SYNTHESIS REPORT

FOR PUBLICATION

F R E D O P S - FAST RESPONSE ELECTROCHROMIC DEVICE ON POLYMERIC SUBSTRATE

CONTRACT N°: BREU-0546

PROJECT N°: **BE-4** 137

PROJECT
COORDINATOR: CONPHOEBUS scrl, Catania, Italy

PARTNERS:

HEF Centre de recherche, Andrézieux-B., France
LIES-ENSEEG, Grenoble, France
CSTB, Semite materiaux, Grenoble, France
NKT Research Centre, Brøndby, Denmark
1ST, Zulte, Belgium
SIV, San Salvo, Italy
Dipartimento di Fisica, Catania University (subcontr.)

STARTING DATE : 1/1/1 992 DURATION: 40 MONTHS

PROJECT FUNDED BY THE EUROPEAN COMMUNITY UNDER THE BRITE-EURAM PROGRAMME

2.2. Consortium Description

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Conphoebus scrl, Catania, Italy;
(main contractor and project coordinator)

Conphoebus is an applied research and technical service company, indirectly controlled by ENEL SpA, the major Italian Electric Utility. Its main areas of activity are: renewable energies, energy management in buildings, advanced energy and environmental technologies. The type of supplied services range from engineering to research studies, from product qualification testing to vocational training courses. Since its foundation as Phoebus in 1979, Conphoebus has been operating in an international environment, and has signed, up to now, more than 40 contracts with European Commission Directorates as DG XII, DG XI, DG XIII, DG VIII.

The development of electrochromic device enters the company's strategy in view of their large potential for solar control as "smart windows". Contacts have been established and are actively searched with Italian and foreign companies interested in this field both as developers and as end users.

CONPHOEBUS was responsible in the project for technical and administrative coordination and management, it performed laboratory work on WO_3 and Nafion H, assembled at laboratory level full devices by preparation and lamination of BPEI, did voltammetric, optical and durability characterizations.

HEF Centre de recherche, Andrézieux-Bouthéon, France

The HEF group is a very innovative SME, whose heart is the Research Centre. HEF performs surface treatments for industrial customers mainly in the field of tribology and optical coatings. The main interest in EC devices originated from the request of a HEF customer to develop EC visors for helmets.

HEF studied several types of counterelectrodes by magnetron sputtering. It developed innovative techniques to obtain very effective W03 coatings on PET-ITO.

LIES-ENSEEG, Grenoble, France

The "Laboratoire d'Ionique et d'Electrochemie du Solide" is a CNRS-associated laboratory, part of the "Institut National Polytechnique de Grenoble". It works on solid state batteries, sensors, fuel cells and electrolysers, and electrochromic devices. The group involved in the project is expert of polymeric electrolytes. LIES-ENSEEG developed the FREDOPS polymeric electrolyte ('cl'BPEI/H_3PO_4), performed voltammetric tests, and applied a new photo-electrochemical characterisation technique to EC layers,

CSTB, Semite Materiaux, Grenoble, France

The "Centre Scientifique et Technique du Batiment" has in Grenoble its Material Centre, that performs research and characterizations on a wide range of material properties interesting for the building. The involved group is a specialist in optical testing services, with unique facilities as the OPTORA platform for optical and radiative characteristics of materials.

In the FREDOPS frame CSTB performed optical and other physical tests on single materials and devices and developed a new multi-task test bench for cycling EC devices.

2. THE CONSORTIUM

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CONTENTS

ABSTRACT

A dynamic control of light and energy transmission properties of glazed systems can be obtained by Electro-Chromic (EC) devices, that modify their optical properties according to the value of the electric voltage applied to the two external electrically conducting layers. The development of EC devices is a world-wide challenge, focused to the solution of reliability and durability aspects, necessary condition for an industrial exploitation.

Glass has been the standard substrate for the EC device development, as it is the most widely used transparent material. On the contrary, the FREDOPS project is addressed to the development of a fast response EC device on a polymeric substrate.

FREDOPS can be widely applied: from building or transport glazing systems to communication displays, light control systems for visual protection (visors, spectacles, etc.. .), architectural applications, etc...

Several alternative materials have been explored and tested for each different layer type. The synthetical description of the finally proposed device is:

PET-ITO / W03 / 'cl'BPEI-1. 5 H3P04 / polymeric fluorindine / ITO-PET

Test results have-shown very good typical performance values for exchanged charge (2-3 mC/cm2), optical density variation (0.4-0.5) and coloration efficiency (average value 145 cm^2/C). Typical transmittance variations are from 60°/0 in bleached state to 1 5% in' colored state (contrast ratio 4:1). Time responses had to be kept slow (60 s coloring, 150 s bleaching) in order not to degrade performance with long term (104) cycling. Temperature operating range is between 5 and 45°C. Storage temperatures are between -20 and 60°C. No UV damage occurs.

The possibility of producing 200 x 160 mm^2 samples has been demonstrated: further efforts are necessary if an industrial product development phase is started.

Important results have been obtained on the technologies for producing new materials for EC devices on polymeric substrate. The best performing ITO transparent coating on polymeric films has been produced, a new temperature stable polymeric electrolyte developed, a new organic electrochromic dye patented, a tungsten trioxide coating on polymeric film, as good as those ones obtained on glass, produced in 250 x 300 mm size, a technique for lamination of EC films based on PET between glasses developed and tested, an innovative characterisation technique (photoelectrochemistry) applied for the first time to electrochromic layers.

NKT Research Centre, Brøndby, Denmark

The NKT interest in the FREDOPS project was related to the subsidiary company Colorlux, which manufactures various types of displays. The intention was to utilise the project results within Colorlux, to make large area communication displays based on electrochromic materials.

The NKT Research Centre participated in the FREDOPS project, developing an organic dye (polymeric fluorindine) as a counter-electrode acting as electrochromic complementary to WO_3; it did also voltammetric characterizations and designed, constructed and tested the pilot units for roll-coating and tape-casting.

1ST, Zulte, Belgium

Innovative Sputtering Technology (I. S. T.) N.V. is a new company, founded in 1991 as a joint venture between BEKAERT (80°/0 of shares) and the Swedish group ES SELTE (20°/0 of shares). The BEKAERT group, with headquarters in Belgium, is the world's largest independent manufacturer of steel wire and wire products, active in the automotive, building and consumer markets. I.S.T.N.V. develops, produces and markets vacuum deposited thin film coatings on flexible substrates (mainly plastic films) for all kinds of technical applications (magnetic, electronic, optical).

I.S.T.N.V. produced ITO-coatings on PET-substrates, developed an EC-half cell by consecutive deposition of ITO and WO_3 in different stations of the same roll coater and performed a lot of basic physical and chemical analyses on the coatings, taking profit of the highly sofisticated BEKAERT-laboratory equipment .

SIV, San Salvo, Italy

As one of the leading European companies in the car glazing market, SIV is involved in production and research on advanced coated glass. Plastic film lamination is now a widely accepted technology for safety glass and SIV thinks that FREDOPS films could be used in this application.

SIV did some lab sputtering tests on Molybdenum doped W03 , developed a lamination procedure for EC films and tested the obtained samples.

Dipartimento di Fisica, Catania University
(subcontractor of Conphoebus)

Dipartimento di Fisica, Catania, has a long term experience in EC devices developed also in collaboration with the Lawrence Berkeley Lab. It tested Mo doped W03 obtained by electrodeposition, tested several techniques for Nafion H. assembly, did physical tests on layers.

3. TECHNICAL DESCRIPTION

Goal of the project is to propose and develop a FAST RESPONSE ALL-SOLID-STATE electrochromic device on polymeric substrate (FREDOPS).

Electro-Chromic (EC) devices allow a dynamic control of light and energy transmission properties of glazed systems, modifying their optical properties according to the value of the electric voltage applied to the two external electrically conducting layers. The development of EC devices is still a world-wide challenge, focused to the solution of reliability and durability aspects, necessary condition for an industrial exploitation.

Glass has been up to now the standard substrate for the EC device development, as it is the most widely used transparent material; instead the FREDOPS project focuses on the development of a fast response EC device on a polymeric substrate. An EC device on flexible rind thin substrates in fact offers new opportunities for applications in the field of building/transport glazing (as adhesive film or between two laminated glass sheets), large size communication displays, light control systems for visual protection (curved visors, spectacles, etc.. .), architectural applications, etc...

In the first project phase several different materials have been identified as possible component of the final FREDOPS device. At Mid-term a selection was made and a final solution accepted. The various materials investigated in this phase were:

substrate: PET

electronic conductor: ITO

EC layer:
-W03
-heterocyclic pentacenes (polymeric fluorindine)
-phtalocyanines containing rare earth medallions (gadolinium or lutetium)

NOTE: phtalocyanines switch electrochromically from yellow-brown to violet, while fluorindines switch from light yellow to blue.

electrolyte:
-Nafion H ™
-PAAM.H_2SO_4;
-BPEI.H_2SO_4;
-BPEI- 1.5 H3P04
-pseudo cross-linked ('cl') BPEI-1.5 H3P04

NOTE: Nafion has adhesion problems **when dry** and is incompatible with fluorindines; PAAM is suitable for electrochromism but too sensitive to water; BPEI performs much better when doped with phosphoric instead of sulphuric acid, The pseudo-cross-linked polymer is thermally stable up to 150°C, while the base polymer becomes viscous at about 80°C.

counter-electrode:
-metal hydrides;
-IrO_2;
-V_2O_5
-polymeric fluorindine

NOTE: metal hydrides are too reflective to be a good layer for transmitting systems; iridium oxide is too expensive, vanadium oxide is unstable with humidity, is yellow, when doped with fluorine (to improve transmittance) its response is slowed down, it shows uncompatibilities with BPEI; polymeric fluorindine is a good complementary electrode for tungsten trioxide as it contributes to the contrast and has no other performance contraindications.

The finally accepted solution was:

PET-ITO / WO_3 / 'cl'BPEI-1.5 H_3PO_4 / polymeric fluorindine / ITO-PET

Several important studies have been performed on specific aspects, leading to very interesting scientific results:

i) The performance of tungsten trioxide EC layers deposited on polymeric substrate has been' explained studying the surface morphology. The columnar structure of the tungsten oxide, deposited at lower temperature than the one normally occurring on glass substrates, explains the mechanism of penetration of the hydrogen ions, which is driven both by diffusion and by the electric field.

ii) The poor performance of the early FREDOPS-samples was explained, by means of factor analysis on Auger Electron Spectroscopical data, as being caused by an intermediate layer between ITO and WO_3. This layer is $In(OH)_3$ or an intermediate phase between In_2O_3 and $In(OH)_3$, and results from the interaction of the ITO-coating with water from the ambient air. This layer decreases the electronic conductivity across the interface ITO/WO_3; to avoid it, consecutive depositions of ITO and WO_3 in the same vacuum were started at I.S.T.

Another instability of ITO when coating with WO_3 was shown by both Transmission Electron Microscopy at I. S. T.-BEKAERT and photoelectrochemistry at LIES. It was shown that due to the thermal load on the amorphous ITO during WO_3 -deposition, the In_2O_3 started to crystallize partially, introducing an extra resistance in the current path through the device. The extent to which this crystallization takes place depends very much on the deposition conditions (free span coating vs. roll coating and drum cooling in the latter case, sputter power density). It is generally assumed that depositing the WO_3-coating from several coating sources will avoid the problem.

Test results on the final EC cell have shown very good performance values for exchanged charge (2-3 mC/cm^2), optical density variation (0.4-0.5) and coloration efficiency (avg. value 145 cm^2/C). This very high coloration efficiency can be explained by the simultaneous EC switching of electrode (WO_3) and counterelectrode (fluorindine) operated with the same amount of charge. The amount of exchanged charge is driven by the amount of H^+ ions stored either in the WO_3 or in the fluorindine layers before assembly. The best performance is obtained when the stored charge corresponds to the full switching charge of the fluorindine.

Typical transmittance variations (see figure 1) are from 60% in bleached state to 15% in colored state (contrast ratio 4:1). This contrast, even if not as large as the one stated in the initial specifications, is still largely satisfactory for most applications. Particularly interesting is the value of visible transmittance in bleached state (600A), that is significantly higher than the values obtained by most systems based on V_2O_5 counterelectrodes (450/0), that are yellow in bleached state.

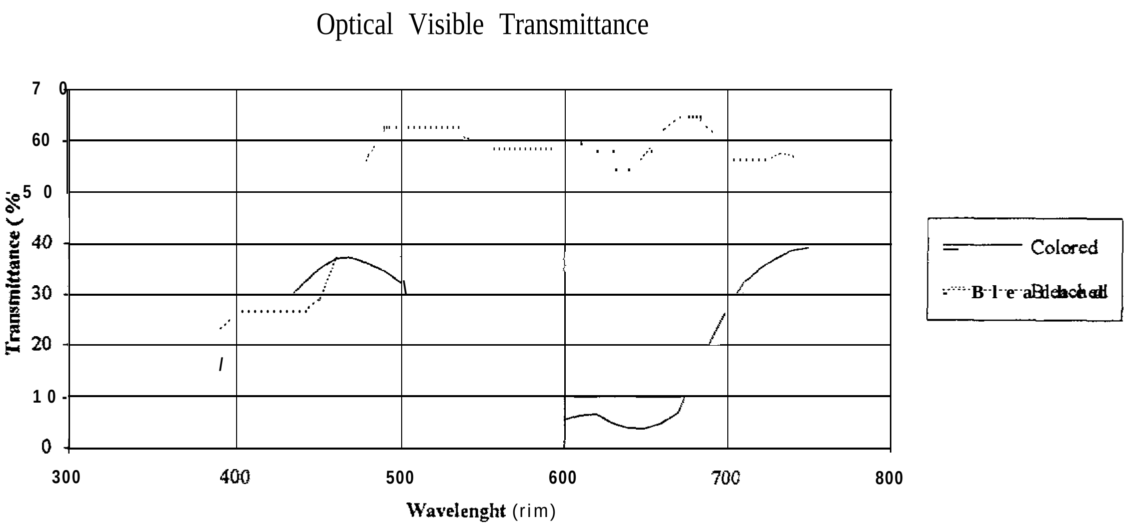

Figure 1: Visible transmittance spectra in the bleached and colored states

Time responses had to be kept slow (60 s coloring, 150 s bleaching) in order not to degrade performance with long term (more than 10^4) cycling. If operated at its maximum possible speed (10-15 s) the device degrades irreversibly within the first 50 voltammetric cycles. The reason is probably related to the excess electric field locally created when the voltage is raised too quickly.

The temperature operating range is between 5 and 45°C. The storage temperatures are between -20 and 60°C. No UV damage occurs.

Beyond the laboratory stage, a pilot unit was assembled to validate the technology for large area devices (200 x 160 mm^2). A precision doctor blade casting equipment was designed, constructed and tested, both for fluorindine coating and BPEI layer casting. The equipment was satisfactory for the first task only. In fact the BPEI coating, that acts as intermediate layer between the two PET foils coated as half-cells, is too sticky to be correctly tasted. Moreover, the experience showed that BPEI has to be very well dried before assembly to avoid bubble formation, but then it becomes hard and not adhesive, therefore it requires a temperature controlled (80°C) process under controlled atmosphere (no oxygen nor humidity) to obtain a satisfactory lamination. To use the method successfully in an industrial manufacturing environment, more development would be needed.

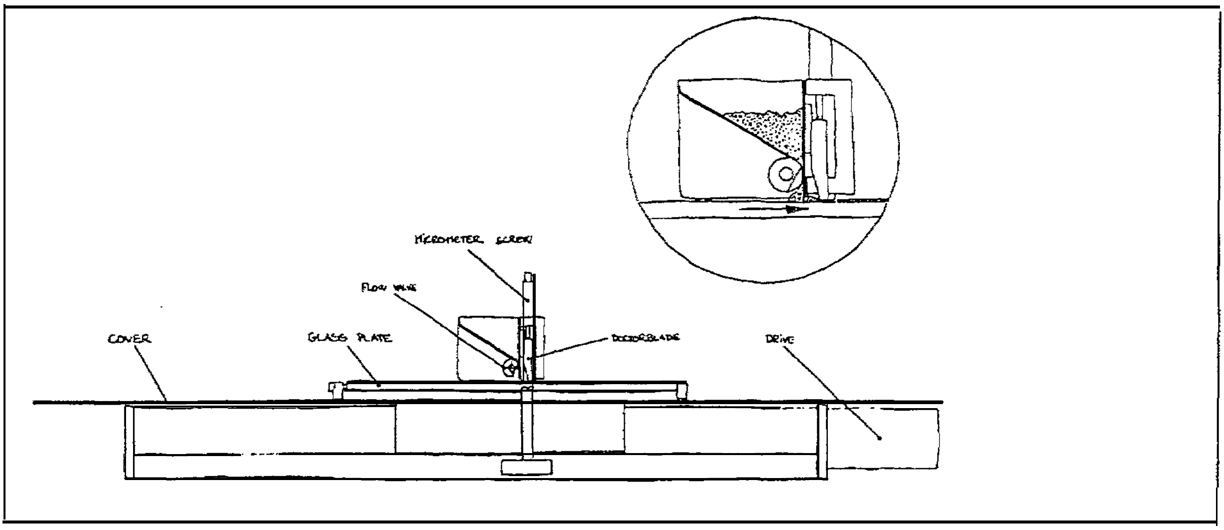

Figure 2: Tape casting pilot unit

Extensive testing has been performed at SIV to develop a suitable technique for the lamination of PET films (of the type used for FRED(3PS devices) between glasses. The best coupling film has been identified, possible surface treatments examined, and the adhesion between glass and PET verified by the peeling test, according to the standards of the car industry.

The other deliverables obtained are technologies for producing new materials for EC devices on polymeric substrate:

a highly performing ITO transparent coating on polymeric film, having 22-24 Ω/□ sheet resistance and >85% transmittance throughout the visible spectrum: the film performance excels the level of all the other products available on the world market;

a new temperature stable (3- 135°C) polymeric electrolyte;

a new patented organic electrochromic dye (polymeric fluorindine);

a tungsten trioxide coating on polymeric film, as good as those ones obtained on glass, produced in 250 x 300 mm size.

a metal hydride sputtered counterelectrode, that has not been adopted by FREDOPS because of its too high reflectance (unsuitable for transmitting systems), but is extremely interesting for EC mirrors (it could play in these devices the multiple function of counterelectrode, specular surface and conducting electrode).

Other deliverables are related to the final application of FREDOPS films:
- a technique for lamination of PET-based EC films between two glass sheets,
to the characterisation of EC layers:
- photoelectro-chemistry, applied for the first time in this field,
to the development of new sputtering targets:
- a process for manufacturing ITO alloy targets

Finally, the FREDOPS project has obtained:
-the first EC device on polymeric substrate, produced at laboratory level.

The fill cell device obtained at the end of the project, nevertheless, does not fully satisfy the initial specifications. It meets quite well the optical performances, but fails in the time response requirements. Therefore the range of possible applications is restricted to communication displays, building glazing and other architectural uses, where conversion times, as long as 1 (coloring) and 2.5 minutes (bleaching), are acceptable. Visual control and transport glazing applications are on the contrary out of reach for this product.
Operating and storage temperature specifications are also not fully satisfied.

4. EXPLOITATION PLAN

Conphoebus, Catania, Italy
As a research and technological services provider, Conphoebus tends to transform the know-how developed in applied research contracts in new services for its customers, primarily ENEL SpA (the largest Italian electric utility), that indirectly controls Conphoebus. Electrochromism could be a very interesting product for a demand-side energy management in the building sector: **in** fact the rate of growth of air conditioning in Italy is really impressive, and meeting the summer peak load could be a serious problem in a near future. Conphoebus therefore intends to perform in the future a continuous survey of the EC technology developments towards possible “smart window” applications, feasibility studies on the possible demand side actions, evaluations of these by least cost analysis, characterisation of new products emerging in the market.
The knowledges gathered during the FREDOPS project will also be used for supporting industrial development efforts: contacts have started with Italian SME's operating in the field of advanced glazing for buildings. In these areas the slow FREDOPS response is not an obstacle, but further efforts are necessary to identify easier manufacturing techniques.
Conphoebus will continue its cooperation with Catania University in the frame of an EC Project, financed by DG XVI Structural Funds (1994-99), through the Italian Multi-regional Programme for Research, managed by the Italian Institute for Materials Physics (INFM). The project, presented in winter 1995, has been accepted by INFM and is now in the definition phase; its objective is to develop and transfer to Southern Italy SME's innovative technologies for EC devices.

HEF, **Andrézieux, France**
HEF exploitation plan was initially to develop EC visors for motorcycle or other types of helmets, based on the request of one customer of its. The project results have revealed that the obtained FREDOPS are not suitable for this development, due to the too slow response (60 to 150 s are the minimum time response for their safe operation, while for visual protection it cannot be longer than some seconds).
HEF policy is not only to make coatings for third parties but also technology transfer: therefore, even if HEF has no plans for internal exploitation, it is open to cooperate with other organisations interested in sputtered EC coatings on films. In fact, at the end of a long and difficult optimisation process, the obtained W03 coating on polymeric substrate is as good as the ones obtained on glass.

The know-how concerning the deveolpment of W03 coating on polymeric substrate is protected by the confidentiality agreement among partners.

LIES-ENSEEG, Grenoble, France

LIES can support the possible industrial exploitation of the polymeric electrolyte developed and tested in the FREDOPS project, selling licenses and supplying assistance. The 'cl'BPEI/H3 S04 is a very promising electrolyte, with very good thermal and conductivity performances.

CSTB, Grenoble, France

The wide testing experience of CSTB in optical materials has produced a new testing bench where the testing procedures developed in the FREDOPS project can be automatically operated. This testing facility can supply services to all manufacturers of electrochromic devices willing to obtain a detailed and independent evaluation.

NKT, Brøndby, Denmark

The organic dye working as counter-electrode (polymeric fluorindine) has been patented by NKT. In fact it represents a very promising EC organic dye, avoiding the main defects of the available alternatives (low visible transmittance caused by the addition of conductive elements, instability, etc.. .).

The original NKT interest in EC devices, was for potential use by the subsidiary company Colorlux, but Colorlux was sold in a management buy out.

NKT is now willing to cooperate with other companies, in the field of communication displays, for further product development.

The word market potential has been earlier estimated in 250 MECU/y for EC information displays. The market shares are **36%** Europe, 42% America, 22% Asia.

I. S. T., Zulte, Belgium

The innovative technology for the roll-to-roll deposition of ITO on polymeric films, developed in the FREDOPS-project frame, has produced very satisfactory results, as PET-ITO films performing better than the ones available on the market can be manufactured at 1ST now. 1ST is strongly interested in starting a production of ITO coated PET-films, that coud be applied for membrane switches, electroluminescent lamps and displays, touch panels, car rear window antennae, electrochromic devices, PD-LCD's [liquid crystal devices), EMI (electro-magnetic emission) -shielding, etc... The only limiting factor is the market size, which should amount up to 10,000 m^2/y to justify the manufacturing start up. The present market size is still far below this number. It is expected that e.g. the large scale production of Electrochromic Devices will be needed to generate enough production volume.

SIV, San Salvo, Italy

The SIV group has been sold by the public Italian group EFIM to the joint venture Tekint-Pilkington. The group interest in EC glazing is large (e.g. Pilkington leads two Joule projects on EC smart windows).

The possibility of laminating EC films between glass layers is very interesting for glass manufacturers, and the technology developed during the Fredops project by SIV is promising. The electrochromic market potential interesting for SIV is firstly the one of sunroofs (5- 10% of the present 3 million pieces/y in Europe). In buildings a first estimate of the European electrochromic market is in the range of at least 10-20,000 m^2/y. The difference between “potential” and “real” market is basically depending on product cost and on the development of an integrated control system.

5. COLLABORATION SOUGHT

The industrial exploitation of the full device needs a further product development. From the partner’s estimates this further phase could be quite long (2-3 years) arid costly.

Polymeric electrolyte

The most delicate point in a possible FREDOPS industrial manufacturing is the polymeric electrolyte, because its development involves technological and cost problems. This development could be shortened if an industry, having experience in the manufacturing of polymeric electrolytes, could participate in this development.

The potential partner should preferably have experience with polymeric electrolytes for batteries or fuel cells.

EC and counterelectrode coatings

Licence agreements can be offered to new partners interested in W03, metal hydrides and fluorindine layers on PET-ITO substrates. All these layers can be part of full EC devices composed of other compatible coatings. Fluorindine and metal hydrides can also be coated on glass substrates and are therefore interesting for glass-based EC manufacturers that are looking for new solutions.

Metal hydrides can reach very high reflectance and are therefore the perfect counterelectrode for EC mirror devices.

PET-IT(3

I.S.T. **is** constantly looking for long-term sales agreements with other industries for ITO coated PET in large quantities. In order to start a production in Europe of PET-ITO, a minimum market of 10,000 m2 is estimated to be necessary. As the application field is wide (EMI-shielding, electroluminescent and electrochromic devices, film based LCD’s, membrane switches, touch panels, car glazing radio antennae,...) - even before the set up of a significant film-based EC market - all companies making products based on this material are requested to contact I. S .T.

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7. KEYWORDS

ELECTRO-CHROMISM, MAGNETRON SPUTTERING, POLYMERIC ELECTROLYTE, SMART WINDOW, COATED FILMS