criterion is for convenience; a paper with a wet strength additive to prevent breaking when the paper web gets wet either by accident or at startup of a run. The second criterion is a thin paper. This maximizes the amount of thin film that can be carried on a roll into a vacuum metallizing system. A satisfactory paper is a tissue manufactured for tea bags.

At the midpoint of the casting tank the web is brought close to the water surface where the freshly developed film is picked up and carried on the top surface of the paper to the windup roll. The clearance between the pickup roll and the water surface can be varied from zero to one cm.

Two overall photographs of the device from opposite directions are shown in Figures 2 and 3. Figure 4 is a photograph of the thin film formation area showing the solution ramp at right and freshly formed film on the water surface, moving towards the pickup point at the left of the photograph. Figure 4 also shows the solution feed system. This system consists of a pressurized reservoir and a feed tube. Solution feed rate is controlled by varying the pressure on the reservoir. The feed tube can be seen in Figure 4 at the right-hand side of the ramp just above it. The tube is driven back and forth above the ramp by a chain drive which is powered by an SCR, variable speed motor. Adjustable left- and right-traverse limit switches control the distance that the feed tube travels across the ramp. This, in turn, controls the width of the solution pool and hence the width of the film sheet. The reciprocation mechanism is also equipped with adjustable time delay relays that can vary the stop time at each end of the

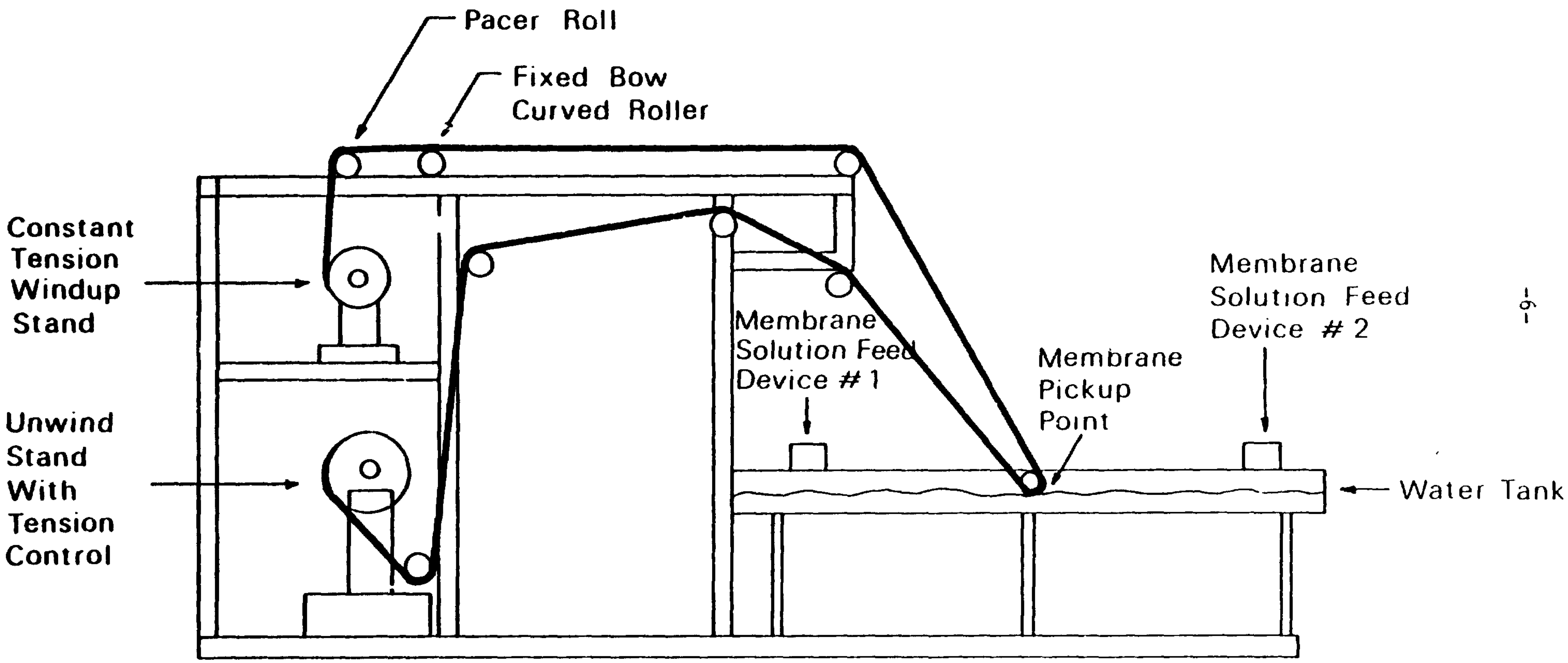

Figure 1. Thin Film Production Facility

Figure 2. Overall View of Membrane Production Facility

Figure 3. Overall View of Membrane Production Facility From Opposite Direction

ERRATUM

The Photographs, Figures 4 and 5 are Interchanged.

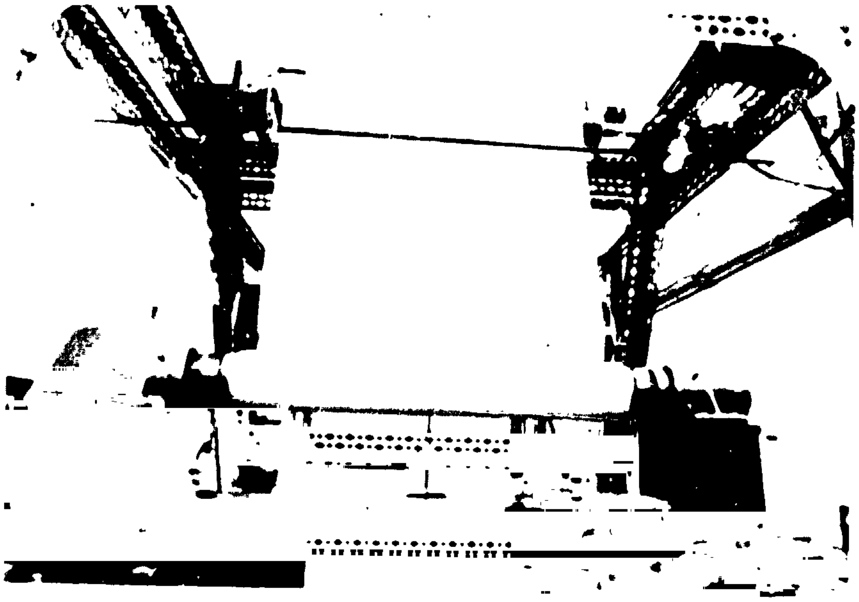

Figure 4. Membrane Casting and Formation Section

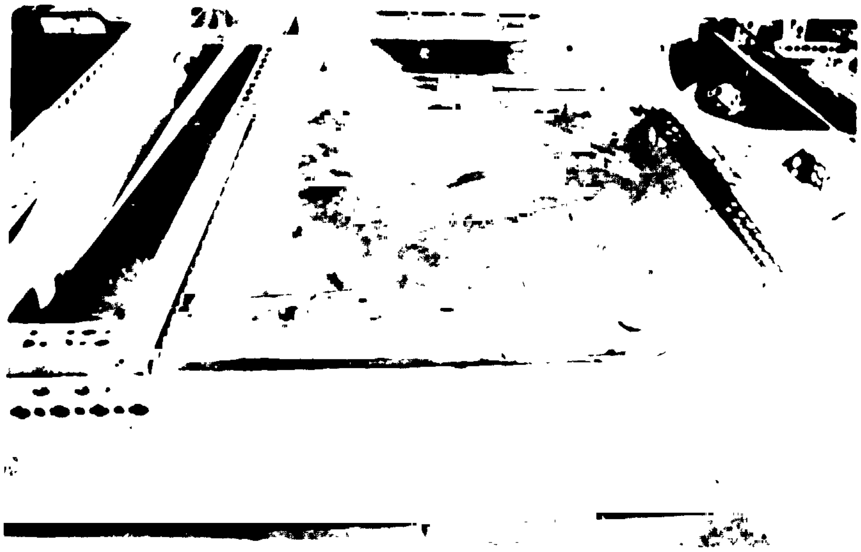

Figure 5. Membrane - Paper Composite Entering Windup

stroke. This stop time control is useful with some casting solutions to maintain a uniform pool of solution on the water surface.

Figure 5 is a photograph of the film-coated paper entering the windup station.

The web handling system is equipped with an automatic tension control on the windup stand, an adjustable speed pacer roll, and a constant tension windup. These controls and a speed read-out are housed in a separate control cabinet. The facility also includes a footage counter.

The velocity of the web can be varied from about 75 cm per minute to about 300 cm per minute. Sufficient power is available for higher speed driving by changing sprockets on the chain driven pacer roll.

The facility has space for, but is not equipped with, a drying unit and a paper web dampening unit. These devices are useful for the production of continuous rolls of film. In this mode, the system takes advantage of an adhesion property of the film; i.e., a thin film applied to a water-wet surface will adhere to that surface when it dries. The adhesion of the film to a water absorbing surface, such as a paper, can be controlled by adjusting the water content of the paper. In operation, the paper is dampened before the film is applied and dried after the film-paper composite is formed. This composite may be used for continuous film treatments such as the application of specialized coatings in vacuum systems.

Thin Film Materials

Polymers

The polymer of greatest interest was Ciba-Geigy's polyimide, P-100. The molecular structure of this polymer includes a variety of heterocyclic units which render the polymer soluble in a variety of common solvents including cyclohexanone. The latter is the solvent of choice for film formation when the MRI system is used.

The statement of work also called for films to be made with E.I. duPont's Liquid H. This material is, as the name implies, a liquid. It is a polyimic acid precursor of a polyimide which can be made into a solid film by curing with heat. The MRI film formation system cannot form films from liquid materials and no work was done with Liquid H.

Other polyimide materials were investigated. A sample of Upjohn's Polyimide 2080 was obtained but it proved to be insoluble in any solvent system useful in the MRI film formation system.

An attempt was made to obtain experimental polyimide materials that were reported by workers at Ashland Chemical Company. The results of this research were sold to Monsanto Chemical Company and Monsanto personnel reported that Monsanto has no current interest in, nor production of, these polymers. These polymers are apparently quite similar to the Ciba-Geigy materials. Films were also prepared using Ciba-Geigy's B-100 polyimide, a polymer similar to P-100 but with somewhat lower heat resistance. In addition, films were prepared using a Union Carbide polysulfone. This polymer has only moderate heat resistance but forms films that have excellent physical properties.

Quantities of B-100 and polysulfone films were shipped to JPL in addition to three shipments of the P-100 film. Each shipment consisted of about 100 meters of membrane with a usable width of 50 cm. All the films were about one μm thick.

Casting Solution Preparation

The preparation of film casting solutions is simple. Measured amounts of solvent and polymer are stirred until dissolution of the polymer is complete. Heat accelerates the process and is also desirable to drive off any water that the polymer and water absorb in storage. The solution is then filtered. This was particularly necessary when P-100 solutions were made since the starting material had been produced on a laboratory scale and was not very "clean." After filtration, minor amounts of low boiling solvents were added to improve film characteristics. These solutions appear quite stable when stored at room temperature.

The concentration of polymer in solvent is one of the parameters that is used to control film thickness. One objective of this project was to prepare films at least one micrometer thick. This is a thick film for the MRI process and required solutions with maximum polymer concentration. There is, however, a limit in solution viscosity which, if exceeded, will not permit film formation. For P-100 and B-100 solutions, the maximum usable viscosity was about 1800 cps. This viscosity is reached with about 13 weight percent of P-100 in cyclohexanone-toluene solvents and about 11 percent B-100 in the same solvent.

Radiation-Emitting Films

To prevent the solar sail from overheating during its journey in space, it is desirable that the front surface be a good reflector (i.e., poor absorber of solar radiation) and the back surface be a good emitter. An aluminized coating would provide a reflector for the front surface. For the back surface, one approach would appear to be impregnation of the polymer film with a dispersion of carbon particles. Carbon black is a good emitter. A dispersion of carbon black in a film could provide a useful emissive surface, although the actual surface of the film would be a polymer which, in itself, is not a particularly good emitter. When the layer of polymer over a particle of carbon black is very thin, it has only a minor effect on the emissivity of the carbon black. It is important that the size of particles dispersed in the film be as small as possible, in order to preserve the mechanical strength of the film. Carbon black is available with ultimate particle size diameters in the order of 0.015 μm which is relatively small when compared to the one μm thick film. Such carbon blacks are notoriously difficult to disperse. Normally, dispersion is carried out using high polymer concentrations and high When high molecular weight polymers are involved, such as P-100, dispersion becomes more difficult.

MRI has developed a carbon black dispersion system useful for preparing carbon black-filled films in quantities large enough for the small-scale production required in this program. In the MRI process, a viscous solution of P-100 solution is prepared and placed in the mixing head of a Braebender Plasticorder. This mixing head contains two blades that turn at different speeds. Enough carbon black was added to form a very viscous paste--viscous enough to be a near-solid. The dispersion was then reduced with P-100 solution in a high shear mixer (a Waring Blender) until a usable dispersion was obtained. This process is commonly carried out in industry using somewhat different equipment in which better dispersions can be obtained.

The resulting dispersion was used in the film production facility and the resulting film was applied to a P-100 membrane that was cast simultaneously from the other end of the formation tank (see Figure 1, where the two casting stations are shown).

COSTS AND DEVELOPMENT OF A FULL-SCALE THIN FILM PRODUCTION UNIT

Costs and Film Capacity of a Single Production Unit

The thin film facility shown in Figure 1 would need to be replicated in a wider version for a full-scale production unit. Table 1 shows an estimate of the annual production of such a device that would produce about one-third of the material required for a solar sail--nominally 10^6 square meters.

Table 1. Annual Production Capacity and Estimated Cost Per Production Unit

Working Days	250
Shifts Per Day	2
Production Rate	1.2 m per min
Production Width	1.25 m
Annual Production Per Production Unit	350,000 m^2
Estimated Cost Per Production Unit	$20,000

A solar sail production unit would require the addition of two sections that were not included in the MRI demonstration facility; a section to control film-to-support adhesion and a film-support drying section. A description of these sections follows.

Film-Support Adhesion Control

A film of polyimide, two-micrometers thick, is not rugged enough to be manipulated on contemporary roll-to-roll web handling systems such as is found in vacuum-coating equipment. Another major problem would be the static charge developed when a roll of two-micrometer film is unrolled. The static charge forces are greater than the film can tolerate. For these reasons, MRI has employed a tissue support which acts as a carrier for the prepared film through any subsequent treatments.

If a film is simply picked up on a tissue support and the resultant composite film is dried and rolled up, the film will be essentially unattached to the tissue. If, on the other hand, the tissue is wet and the film/tissue composite is dried before rolling up, the film adheres strongly to the tissue. What MRI has discovered is that the amount of water in the tissue can control this adhesion. It has also been discovered that roll-to-roll vacuum metallizing requires only minimal adhesion. Such minimal adhesion results in less film damage than that caused in passing through roll-to-roll devices. In practice, MRI has found that relatively large areas of membrane can be completely free of the support during metallizing; at least in the metallizing system that was used during a program requiring the production of many thousands of square meters of aluminum-coated membrane.

The application of a controlled amount of water to the tissue support can be done using transfer rolls. In its simplest form, such a device consists of a roller partially immersed in water that also is in contact with the paper. More precise control of the amount of water applied can be achieved by addition of one or two intermediate rollers whose contact pressure can be adjusted to transfer more or less water to the tissue.

Film-Support Drying Section

The lightly dampened tissue and film composite is readily dried by simple radiant heating. More troublesome are drops of water on the film. Such drops are quite difficult to remove and MRI has found it simpler to wind them up into the final roll where they are absorbed by the dry tissue. The small amount of moisture is wicked over a wide area of the paper and can be readily evaporated in a second drying step.

Total Production Costs Including Raw Materials

The estimate of total cost for producing 10^6 m^2 per year is shown in Table 2. An explanation of the various line items follows.

Production Units

As described in the preceding section, one production unit would produce about 350,000 m^2 per year and three would be required. It is estimated that such a unit would cost about $20,000 and would include the features shown in Figure 1 plus a drying section and an auxiliary drying unit. This relatively low cost is in large part due to the low web speed of the system. A low web speed requires small motors, a light framework, simpler rollers, etc. A three-year lifetime is proposed for the equipment. Hence, the $20,000 annual charge.

Labor

It is estimated that three machines would require only one operator. A half-time worker would prepare the filter solutions, do control tests, etc.

Polymer

One million square meters of film, 2 μm thick, is two cubic meters of polymer. Assuming a density of about 1.5 g/cc, 3 metric tons of polymer would be required. This is a small amount of polymer and the assigned unit cost of $50 per pound for Ciba-Geigy's polyimide P-100 may be overly optimistic. Note that this cost plays a major role in determining the unit cost of the product.

Table 2. Annual Production Costs (10^6 m^2, 2 μm thick, polyimide film)

Production Units (3 each)	$ 20,000
Labor (1-1/2 persons)	40,000
Polymer at $50 per pound	330,000
Solvent at 40¢ per pound	20,000
Paper Support at 5¢/m^2	50,000
Utilities, Space, etc.	10,000
	$470,000
Overhead & Profit	230,000
Royalties	100,000
Total	$800,000

Cost of Film = 80¢/m^2

Solvent

The current price for cyclohexanone in the Oil and Drug Reporter is about 40¢ per pound. About 75 percent of the casting solution is cyclohexanone with the remainder being polymer and toluene. It may be practical (or required) to recover the cyclohexanone from the casting bath. This would result in a capital outlay for a solvent recovery system; probably based on adsorption on (and recovery from) activated carbon. This outlay would be largely offset by the ability to use recovered solvent which usually costs a few cents per gallon.

Paper Support

The cost estimate is based on using a high wet-strength tissue which is commercially available as a tea-bag paper. It is in the order of 3×10^{-3} cm thick and costs about $2.00 per pound. Such papers are sold on a "basis weight" which defines a ream as being 480 sheets, each sheet being 24 x 36 inches, and the ream weighs about 3.3 kg.

Royalty

MRI is the owner of a patent covering the production of ultrathin membranes and would expect to receive some royalties from commercial production. For cost purposes we used a royalty of 10¢ per m^2, although we have no precedent for such an amount. The line item in Table 2 is only indicative that such an item would occur in production costs.

Utilities, Space, Etc.

We have assigned a cost of $10,000 to this item. Very little would be required beyond a simple, open space and most of the utility bill would be consumed by the dryers. The casting section must be provided with proper ventilation.

Overhead and Profit

As can be seen from Table 2, the unit cost of the film is mostly material costs and we find it difficult to assign a reasonable overhead and profit cost. It can be assumed, however, that at least a man-year of professional and managerial staff time would be consumed in the design, assembly and startup of the production facility and these costs do not appear in the production costs. Therefore, we have arbitrarily set the overhead and profit item equal to one half the production costs. This results in a film cost of less than one dollar ($1) per square meter.

Metallizing: Capabilities and Costs

About two years ago, MRI undertook to find vacuum metallizing companies that could apply closely controlled thicknesses of aluminum and nickel to very thin polymer films. Two companies were found. The first, the Dunmore Corporation, New Town, Pennsylvania, was capable of applying closely controlled amounts of aluminum and chromium using a feedback system to control the metal application rate. The other company was 3M Corporation, St. Paul, Minnesota.

At the time of this search, MRI was interested in metallizing tests on rolls of film on the order of 30,000 meters in length. Prices of about 50¢ per linear meter were quoted for the pilot runs.

Two of the problems of vacuum metallizing thin films are the effects of radiation from the molten metal source and the heat of condensation of the metal on the polymer film. Commercial metallization of most films has been done to provide decorative Mylar material and thick coatings of aluminum are applied from ceramic boats of molten aluminum. Apparently, some of these operations use a large water-cooled roller to carry the film past the region where metal is applied.

In work at MRI, aluminum coatings have been applied *in vacuo* to small samples using electrically heated aluminum filaments and polysulfone films in the order of 0.5 μm thick. No attempt was made to provide a heat sink for the films. Attempts to apply aluminum layers, 0.1 μm or thicker, resulted in films that shattered into fragments when removed from the vacuum chamber. However, aluminum coatings in the order of 0.04 μm were applied without apparent damage to the film. It would appear, therefore, that 0.05 μm thick aluminum coatings could be readily applied to 2 μm films mounted on tissue in a standard roll-to-roll vacuum system.

Film Construction Techniques

The manipulation of ultrathin films requires special techniques. MRI has never found any satisfactory method to manipulate free, unsupported membranes. If the films are dry, static electricity causes the film to cling to itself and other surfaces with forces strong enough that further attempts at manipulation cause severe damage. If the films are wet, surface tension of the water tends to roll up the film. Therefore, films have been carried through any processing mounted on a support. Thin, high wet strength tissue papers have proven to be the best material for this purpose.

Metallization of the film drastically alters its manipulation characteristics. The application of as little as 50 Å of aluminum to one side of the film eliminates the problems of static electricity. A piece of aluminized film can be readily crumpled and unfolded by hand. It would appear, therefore, that fairly large sheets of two-micrometer thick, aluminized film could be readily picked up, carried and attached to a structure. It is doubtful, however, that such a film could be run on standard roll-to-roll equipment. The film would have to be processed and carried to the point of use on a tissue support. At that point the film could be freed from the tissue by dampening the tissue with a mist of water or stream. Some experimentation is obviously necessary to develop a usable technique.

The assembly of large film structures will require methods of sealing the film to itself and the supporting structure. In discussions with JPL personnel, it was learned that JPL has sealing requirements for the solar sail which MRI has never considered and that JPL has advanced this work beyond the point where MRI can make any useful suggestions.

The annual quantity of 10^6 m^2 is small when compared with typical film production and could well be considered a pilot plant production. Whether or not MRI would be willing to undertake such an endeavor is uncertain. A recently formed company, FilmTec Corporation (Minnetonka, Minnesota) has management and technical personnel that have had considerable experience with the large-scale production of ultrathin films using the MRI technique. This company has expressed interest in commercially producing ultrathin films.