TECHNICAL PROGRESS REPORT

I. Improvement of Metallization Procedures

In a first step, we wanted to precise the experimental conditions of the pretreatment of polyimide films along the chemical metallization process which has been previously set up.

I.1. Preliminary Remark

Industrially polyimide films are obtained by casting-evaporation and the technique of implementation requires a meticulous control of the different parameters governing the process, in particular the nature of solvent, the temperature of drying as well as the factor time of the various operations. We noticed that, for the same sample Kapton 100 HN coming from different batches, a notable differences in behavior in the process of metallization. This observation is due to weak modifications in the structure even of the film polyimide. Thus by FTIR we could observe, for the same chemical treatment, a light difference between polyimide giving a bad metalization fig.1 (Polyimide A) and a good metalization fig. 2 (Polyimide B).

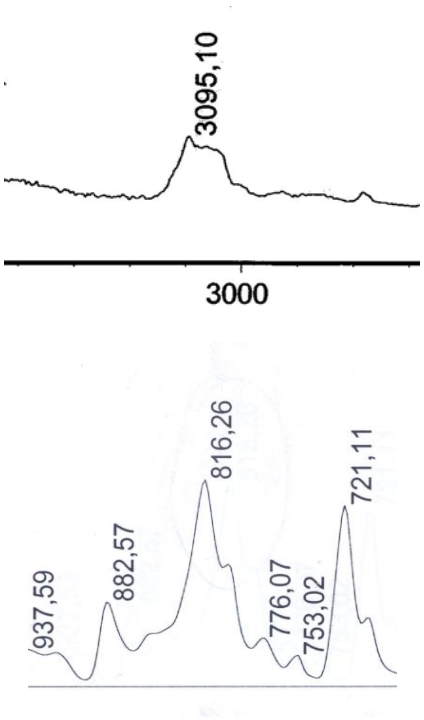

Figure 1. Polyimide A

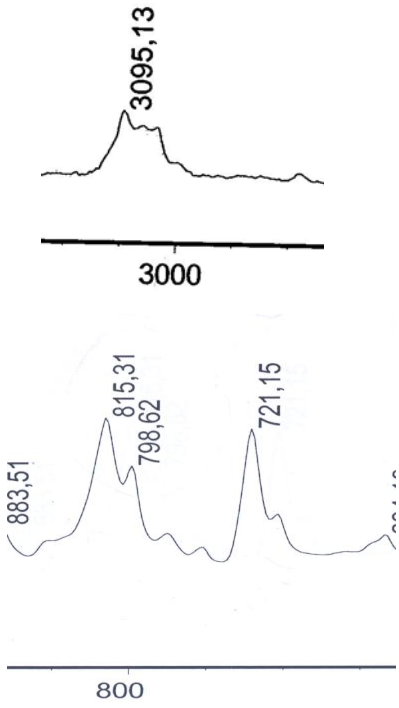

Figure 2. Polyimide B

One notes a light difference in the shoulder at 798 cm^{-1} corresponding to the movement of H apart from the plan in position p-substituted of the phenyl group. These two samples are used in a comparative study to explain the difference in their behavior. The samples are treated in methanol during 6 hours, then dried with 120°C during 1 hour; they are respectively weighed before and after treatment.

	Polyimide A			Polyimide B		
	before	after	difference	before	after	difference
1	17.020	15.949	1.07 (-6.29%)	12.010	11.763	0.25 (-2.06%)
2	20.115	19.454	0.66 (-3.29%)	11.782	11.944	0.16 (+1.37%)
3	17.206	15.944	1.26 (-7.33%)	16.149	14.667	1.48 (-9.18%)
	total		- 16.91			- 9.87

Table 1. Variation of polyimide film weight treated with methanol

One observes - Table 1, that sample A lost more weight than B, which implies that A contains more impurities (soluble in methanol) that B.

The same experiment taken again with the dibutylphthalate - Table 2, confirms the greatest loss of weight of sample A compared to B.

	Polyimide A			Polyimide B		
1	26.927	26.940	0.013 (+0.05%)	33.299	33.190	0.109 (-0.33%)
2	27.895	27.809	0.009 (-0.09%)	35.670	35.623	0.047 (-0.13%)
3	21.899	21.865	0.034 (-0.16%)	35.564	35.403	0.161 (-0.45%)
	total		- 0.20			- 0.91

Table 2. Variation of polyimide film weight treated with dibutylphthalate

These preleminaries experiments confirm that sample A has more impurities that B (solubility in methanol) but has lower porosity than B (profit of weight with a non volatile solvent).

I.2 - Chemical Process of Metallization

I.2.1 - Pretreatment of Virgin Film

Three distinct phases represent the conditioning of the surface of neat film :

- the film is initially washed with the isopropanol to clean film and to remove the prints of finger. Other solvents were used, but the isopropanol proved to be the best,
- then the film is dried with the drying oven has 200°C during 1 hour in order to eliminate any trace from solvent as well as the surface tensions of film resulting from the process of implementation,
- finally the swelling of film pi in a solvent adequate. It will be shown that the process is optimized with the DMF during 20 min. This stage proved to be crucial and determining for the continuation of the operations because it ensures a porosity film, facilitating of this fact the penetration of metal through the film during the treatment chemical.

I.2.2 - Hydrolizis

The hydrolysis of polyimide led to the opening of the imide cycle, necessary following the operations of metallization - fig. 3.

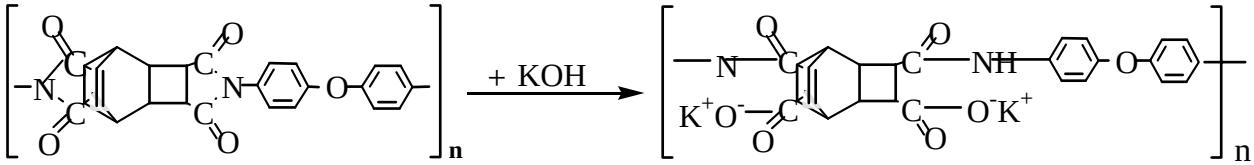

Figure 3. Basic hydrolysis of Polyimide

This reaction of opening of cyle is confirmed by infrared spectrometry FTIR, fig. 4 where one observes the disappearance of the imine function (1,755 cm^{-1} and 1,090 cm^{-1}) with carboxylate appearance function (1,555 cm^{-1}) and the vibrations of valence of the OH to 3,500 cm^{-1}).

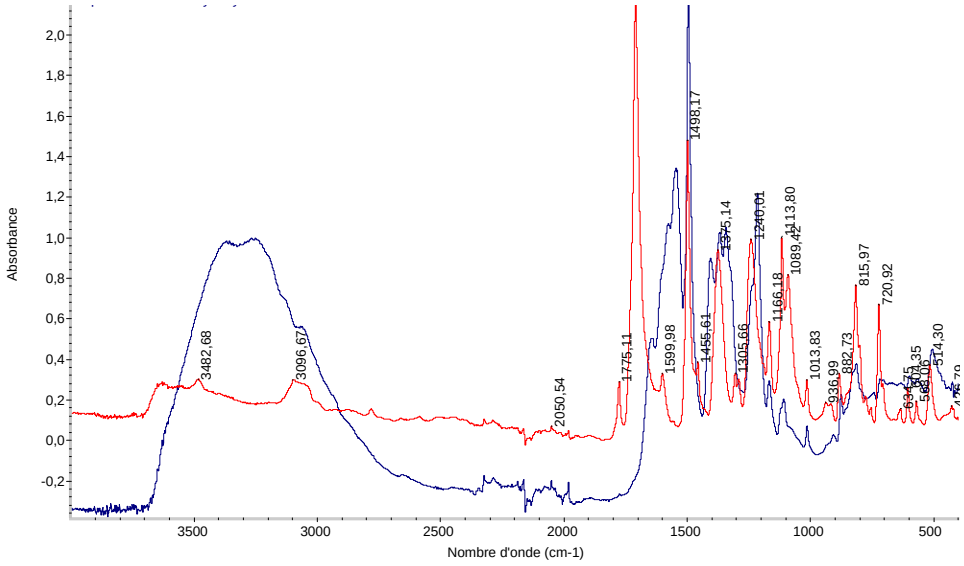

Figure 4. Infrared spectrum of neat Polyimide film (red) and after hydrolysis (blue)

Three solvents for the swelling of virgin film were tested : methanol, the diméthylformamide and mix of DMF/MeOH/acetone in ratios 2/1/1. The conditions of hydrolysis are led respectively with KOH, NaOH and $Ca(OH)_2$. The solutions of hydrolysis contain a mixture of isopropanol /water in the ratio 20/1 and the concentration of alkali is of 0.002 mol/L for KOH and 0.003 mol/L for NaOH and $Ca(OH)_2$. The results are carried in Table 3 being understood that the process is led at its term, the best note is allotted to the perfectly metallized sample.

Alcali	Solvent Treatment		
	Methanol	DMF	Mix
Swelling time of the film during **20 min**			
KOH	4	8	3
NaOH	5	10	6
$Ca(OH)_2$	0	0	0
Swelling time of the film during **1 h**			
KOH	5	7	3
NaOH	4	0 ?	8
$Ca(OH)_2$	0	0	0
Swelling time of the film during **3 h**			
KOH	4	2	0
NaOH	0	8 (shrinkage)	0
$Ca(OH)_2$	0	0	0

Table 3. Influence of solvent and alkali hydrolysis on the metallization process

Two important parameters can be optimized, the best result being obtained for a swelling with the DMF during 20 min followed by hydrolysis in the presence of NaOH. One can think that the size of the atom of the metal of alkali plays a part and that the hydrolysis is done better with an atom of reduced size. The sample is then washed with the mixture isopropanol/water 20/1 during 10 min.

I.2.3 - Metallization

This operation makes it possible to make the exchange metal/alcali-metal, in other words to transform the function $-CO_2^-Na^+$ in $-CO_2^-Ag^+$. The reaction is carried out by an aqueous solution of $AgNO_3$ with 3% in weight, during 20 min, followed by a washing to water during 10 min.

With silver,

- $8\ Ag^+ + BH_4^- + 8\ OH^- \rightarrow 8\ \underline{Ag} + H_2BO_3^- + 5\ H_2O$

Other metals have been used such as Co, Ni :

- $4\ Ni^{++} + BH_4^- + 8\ OH^- \rightarrow 4\ \underline{Ni} + B(OH)_3 + OH^- + 4\ H_2O$

- $2\ Co^{++} + 4\ BH_4^- + 9\ H_2O \rightarrow 2\ \underline{Co} + B(OH)_3 + B + 12.5\ H_2$

or Cu :

- $\underline{a\ \alpha = 0.1 - 0.25\ ;\ pH\ 9 - 9.5\ :}$
- $CuCl_2 + 2NaBH_4 + 6H_2O \rightarrow Cu + 2H_3BO_3 + 2NaCl + 7H_2$

- $\underline{at\ \alpha = 0.25 - 0.5\ ;\ pH\ 7 - 9}$:
- $CuCl_2 + 2\ NaBH_4 + 6H_2O \rightarrow CuH + 2H_3BO_3 + 2NaCl + 6.5H_2$

- $\underline{at\ \alpha = 1\ ;\ pH\ 5}$:

- $2CuCl_2 + 2NaBH_4 + 6H_2O \rightarrow CuCl + CuH + 2H_3BO_3 + 2NaCl + HCl + 6H_2$

II.2.4 - Reduction of Metal

The reduction of the function -CO2-Ag+ into Ag is carried out using a NaBH4 solution to 0.035 % in weight during one minute following the reaction :

$$-CO2-Ag+ + NaBH4 \rightarrow Ag + -CO2H$$

The sample is then washed with water during 10 min to eliminate salts. Recent studies carried out with ICS, Almaty (Dr. Rinate Iskakov) showed all the importance of washing with water on the thermal properties of metallized film. Three-days dialysis with daily changed distilled water (red plot – 585°C) shows on the enhancement of thermostability of the annealed construct (black plot – 445°C) fig. 5. Thus a dialysis during at least 24 hours makes it possible to eliminate salts and to ensure the good thermal behavior of metallized film.

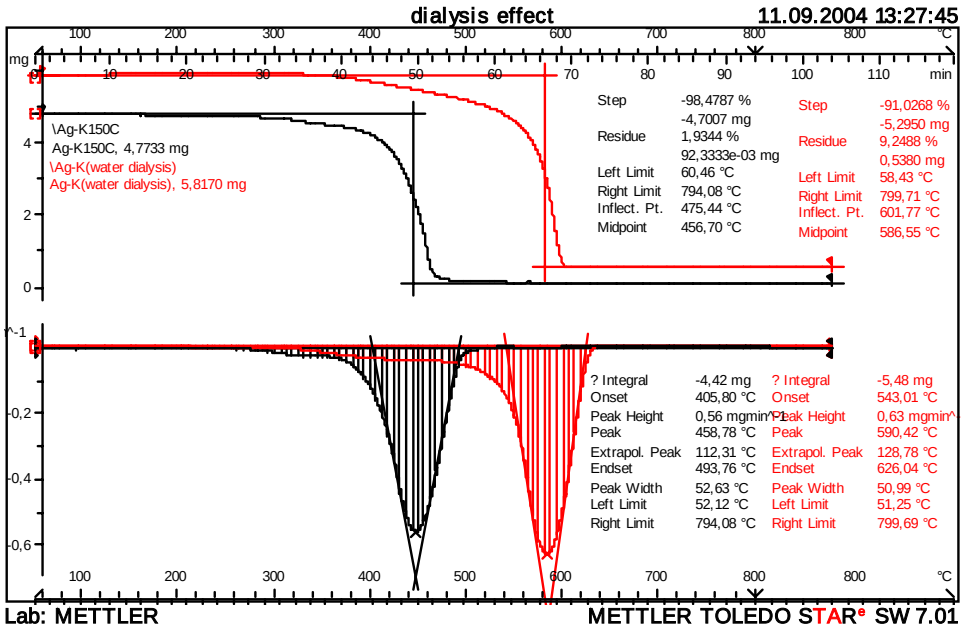

Fig.5. Effect of water dialysis on thermostability of metallized Kapton 50HN films. As was shown by X-ray analysis there were no traces of alkali ions in dialyzed metal-polyimide construct. The further annealing of alkali-free samples leads to cyclization of silver-amate complex to the imides and reduced metal.

I.2.5 – Thermal Treatment

I.2.5a TGA Analysis

Kapton 100HN metallized Ag by Montpellier University have been studied by TGA under nitrogen with this programme temperature :

- isotherm during 1 min at 25°C

- turn up from 25 to 900°C at 10°C/min
- and a plateau during 60 min at 900°C

A new calculation method (Journal of Thermal Analysis, 2005) of the kinetic energy (Ea) has been used. The activation energy of this thermal degradation is 166 kJ/mol. In comparison with Ea = 386 kJ/mol for Kapton 100 HN reference.
Concerning the temperature corresponding to maximum rate of the thermal degradation, (610°C for Kapton 100 HN reference), the data for metallized Kapton is 550°C – fig. 6.
Temperatures corresponding to 20% of weight loss for Kapton reference is 640°C, and after metallization process is 500°C – fig. 7.
Percentages of residual weight at the end of analysis is 18% for Kapton reference, and 33,5% for metallized film.

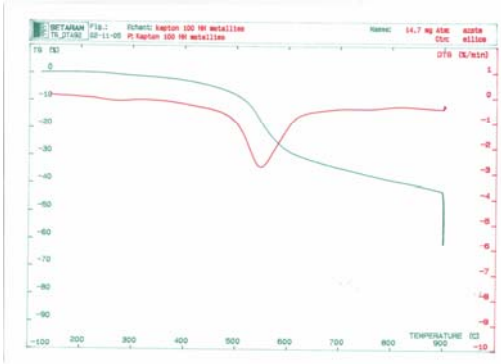

Figure 6. TGA of Kapton 100HN metallized Ag versus temperature

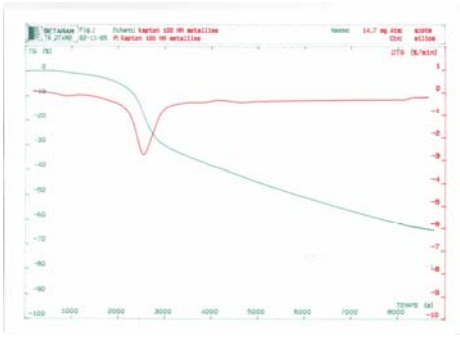

Figure 7. TGA of Kapton 100HN metallized Ag versus time

I.2.5b Thermal Curing

The thermal treatment of the sample is then necessary for two principal reasons :

- initially to allow metal Ag to diffuse on the surface to ensure a good homogeneity of the metal layer - fig 8,

Figure 8. Diffusion of metal with migration on the surface

- then to allow the reaction of cyclization of the function imine, beforehand open at the time of the hydrolysis to ensure the reaction of metallization - fig. 9. This reaction of cyclization of the amic-acid function makes it possible to ensure and find good the inherent properties in any polyheterocyclic structure.

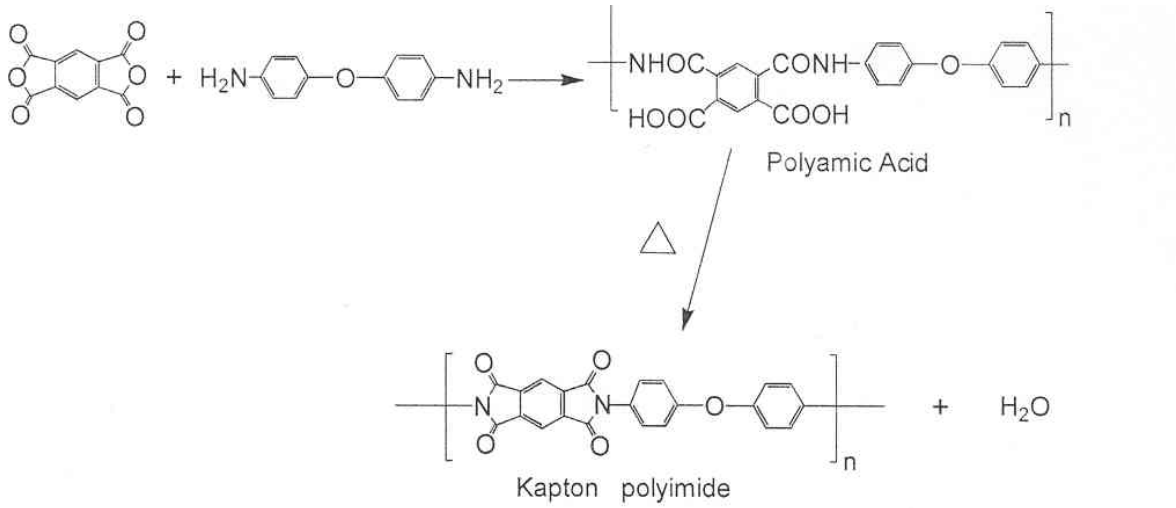

Figure 9. Reaction of synthesis of the Kapton polyimide

The heat treatment was optimized for 2 hours with 180°C. Observations with electronic scan microscopy showed infusion of metal through the thickness of film - fig. 10 & fig. 11, which confirms the good adherence of the metal layer on the surface of the polyimide film.

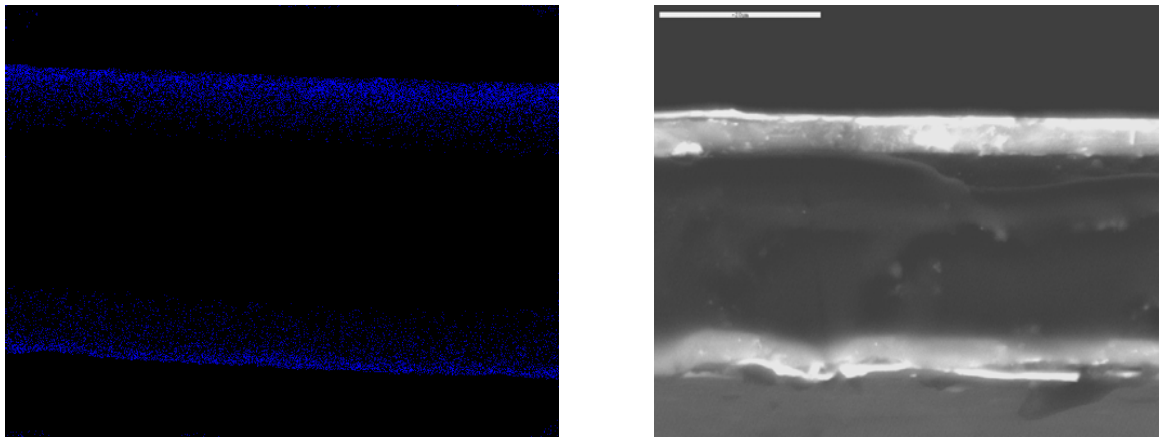

Figure 10. Cartogrphie with the x-rays of film of metallized polyimide with the silver (left photo) and observation with the SEM (right photo)

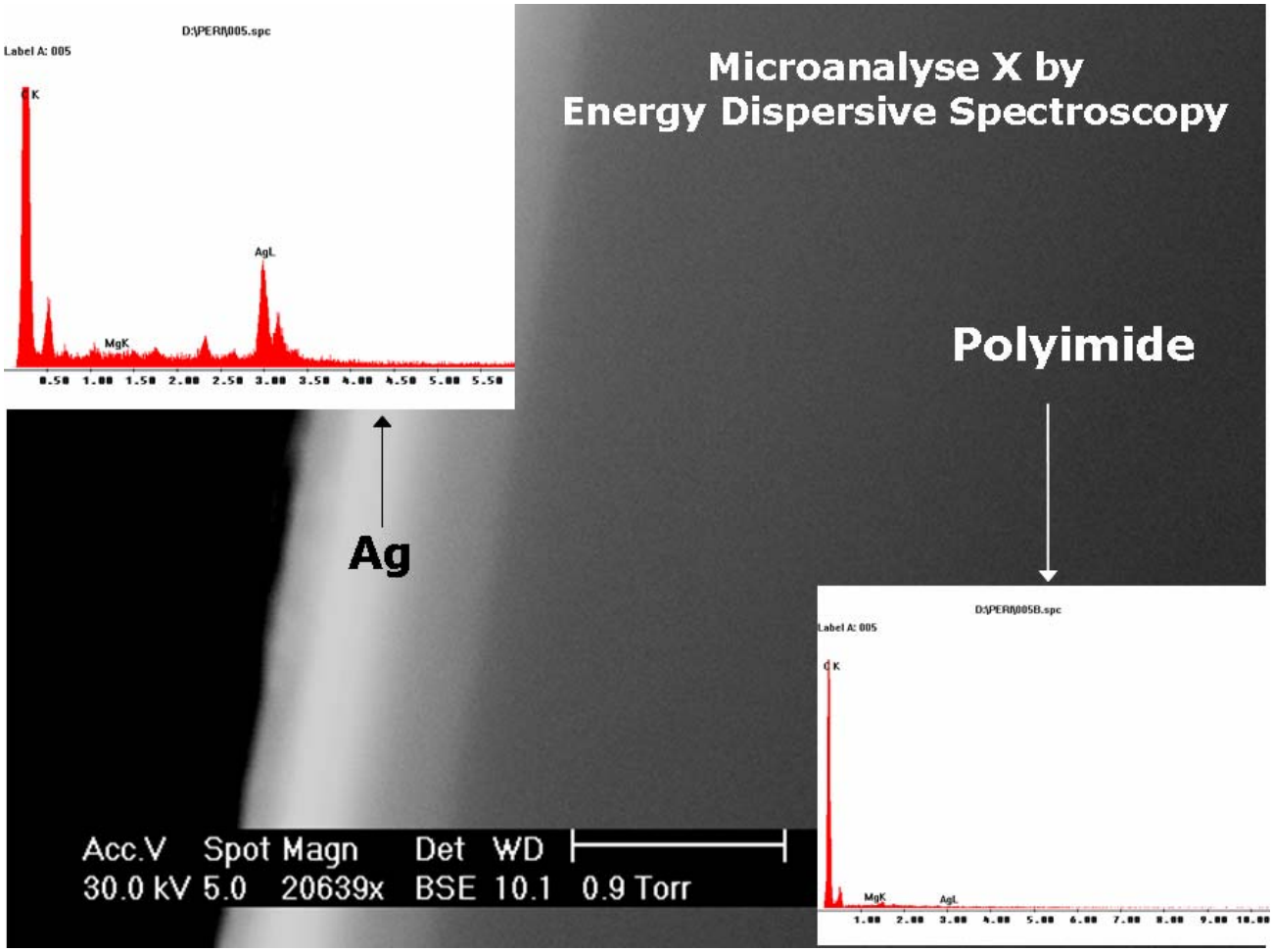

Figure 11. TEM and X Microanalysis by energy dispersive spectroscopy

The strong adherence of the metal layer was also confirmed by the observation of samples subjected to a stretching, causing on the surface of the cracks without causing delamination of the metal layer - fig.12.

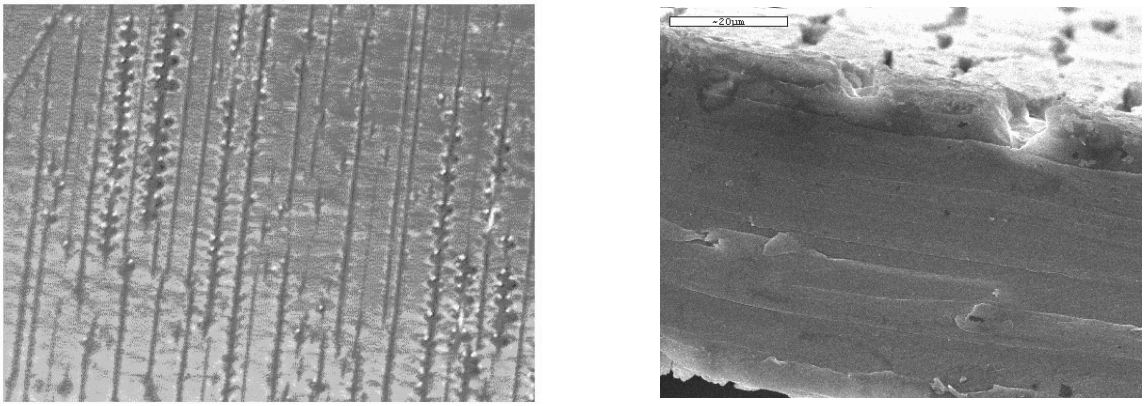

Figure 12. Polyimide subjected to stretching with appearance of cracks on the surface (photo of left) and seen section of the film polyimide (photo of right-hand side)

I.2.6 Cristallography

In order to increase the effect of plasma pre-treatment on PI films (Upilex or Kapton), we have tried to swell films in a solvent. In order to do that, we have follow this procedure :

- cleaning of PI film by isopopanol
- heating at 200°C during 1 hour
- swelling in DMF during 20 min.

We have obtained the following results – fig. 13 & 14 :

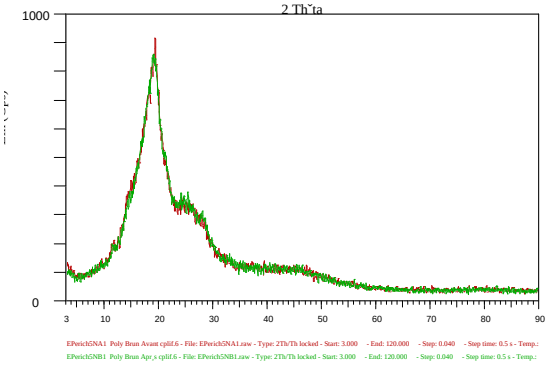

Figure 13. Crystallography analysis of Upilex PI films before (in red) and after swelling (in green)

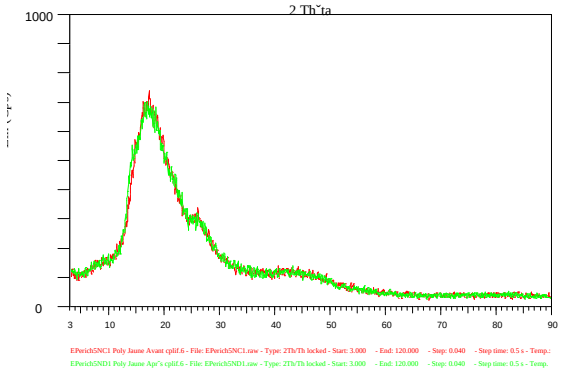

Figure 14. Crystallography analysis Kapton PI films before (in red) and after swelling (in green).

As shown on fig. 13 and 14, the swollen films of Upilex or Kapton do not present an increase of the amorphous part. In other words, the solvent pre-treatment of the neat polyimide film does not change the cristallinity of the product.

II. Application

Applied technique allows to produce metal-polyimide composites with surface distribution of metal into the polyimide matrix. The depth of silver penetration is 2-4 microns in 30-50 micron films, moreover it is identical along the surface due to uniform distribution of metal by the applied metallization technique. In fig. 9 the uniformity of silver layers onto polyimide surfaces are shown as cross-section data of Energy Dispersive Spectroscopy and layered data of X-ray analyses. The most concenrated area of silver is around the surfaces penetrating in 2-3 microns depth. There are a presence of silver in the inner part of polyimide matrix, which is visible in X-ray adat hardly. Uniformity are generally provided by the use of large amount of aqueous solution in a bath which is large than square of metallizing film. Equal deposition of metal ions is also provided by constantly flowing solution through the bath without mechanical stirring which can damage a growing metallic layer or scratch the surfaces. Any mechanical disturbances of the film surfaces lead to uncontrolled formation of defects of metal crystal grains forming onto the surfaces of polymer. Data of mathematical simulative analyses of silver distribution based on X-rays and

silver diffusivity data shows dominant location of metal as growing grains in the surface part of polyimide matrix fig. 15.

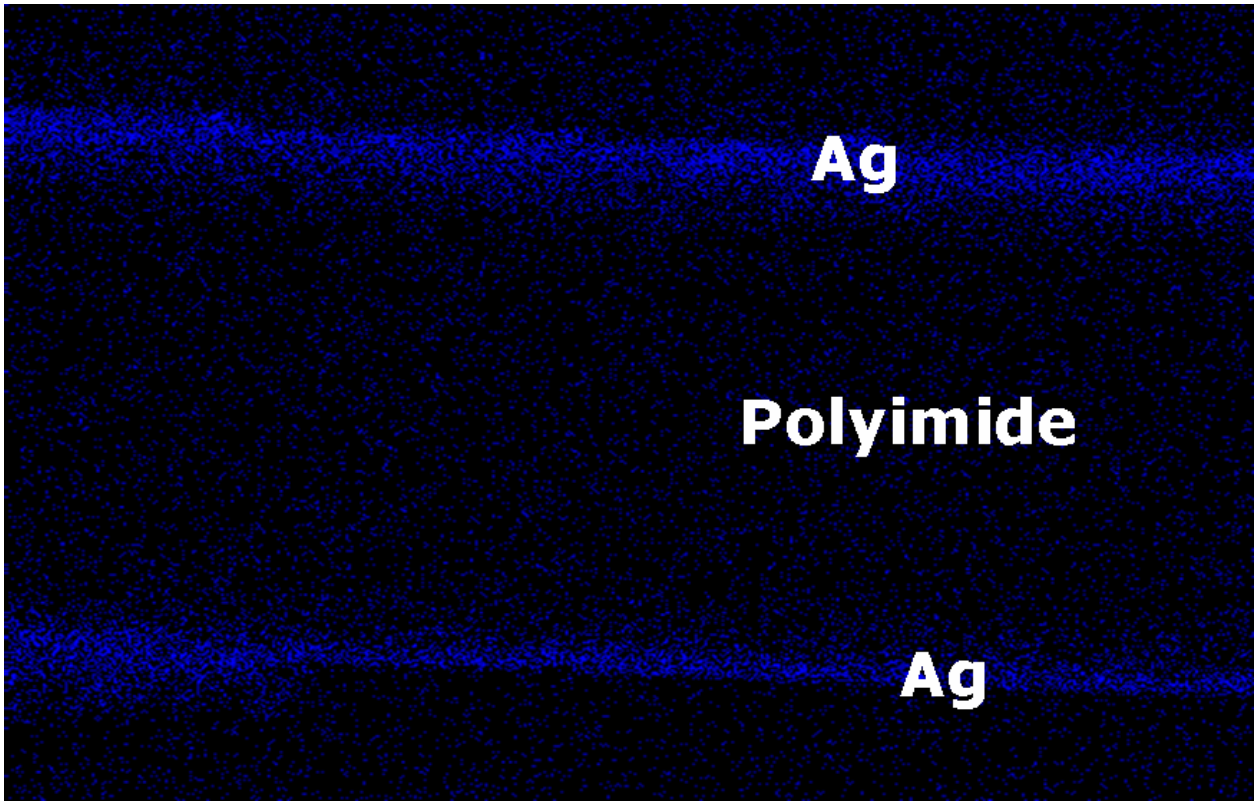

Figure 15. Distribution of silver in Polyimide film from X ray chemical cartography

III End Users

III.1 Joint Stock Company Ust-Kamenogorsk Capacitor Plant

Since September 21 the development of technology for metallization of indistrial polyimide film (PM, Russia) and installment of technological equipment were started. Technology procedure leads to formation of metallized coating onto a tape of the polyimide film using our patent methods of chemical deposition of metals. Scheme of technological chain is demonstrated in fig. 16.

III.2 USA-Kazakhstan Joint Venture "KKInterconnect"

In June of this year we started a pilot production of flexible microchips based on polyimide films and using our patent technique of chemical deposition of metal with pattern (discrete) distribution of metal layers. The producing chips are planned to apply as flexible elements of computer keyboards which are key product of the company.

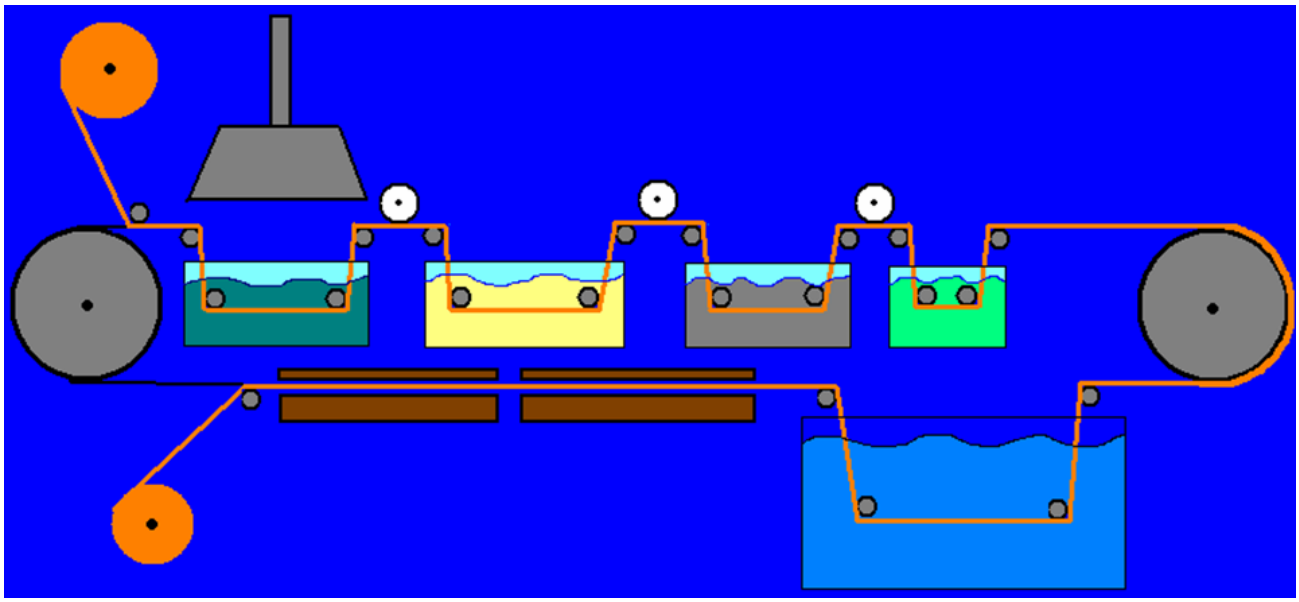

Figure 16. Scheme of technological procedure for metallization of polyimide film consisting of modification in organic solvent, alkali hydrolysis, metal ions deposition, chemical reduction of metal, washing and annealing.

Conclusions

The process of metallization by chemical way was optimized by consigning the experimental conditions. The good integration of metal film on the polyimide support was shown and confirmed. With regard to metallization with the silver of the films Kapton® polyimide, the glare obtained while proceeding by hydrolysis with NaOH is higher and of better aspect (frozen aspect) compared to the hydrolysis in KOH medium. In addition and because of its smallness, the migration of Na is higher than that of K, which causes thereafter a better adhesion of metal Ag. Lastly, of the experiments carried out in the presence of agitation showed in all the cases - modification, hydrolysis, metalation taken separately or successively, the preponderance of the non use of agitation on the final result of metallization.