1. Project Title

Development of New Technology of Electra- and Heatconductive Metallized Polyimide Constructs with High Reflectivity

2. Project Manager

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3. Participating Institutions

3.1. Leading Institution

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3.2. Other Participating Institutions

Participant Institution 1

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Participant Institution 2

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4. Foreign Collaborators/Partners

4.1. Collaborators

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5. Project Duration

36 months

6. Project Location and Equipment

Institution	Location, Facilities and Equipment
Leading Institution	Institute of Chemical Sciences **106 Walikanov Street, Almaty, Kazakhstan** Totally – 6 spacious rooms (#126, 130-134, 140) 1. Termogravimetry Analyzer (TGA) Metler-Toledo Star 2. IR-spectrometer Jasco IR-810 3. UV/VIS-spectrometer Jasco UV/VIS 7850 4. Melting TA Metler-Toledo FP900 5. Microcalorimeter Metler-Toledo SDTA 851 6. NMR-spectometer Varian
Participant Institution 1	Al-Farabi Kazakh National University, Department of Chemistry (1), **95a Karasay Batyr St.** and Department of Physics (2), **96a Tole bi St.** Totally – 2 laboratories, including 1 auditorium and 5 rooms 1. Universal electrochemical station AUT 30 Ecolab 2. Coupling to AUT 30 with contact electrodes 3. Ionometer 4. Universal station for measurement of current, voltage and resistivity S302-S68003 5. Spectrofotometer for measurement of reflectivity SF18 Lomo 6. Voltmeter universal with contact electrodes 7. X-ray small angle spectometer
Participant Institution 2	Academician I. Vekua Sukhumi Institute of Physics and Technology**, 0108, Rustaveli Ave 52, Tbilisi**. The Project will be conducted at the Institute of Physics and Technology, in the building of Academy of Sciences of Georgia (rooms#202,403 office facilities), 0108, Rustaveli Ave 52, Tbilisi and in the building of the Institute of Mining Mechanics Academy of Sciences of Georgia (rooms#438,442,449, experimental and measuring devices), 0116, Mindeli str.7, Tbilisi

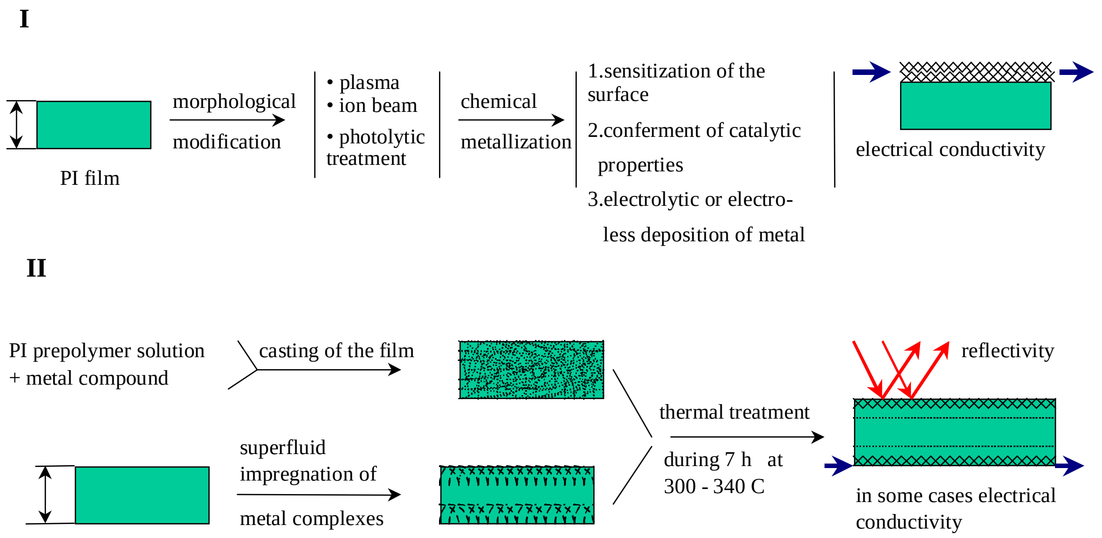
II. Specific information

1. Introduction and Overview

The development of the whole class of heterocyclic polymers, polyimides particularly, determines the progress in the creation of thermal and radiation stable polymer composites that have been used in airspace apparatuses, micro- and radio electronics. Scope of mechanical, dielectric and radiation durability of polyimides (PI) set new tasks for expansion of their application range by way of imparting specific physical properties to the materials on their basis. The imparting of such properties as electric and heat conductivity, magnetic activity as well as optic properties to the polyimide materials are related to the formation of metallized polyimide films. But the most classic methods of polyimide films metallization are not acceptable for polyimides and are of principal difficulty because of their low adhesion that is limited by chemical structure.

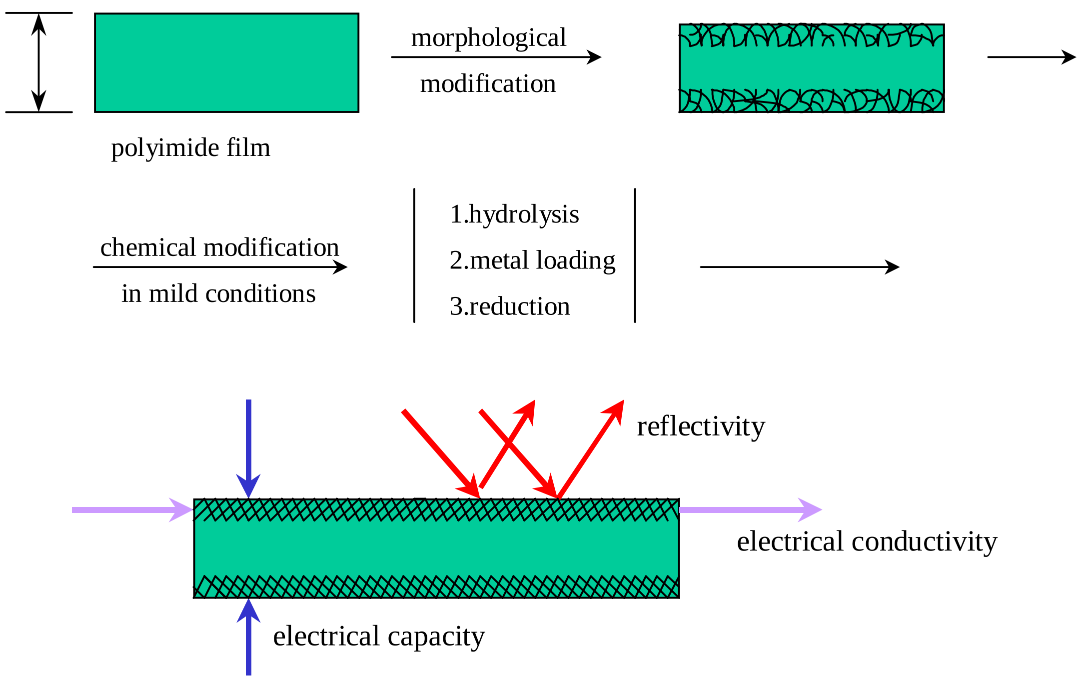
At the present time the aluminized polyimide films find their application as thermo- regulative coatings in the elements of airspace constructions. However, the new demands in airspace exploring and development of the modern communication facilities dictate a search for the novel materials with a high reflecting ability to make them usable as antennas on space apparatuses and as light reflectors and collectors for solar energy accumulation. Silvered polyimide films are considered to be the most effective ones as they could provide high degree reflection in IR-regions of spectra of solar emission and may endure electromagnetic radiation. For these purposes expensive multi-staged technologies providing surface modification (by plasma-chemical etching, ion implantation, laser ablation, etc.) with a further vacuum deposition of the metal are used. At Langly NASA Centre a new method of superfluid silver metallization has been developed. The method consists of the treatment of PI films by supercritical liquids, impregnation of silver organic complexes with the following thermolysis at high temperatures (300°C). Also there ahs been developed a method of inner-self-metallization of the films by doping of prepolymer solutes with solubilized silver complexes and also by films casting and their thermal treatment at 300°C with a long treatment exposure. These methods do not always allow obtaining of both electroconductive and reflective surfaces simultaneously on the films. Besides, such materials can not be formed on the basis of industrial PI films that makes the cost of the final products rather expensive.

CURRENT STATUS . PRINCIPLES OF THE TECHNOLOGIES FOR METALLIZATION OF POLYIMIDE FILMS DESCRIBED IN THE LITERATURE



<u>Currently a new non-traditional method of non-traumating polyimide metallization is being developed at the Institute of Chemical Sciences in the Laboratory of Polymer Synthesis</u>. That enables one to obtain polyimide films with durable and non-removable coatings of both sides of films. Crystallity, considerable thickness (to several microns) of the coating as well as the impregnation of metal layers into the polymer base lead to high electrical and heat conductivity of the construct. The formed coatings represent primary mirror surface with high reflection coefficients in visible and IR ranges of spectra (up to 98% relative to silver mirror at the normal angle of light incidence). The new developed technique, enclosing a unique combination of physical and chemical procedures allows one to obtain prompt and technically non-complicated metallized films on the basis of industrial polyimides (Kapton, DuPont, USA; Upilex, Ube Corp. Japan; PM Russia). The method is based on consequent steps of surface alkali hydrolysis of imide group to amide ones; so-called metal chelation or loading of metal ions in their aqueous solution; chemical reduction of the chelated metals; and final annealing of the films. An appropriate price of the method is at least by 2.5-3 times cheaper than the methods of vacuum deposition or radiation etching, both being produced at the NASA Centre. Moreover, by using the multicracking methods to estimate a metal-polymer adhesion degree it was manifested that **<u>chemically metallized layers are by 3.5-5 times adhesively stronger than those of chemically vapor deposited</u>**.

OUR STATE OF ART. I. PRINCIPLE OF THE TECHNOLOGY FOR METALLIZATION O
POLYIMIDE FILMS **(ICS**



Another direction in the field of polyimide metal-construct is the creation of the new composite materials with discontinuous distribution of metallized phase in polyimide matrix. **<u>Application of the developed at the ICS methods of catalytic condensation makes it possible to invent polyimide blends with different polymers that are of high compatibility and similar in thermal-life characteristics.</u>** Further chemical metallization of those polyimide-polymer blends of certain surface morphology enables one to vary the physical and chemical properties of the composites in the wide ranges. The suggested approach to the composite materials creation with the set sizes, form and structure of metal clusters that determine the physical properties of composites is principally novel in material research. The catalytic method is mainly based on polycondensation of alicyclic polyimide in the presence of another polymer and a catalyst. The reaction takes place between a photoadduct of benzene and maleic anhydride with oxydianiline in the presence of the second polymer in methylpyrrolidone medium through matrix polycondensation of polyimides along the second polymer chains. The next steps do not require thermal imidization due to fact that metal chelation occurs between amide groups of polyimide with metal ions. However, the imidization of films is finally reached within the last step of metallized film annealing.

Metallized polyimide films on the basis of both industrial materials and ICS developed blends are potentially good ultra-thin condensers of a high capacity. The priority of works currently carried out worldwide is the result of high characteristics of polymer constructs. With the aim to recommend the metallized films (with silver, cobalt, nickel) applied in the open space at low-earth orbit the stability attributed to the major destructive factor (basically atomic oxygen) must be increased. To achieve this point an electrochemical deposition of thin coatings of precious metals: gold, platinum, palladium and radium) under mild conditions is suggested, as well as casting of polyimide thin layer on the films for surface passivation. To introduce the developed metallized films with metallized phase surface distribution as reflectors and collectors, antennas for space apparatuses it is necessary to carry out a whole series of works for the determination of the open space effects (different types of radiation, abrasive factors) upon their structure and properties. **<u>This project offers a unique possibility of exercising of joint works in inter-disciplinary field for the development of the material creation technology for its use in various civilian fileds. First stages of the investigation of physico-chemical procedures of chemical metalization have been implemented in the frame of NATO (SfP978013) project and passed successfully the international scientific expertise.</u>** All the works for the formation of thermally stable metallized polyimide films will be accomplished in the Laboratory of Polymer Synthesis, ICS **<u>that is well experienced in synthesis and modification of heterocyclic polymers.</u>** The KazNU will carry out electrochemical part of the works. The structure and properties of PI films will be studied by the modern methods of physical analysis (X-ray phase analysis, Auger-spectroscopy, thermal -mechanical analysis) in ICS. Laboratory of Organic Polymer Materials at the Montpellier II University, France (collaborator) will provide consulting in molding, filming and passivation techniques. KK Interconnect

Joint Stock Company will produce a large-scale metallized polyimide film as a solar light collector, as well as will assist for the development of mask metallization technique for pattern chip-like metallized films through subcontracts. As a final part of the project we plan to design a light cone mirror for a diminutive IR-spectra device (subcontract with Department of Solid State Physics of Moscow State Pedagogical University [MSPU] for installation of the light cone mirror to a IR-spectra device), lab-on-a-chip electroforetic tool, and technology of large-scale film metallization as examples of method applicability (subcontract with KK Inetrconnect Joint Stock Company). The project also assumes that Thermogravimetry analyzer TGA Metler Toledo equipment (ICS) and Universal electrochemical station AUT 30 Ecolab (KazNU) will be reconstructed for fitting their holders to analyze metallized polyimide samples through two additional subcontracts with Metler Toledo Central Asia Company.

Thus, the main aim of the project leads to property design of polyimide materials for their further industrial application as constructs in aerospace and electronic civilian fields.

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PUBLICATION OF PROJECT PARTICIPANTS:

1. S. Kudaikulova, G. Boiko, B. Zhubanov, O. Prikhodko, V. Voytekunas, M. Abadie. Synthesis of new metallized polyimide films with high optical and physical performances. *Eur. Chem.-Technol. J.* v. 6 (1), 2004, p. 57-66.
2. O. Prikhodko, S. Kudaikulova, M. Abadie. Electric and optical properties of polyimide surface films modified by metals. *Eur. Chem.-Technol. J.* v. 6 (1), 2004, p. 31-36.
3. S. Kudaikulova, Z. Musapirova, R. Sarieva, M. Abilova, R. Iskakov, B. Zhubanov, M. Abadie. Novel polymer composites on the basis of arylalicyclic polyimide blends. I. Polyimide/polycarbonate & polyimide/polysulphone blends. *Eur. Chem.-Technol. J.* v. 6 (1), 2004, p. 7-10.
4. S. Kudaikulova, Z. Musapirova, N. Sobarina, M. Umerzakova, R. Iskakov, B. Zhubanov, M. Abadie. Novel polymer composites on the basis of arylalicyclic polyimide blends. I. Polyimide/polyethyleneterephthalate blends. *Eur. Chem.-Technol. J.* v. 6 (1), 2004, p. 11-16.
5. S. Kudaikulova, A. Syzdykova, R. Iskakov, B. Zhubanov, J. Akhmetova, O. Moiseyevich, A. Kurbatov, T. Akhmetov, M. Abadie. Effect of modification on electrochemical chelation of polyimide films. *Eur. Chem.-Technol. J.* v. 6 (1), 2004, p. 23-26.
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7. S.Kudaikulova, G.Boiko, B.Zhubanov, N.Ashurov, O.Figovsky, M.Abadie Formulation of polyimide macromolecular blends by one step matrix polycyclocondensation, *Sci.Israel – Technol. Adv.*, v1, p 5, 1999, p. 1-9.
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10. *Patent of the Republic of Kazakhstan # 13815.* Bimetallized polyimide film and method of its preparation. S. Kudaikulova, B. Zhubanov, M. Abadie, T. Akhmetov, et al

2. Expected Results and Their Application

The suggested project is related to material processing and technology development in the term of rather development stage. The principally new non-traumatic metallization of polyimide films enables one to considerably reduce the price of metallization methods, to obtain mechanically stable and high adhesive metallized films containing metal of different nature, to demonstrate the expanded sphere of their application in different civilian fields, such as aerospace tools and base of microelectronics chips.

- New data on the principles of metal loading, polymer-metal interaction, metal distribution and its morphological structures;
- Metallized polyimide constructs with broad physico-mechanical properties and high thermal stability based on new polyimide blends with polycarbonate, polysulphonate, polyethyleneterephthalate, polyaniline, polyurethane, poly(acrylic- or metacrylic acid)s;

- Thermo-, radio- and oxygen-stable metallized polyimide constructs with secondary-metallized coatings making use of electrochemical metal deposition on the primary metallized polyimide films;
- Technology for large-scale polyimide metallization based on the developed method;
- Technology for pattern chip-like metallization of polyimide films by mask metallization technique;
- Technological documentaion and patenting for the production of large-scale metallized polyimide films by the so-called chemical metallization technique.

Thus, the project leads to both the development of new metallization technology of polyimide films and the its implementation as functional materials (large-scale mirrors) or new products (lab-on-a-chip devices and ultra-thin capasitors ans so on).

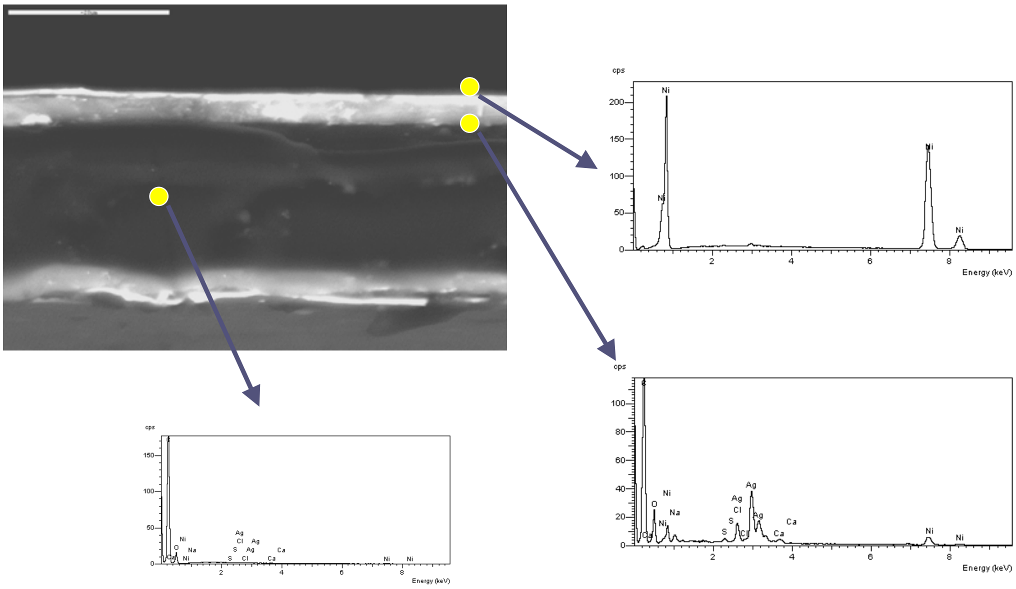
3. Meeting ISTC Goals and Objectives

- conversion of the initial PI material needs for military purposes to peaceful aerospace and electronics application
- involvement of weapon scientists in the development of polyimide materials for the civilian purposes, such as aerospace material researchs, microelectronics and bioanalytical fields
- integration of the Kazakhstani scientists into the international scientific society with the support of their fundamental and applied investigations to the worldwide civilian needs
- development of new advanced Hi-Tech technologies satisfied the national interests of Kazakhstan and Georgia in order to the further growth of national economy.

4. Scope of Activities

The majority of works will enclose the development of a metallization technology of different PI materials through the analysis of composite structures and their physico-mechanical performances as well as their thermal and radiation stability.

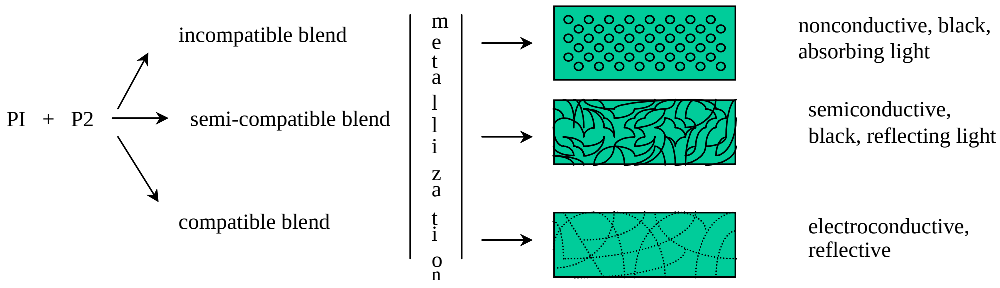
Task 1



Task description and main milestones	**Participating Institutions**
Development of a metallization technology of industrial polyimide films.	**1-ICS** **2-KazNU** **3-SIPT**
1.1. Analysis of scientific and industrial literature concerning processing of metal/polyimide composites.	**1**
1.2. Development of technological approaches of the initial steps of industrial polyimide film metallization. Elaboration of time and concentration factors for both polyimide film surface modification and its surfacial alkali hydrolysis by the analyses of FTIR, UV, and SEM/XR methods.	**1**
1.3. Development of technological procedures of one- and two-film side metal chelation of the modified industrial films by the analyses of TGA, SEM/XR and TGA/FTIR methods.	**1**
1.4. Development of metal reduction technology of the chelated polyimide films by both chemical and thermal methods. Choice of appropriate chemical agents and metal distribution in the polyimide film by means of XR, Auger, and SEM analyses.	**1, 2**
1.5. Development of passivation techniques by casting of polyimide thin layers on the metallized construct.	**2**
1.6. Investigation of the physical properties: electric - by a four-contact method; optical properties – by spectrometrican analysis in UV-, visible and IR- regions of spectra; magnetic ones – by the definition of magnetic permeability, magnetic receptivity and magnetizing.	**1, 2, 3**
1.7. Creation of a metallization technology for large-scale industrial polyimide films with high reflective and electroconductive performances. Stimulation of the effect of low-earth orbit radiation and analysis of their influences.	**1**

Task 2

OUR CURRENT IMPLEMENTATION . II. METALLIZATION OF POLYIMIDE (PI) FILMS BASED ON MACROMOLECULAR COMPOSITES (BLENDS)



Morphology of the films, based on PI blended with P2 polymer determines physical properties of final metallized composites

Metallization of PI blends provides:

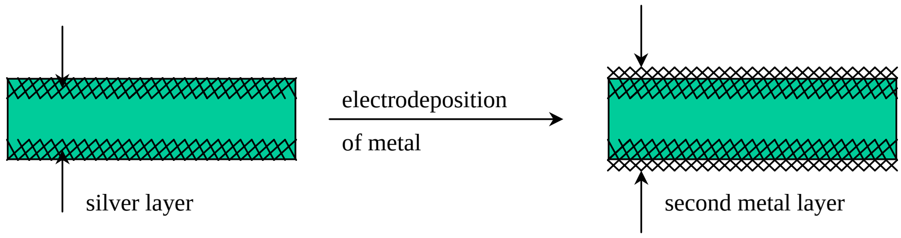
- regulation of electrocoductivity and reflectivity
- magnetic properties
- increase of metal content without embrittlement effect

Task description and main milestones	Participating Institutions
Development of pattern metallization technology of polyimide blend films.	**1-ICS** **2-KazNU** **3-SIPT**
2.1. Preparation of compatible polyimide-polymer blends on the basis of polycarbonate, polysulphone, and polyethyleneterephthalate.	**1**
• Synthesis and definition of optimal conditions (temperature, time, concentration and molecular weight of polymer matrix) of polyimide-polymer formation by way of one-step high temperature catalytic polycondensation of benzene photoadduct with oxydianiline in the presence of a second polymer.	**1**
• Investigation of the structure and morphology of blends by SEM/XR and TGA/FTIR analyses.	**1**
• Study of the effect of the second polymer content on metal loading degree and composite structure.	**1, 2,3**
• Selection of optimal second polyimide-polymer blends and study of their physico-mechanical performances.	**1**
• Study of procedure peculiarities for each steps of chemical metallization. Analogues and discrepancies with the industrial polyimide film metallization.	**1**
2.2 Elaboration of a technology for pattern metallization of polyimide blend films.	**1,3**
2.3. Investigation of physical, mechanical, and thermal properties of composites, such as surface and volume electroconductivity and their temperature dependence; the effect of resolution of metal layer thickness on the quality of surface electroconductivity; correlation between blend content and electroresistivity, mechanical properties.	**1,2**
2.4. Design of polyimide blend coating, silvering of polyimide	

	surfaces for the development of light cone mirror in a diminutive IR-spectra device.	**1, 2**
2.5.	Development of the technological documentation for the obtaining of pattern metallized polyimide blends.	**1, 2**

Task 3

OUR CURRENT IMPLEMENTATION. III. DEPOSITION OF SECOND METAL COATING ON THE SURFACE OF SILVERED POLYIMIDE FILM (ICS in co-operation with KZNU)



Electroconductive silver layer provides the possibility for deposition of different metals: palladium, platinum, gold, rhodium, cobalt, nickel and their alloys in mild coditions.

Result:

- supposed increase of stability to the effect of atomic oxygen - main damaging factor of space environment
- raising of abrasive stability
- no delamination effect

Task description and main milestones	Participating Institutions
Development of electrochemical polyimide metallization technology as secondary coating.	**1-ICS** **2-KazNU** **3-SIPT**
3.1. Development of electrochemical non-traumatic metal deposition on the primary metallized polyimide films. Effects of metal type, electrolyte compositions on the quality of the secondary metal coating.	**2**
3.2. Study of kinetics of electrochemical metal deposition on metallized polyimide films; study of electrochemical principles of secondary metal coatings.	
3.3. Testing the diffusion characteristics of the films for different metal cations at the electrochemical metallization processes *in situ* and metal distribution along the film by SEM/XR analyses.	**2**
3.4. Analysis of different electrochemical factors, such as metal type, electrolyte, voltage characteristics on coating of the primary metallized large-scale films, study of surface passivation by means of electrochemical deposition of noble metals on the primary coating.	**2, 3**
3.5. Preparation of electrolyte-stable metallized polyimide films of various shapes as an element of ultra-thin condensers.	**1, 2**
3.6. Development of the technological documentation on new technology of electrometallized PI constructs. Stimulation of cosmic effects on secondary coated films with passivated surfaces.	**1,2,3**

From the viewpoint of the formation of the primary reflecting mirror surface the methodology of polyimide films metallization in the suggested project is a principally new one. There are two major advantages as compared to all other procedures, which could be attained in case of the technology succeed – cheap price of the final construct and powerful adhesion of metal to the polyimide base. Chemical modification of the polyimide film surfaces, films on the basis of polyimide-polymer blends, carrying out of the consecutive chemical reactions in the modified layer with the use of surface and diffusion effects make it possible to create a metal phase with different gradient of distribution and ultimately allow one to vary physical properties of composites within a wide temperature range with non-laminated metal layers. **The developed method of metallization by chemical modification enables one to obtain films of high quality and any sizes under simple and available conditions on the basis of both industrial polyimide films Kapton (Du Pont, USA), Upilex (Ube Corp., Japan), and new polyimide blend films based on alicyclic polyimides, developed in ICS. The fullfillment of the set tasks is guaranteed by high qualification of scientists and essential modern equipment.**