Thermal Analysis of Silver Coatings Used for Tantalum Capacitors

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SYNOPSIS

Silver-filled polymer coatings are used to ensure the cathodic junction of tantalum capacitors. To polimerize new materials able to resist to the RTSH industrial test, we studied first the physical chemistry of the main commercial coatings used at the present time. Four commercial silver coatings (epoxy, polyester, polyimid, and polyacrylate binders) and one conductive epoxy adhesive were tested. We separated the silver flakes from the polymer binder by centrifugation and filtration. We analyzed the thermal degradation and stability of the two kinds of sample (with and without silver flakes) using DSC and TGA. The influence of fillers mixing is discussed. This article reports, also, the main chemical structures of the binder components, determined using ^{1}H- and ^{13}C-NMR and elemental analysis, after HPLC or GPC fractionation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Tantalum capacitors are, at the present time, the most stable electrolytic capacitors. Pure tantalum, one of the scarcest chemical elements, is a gray-silver colored metal. It was discovered in 1802 by a Swedish chemist: Ekeberg. It resists the acids and bases currently used under 175°C. Moreover, its oxide (Ta_2O_5) is extremely stable, possesses very good dielectric properties (Table I), and its thickness can be controlled exactly.

An electrolytic capacitor consists of two conductive layers separated by a dielectric one: tantalum pentoxide (Ta_2O_5), for instance (Fig. 1).

The capacitance is given by the formula

$$C = \varepsilon A / e$$

where ε is the dielectric constant; A, the area of the conductive surfaces, and e, the thickness of the dielectric. Reducing the thickness e in order to increase the capacitance is limited by the appearance of leakage currents. Higher capacitances are obtained through the increase of the A-specific area by using industrial sintering process.

Manufacturing Process

The chip tantalum capacitor with solid electrolyte is made up of five parts[1,2]:

- A macro porous anode of sintered tantalum.
- A dielectric layer of tantalum oxide (Ta_2O_5).
- A manganese dioxide (MnO_2).
- Surrounding outer layers consisting of graphite, silver coatings, and a lead frame.
- A protective capsule of resin.

Pressing

The tantalum powder is pressed like a cylindrical or parallelepipedical pellet. Its dimension is determined according to the final capacitance and tension required. The pellet composes the anode (+) of the capacitor.
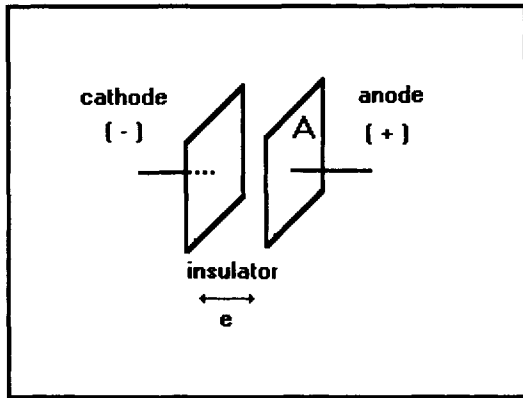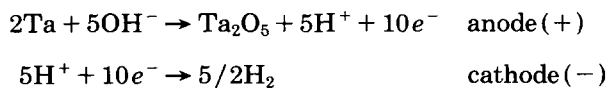

Figure 1 Schematic representation of a capacitor.

Sintering

The grains of tantalum are sintered, between 1500 and 2000°C, to form a conductive network.

Creation of the Dielectric Layer

By electrochemical oxidization, the oxide layer is shaped on the surface of the tantalum sintered pellet:

$$2Ta + 5OH^- \rightarrow Ta_2O_5 + 5H^+ + 10e^- \quad anode(+)$$

$$5H^+ + 10e^- \rightarrow 5/2H_2 \quad cathode(-)$$

Creation of the Cathode

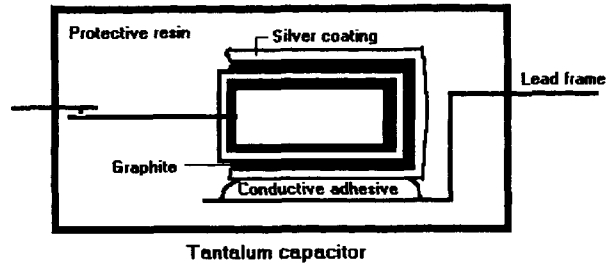The pellet is dipped into a manganese nitrate solution $[(Mn(NO_3)_2]$, which, over 260°C, is trans-

Table I Dielectric Constant of Different Materials Used as Insulators in Capacitors

Dielectric Materials	Dielectric Constant ϵ
In a vacuum or air	1
Paper	2.0–6.0
Plastics	2.1–6.0
Mineral oil	2.2–2.3
Quartz	3.8–4.4
Glass	4.8–8.0
Porcelain	5.1–5.9
Mica	5.4–8.7
Oil ASKAREL (synthetic flammable)	5.6–5.9
Aluminium oxide	8.4
Tantalum pentoxide	26
Ceramics	12–400,000

Figure 2 Schema of a solid electrolytic tantalum capacitor.

formed into manganese dioxide, a good semiconductor:

$$Mn(NO_3)_2 + H_2O \xrightarrow[T>260°C]{} \beta MnO_2 + H_2O + NO_2$$
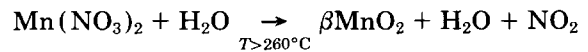
To connect the anode to an external support, it is sufficient to solder a nickel wire on the tantalum metal, but on the manganese dioxide, it is impossible to solder anything.
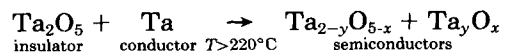
Cathode Connection

At first, the pellet is overlaid by a thin layer of graphite. Then, also by dipping, a thin-layer silver coating is deposited on the graphite. To create the second external connection, the pellet is fixed on a lead frame through the medium of a silver conductive adhesive (Fig. 2).

Plastic Packages

Epoxy moldings compounds are usually used to encapsulate the raw capacitor.

N.B.: It is important to note that over 220°C the tantalum oxide is modified and oxygen ions migrate through the oxide layer to the tantalum metal:

$$\underset{\text{insulator}}{Ta_2O_5} + \underset{\text{conductor}}{Ta} \xrightarrow{T>220°C} \underset{\text{semiconductors}}{Ta_{2-y}O_{5-x} + Ta_yO_x}$$

Silver Conductive Coatings

Advances in surface-mounting technologies demand polymer materials that have extremely low thermal stress and excellent stability at high temperatures to be used in reflow soldering. One of the important electric characteristics of tantalum capacitors is the

equivalent serial resistance (ESR) value. Measured at 100 kHz, this characteristic is intimately related to the quality of the anodic junction realized with two conductive silver coatings.

At present time, to evaluate the thermal resistance of the tantalum capacitors, industry uses the rapid test solder heating (RTSH) test. It consists of dipping the chip capacitor into a 260°C soldering bath for 10 s. Before and after the test, the main electric values are measured (ESR, capacitance, dissipation factor δ, leakage current i_F). The evolution of the ESR value is noted and compared to those before the test. In case of an unacceptable increase (each manufacture determines its percentage), all the production is scraped.

The industrial finality of this study was to synthesize new materials for electronic devices. These conductive coatings have to resist at high temperatures (260°C/10 s, but, soon, 300°C/60 s) and to keep good mechanical properties up to 150°C. Publications reviewing thermal or mechanical properties of silver coatings used for tantalum capacitors or other electronic devices are scarce[3-9] or written in Japanese. Indeed, the manufacturers protect their research against competition. So, to evaluate the qualities of a "good" resin, we began to study the physical–chemical properties of five commercial coatings usually used in industry. We selected four representative kinds of binder (epoxy, polyester, polyimid, and polyacrylate). The samples received from the manufacturers were silver-filled polymer coatings. In order both to understand the effect of metal blending and to fractionate the binder components, we separated silver flakes from the rest.

This article deals with five commercial conductive silver coatings. The aim of the study was to make a precise evaluation of the chemical composition of the samples and of their thermal properties (T_g and thermal degradation).

EXPERIMENTAL

Chemical Composition

Silver Conductive Coatings

The five coatings used are commercial resins called A, B, C, D, and E:

   A: Solvent-free epoxy adhesive;
   B: Polyacrylate resin; solvent: butyl acetate;
   C: Polyester resin; solvent: 3-methoxy butyl acetate;
   D: Epoxy resin; solvent: 2-butoxy ethyl acetate;
   E: Polyimide resin; solvent: N-methylpyrrolidone.

All the five are one-component, silver-filled coatings. All the main components have been identified by IR, NMR, and elemental analysis,[10] except the polyimide one.

Preparation of Samples

To identify the structure of the main component of each coating, we first separated the silver flakes from the resin by filtration and centrifugation. The solvents were removed from the resin under vacuum. When it was necessary, the resins were fractionated by semiquantitative GPC or HPLC.

HPLC Fractionation

Apparatus:

   Two pumps, Waters 510
   Gradient controller, Waters 680
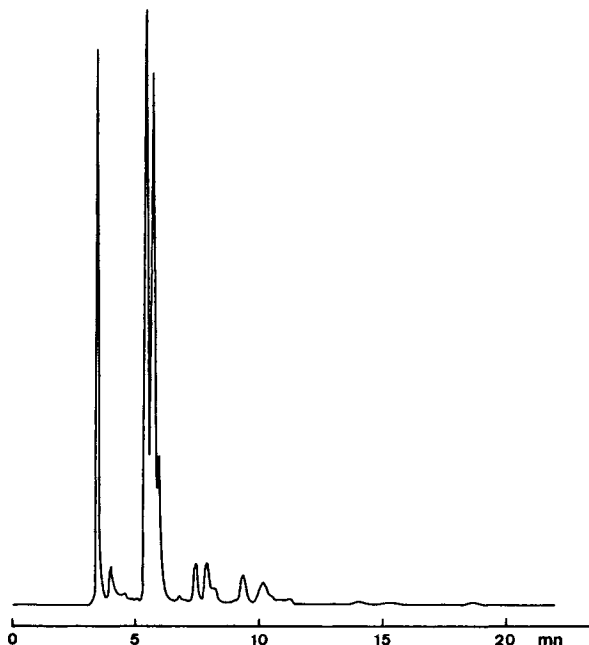   Manual injector, Waters U6K
   UV detection apparatus, Waters 481

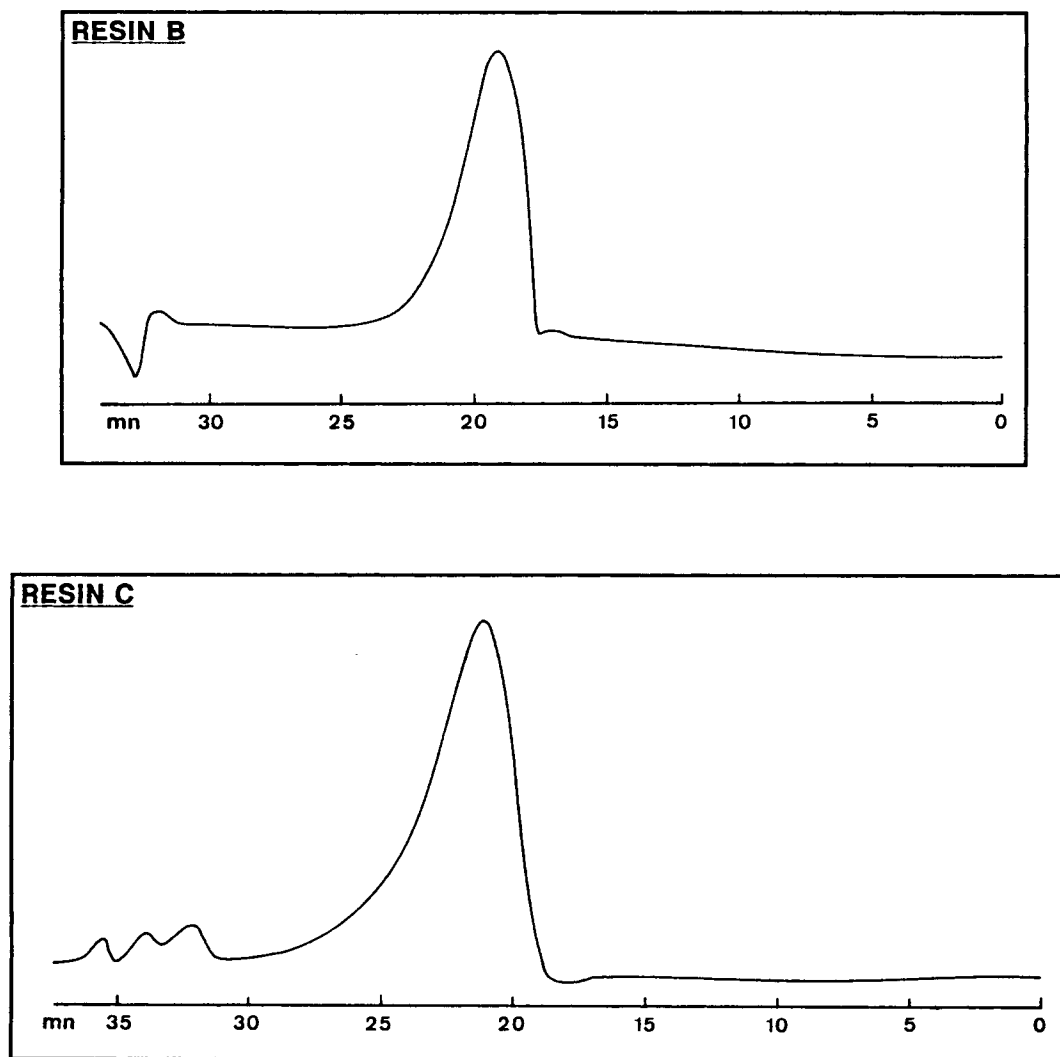**Figure 3**   HPLC chromatogram of resin A.

Figure 4   GPC chromatograms of resins B, C, D, and E.

Experimental conditions:

Column Interchrom Nucléosil 300 Å; C18; 5 μ
(250 × 10 mm)

Flow: isocratic 4 mL/mn; 45% H_2O/55% CH_3CN

Injection: 200 μL; 10% by weight

Detection: UV 230 nm

Fraction purity: The purity of each fraction was verified by HPLC using the following conditions:

Column Interchrom Nucléosil 300 Å; C18; 5 μ
(250 × 4, 6 mm)

Flow: isocratic 1 mL/mn; 45% H_2O/55% CH_3CN

Injection: 20 μL; 0.5% by weight

Detection: UV 230 nm

GPC Fractionation

Apparatus/experimental conditions: The apparatus used to fractionate the resins was a Waters GPC and the columns used are Phenomenex ones. The experimental conditions depend on the samples.

Samples B and C:

Columns: $500/10^3/10^4$ Å

Injection: 100 μL; 10% by weight

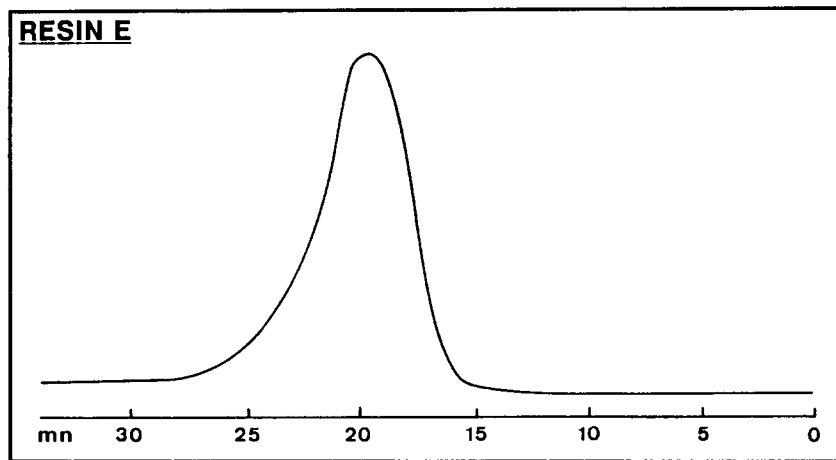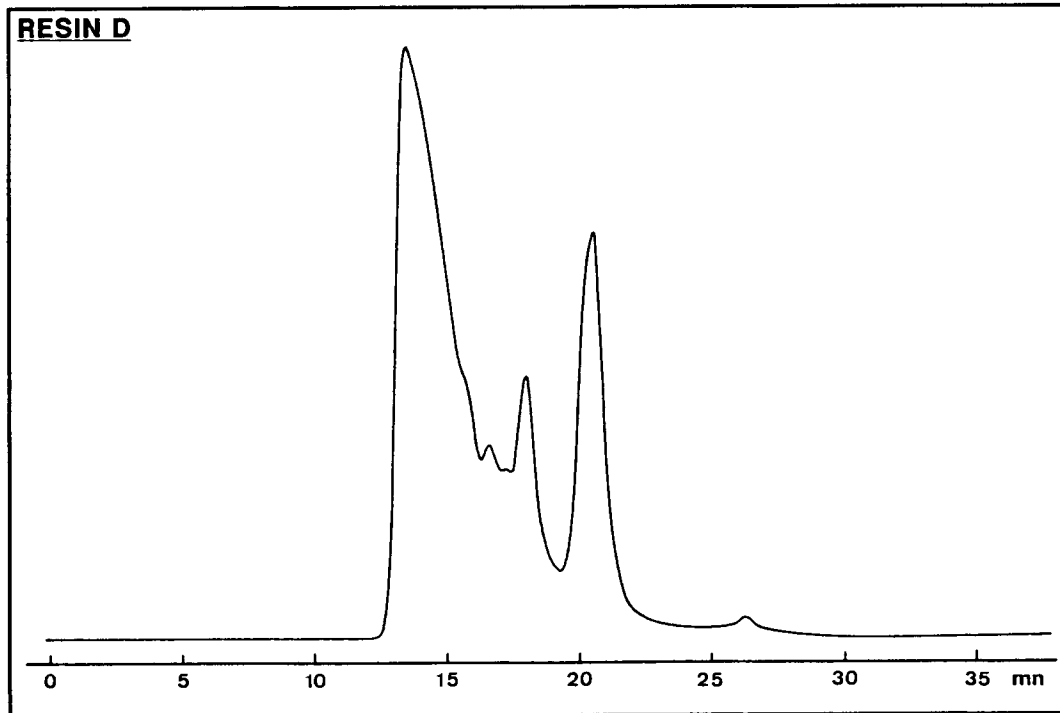Toluene 1 mL/mn; detection: RI

Figure 4 (*Continued from previous page*)

Sample D:

   Columns: 100/100/50 Å

   Injection: 100 μL; 15% by weight

   THF 1 mL/mn; detection: UV 230 nm

Samples E:

   Columns: 100/100/100/50 Å

   Injection: 100 μL; 5% by weight

   DMF 1 mL/mn; detection: UV 280 nm

We used the same conditions to determine the equivalent polystyrene (PS) molecular weight. Molecular weight conversion to correct values for studying molecules is required when a PS-based calibration is applied to estimate the MW of materials other than PS, but our results ignore these corrections.[11]

Fraction purity: The purity was verified for each fraction by GPC analysis using the same conditions

Table II Liquid Chromatography System Used to Separate the Main Component of Each Type of Resin and the Number of Fractions Separated

| Resins | Mode of Fractionation | | No. Fractions | Molecular Weight | |
	Mode	Elution Solvent		MW (g/mol)	Elution Solvent
A	HPLC	CH_3CN 55/H_2O 45	8	410	THF
B	Filtration	Acetone	1	39,000	Toluene
C	Filtration	Acetone	1	26,000	Toluene
D	GPC	THF	4	3,400	THF
E	GPC	DMF	1	Undetermined	

as for fractionation, except the quantity injected: 100 μL, 1% by weight.

Analytical Apparatus

A Perkin-Elmer 882 was used for IR spectra. A Brücker AM 400 and Brücker CXP 100 were used for, respectively, liquid and solid ^{13}C- and ^{1}H-NMR.

Thermal Study

Analytical Apparatus

A Setaram DSC 101 and a Perkin-Elmer 7 DSC were used for the glass transition temperature measurements and thermal analysis. A Setaram TG 85 apparatus was used for the thermogravimetric tests.
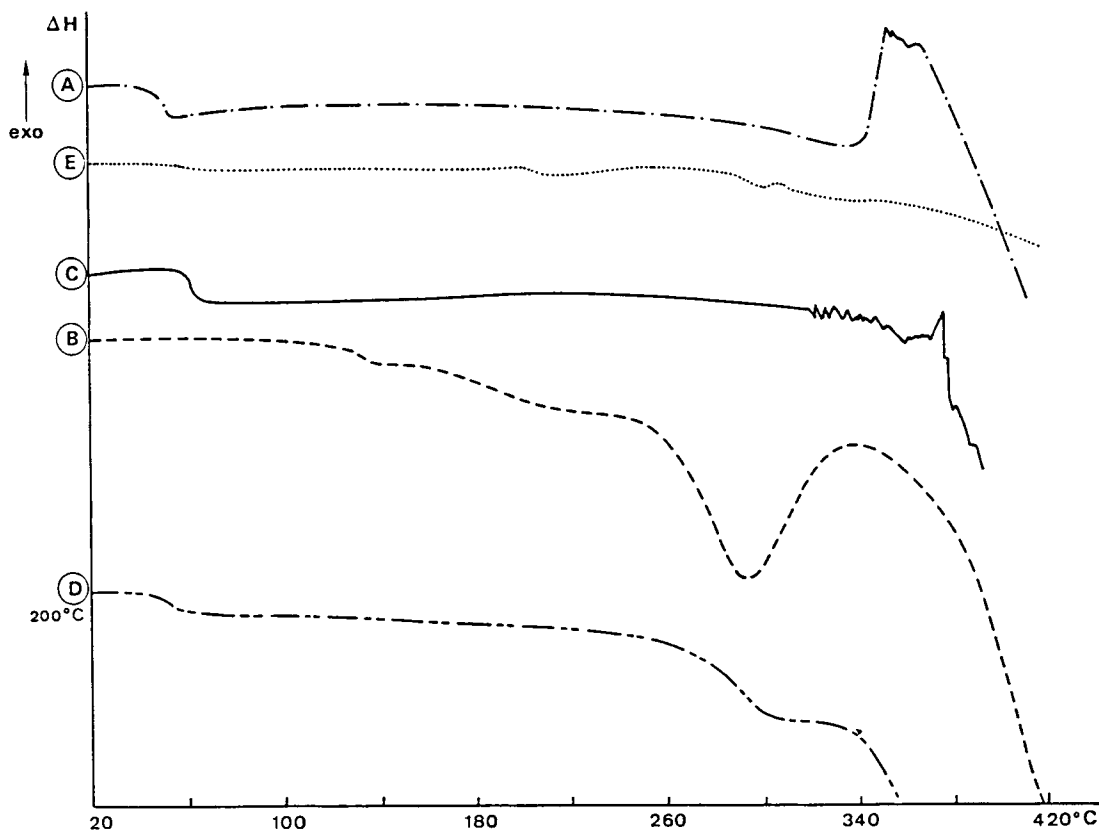

Figure 5 A–E extracted resin (without silver flakes) DSC thermograms after curing DSC heat rate: 10°C/mn. $A_{170°C/1h}$: m = 22.75 mg; B: m = 8.00 mg; C: m = 8.56 mg; $D_{200°C/1h}$: m = 14.10 mg; E: m = 9.80 mg.

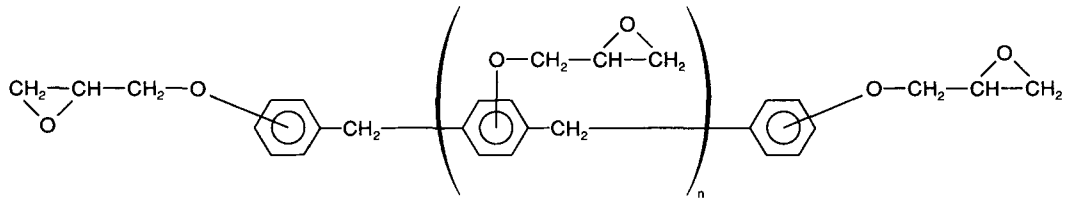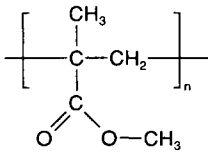**Table III Formulas of the Main Components of Each Resin Except E**
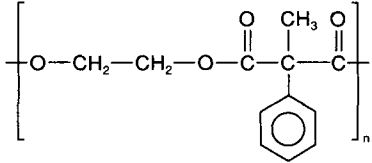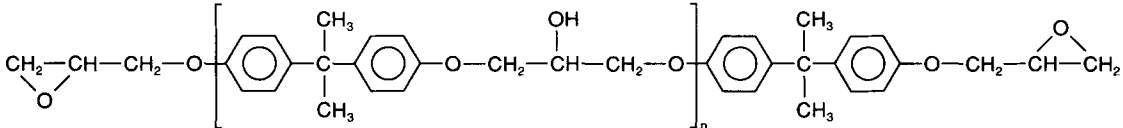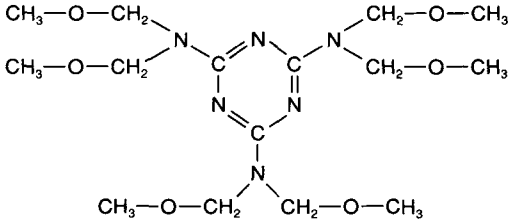
A	**DGEBF** Di Glycidyl Ether of the Bisphenol F Each of the 8 peaks of the HPLC chromatogram was identified except one. The 7 others correspond to the different isomers of the DGEBF $[(p-p')_n ; (o-p')_n ; (o-o')_n]$
B	**PMMA** Polymethylmethacrylate
C	Poly[ethylene(methyl-2-phenyl-2-propionate)]
D	**DGEBA** Di Glycidyl Ether of the Bisphenol A **HMMM** Hexa methoxy methyl melamine Latent curing agent
E	Polyimide

Table IV   Weight Percentage of the Different Silver-coating Components, Given by Different Manufacturers

	Weight %				
Coatings	Silver	Solvent	Resin	Shelf Life	
A	88–92	< 1	8	6 months	−10°C
B	68–72	20	10	12 months	0°C
C	49–51	43–45	6	12 months	0°C
D	68–72	15–20	8	12 months	0°C
E	69–71	25	6	6 months	−40°C

The experimental conditions are repeated under each figure.

Samples

Two kinds of samples were prepared: with and without silver flakes. Indeed, to study the effects of the presence of metal, we separated the polymer resin from the silver fillers by centrifugation and filtration.[10]

Cure Cycles

Silver-filled Coatings. They are dried 30 mn at room temperature both to remove one part of the solvent and to film the coating; then, they are cured. **Extracted Resins from Silver Coatings.** The major part of the solvent is removed under vacuum, at room temperature, to prevent the polymerization; then, the preparation is as described above.

N.B.: It is practically impossible to cure the poly-imid resin over 200°C because of the migration of the oxygen ions through the oxide layer (Ta_2O_5) of the tantalum capacitor anode.

RESULTS AND DISCUSSION

Chemical Composition of Silver Coatings

Chemical Structure of the Main Components of the Resins

After fractionation of the five different resins by HPLC or GPC (Figs. 3 and 4) and removing all the solvent, we determined the equivalent PS molecular weight (Table II); then, we identified the main components of all the resins except the polyimid one that was included in the study as a reference. The results are given in Table III.

We studied four different chemical series of resins that are the most representative of the market at the present time. The PMMA resin as well as the

epoxy are now well known and used for many other industrial applications. But the polyester and poly-imid resins are especially synthesized for microelectronic devices. Of course, a lot of other components are blended into the mixture, such as

- the wetting agent,
- antioxidizing agents,
- thyxotropic agents.

But they are present in so-infinitesimal quantities that, with the technics of separation used, it was not possible to identify their chemical structure.

Weight Percentage Composition

Results are summarized in Table IV.

Thermal Study

To compare the thermal stability of the different coatings, we prepared two kinds of samples, with and without silver flakes, as seen in the Experimental section, and cured as seen in Table V. The following paragraphs deal with the thermal study, with Figures 5 and 6 representing DSC thermograms of resins A–E, respectively, with and without silver flakes, whereas Figures 7 and 8 deal with TGA thermograms.

Glass Transition Temperature

The T_g values increase from 50 to 200°C (Table VI). They depend on the cure cycles and silver flakes

Table V   Cure Cycles of the Five Silver Coatings

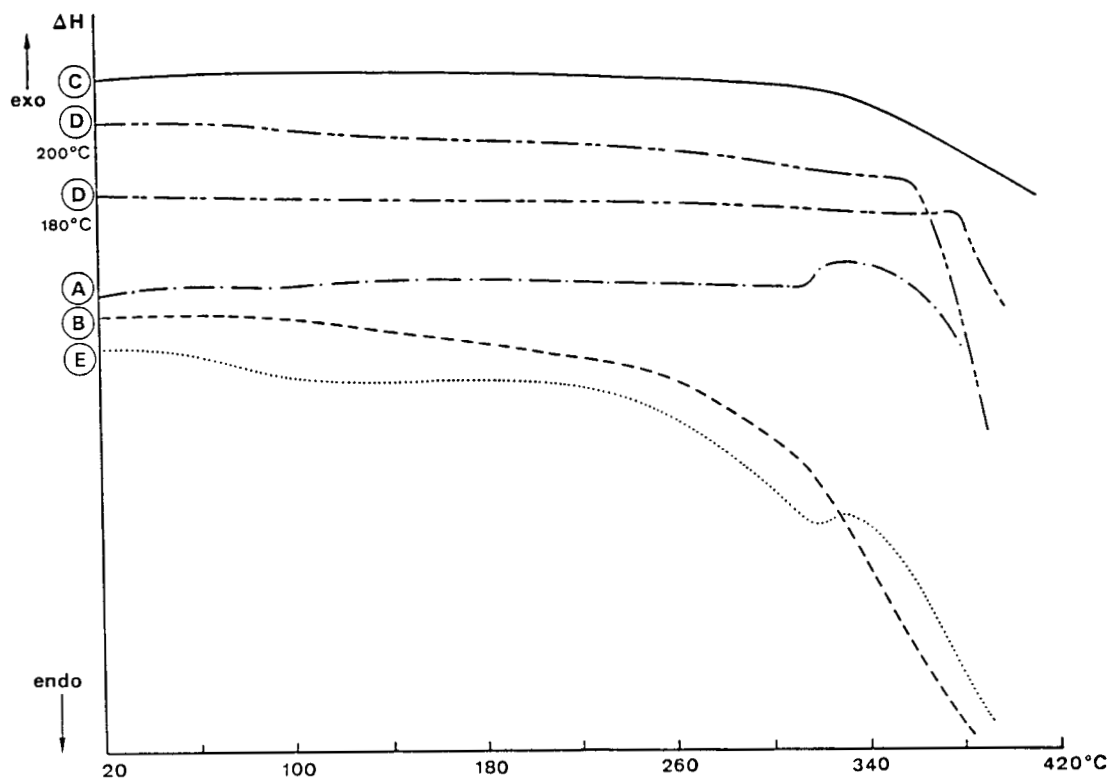| Silver Coating or Extracted Resin	Cure Cycles
A	170°C/1 h
B	150°C/1 h
C	180°C/1 h
D	180°C/1 h
	200°C/1 h
E	200°C/1 h

Figure 6 A–E silver-coating DSC thermograms after curing. DSC heat rate: 10°C/mn.
$A_{170°C/1h}$: m = 96.33 mg; B: m = 43.50 mg; C: m = 25.00 mg; $D_{180°C/1h}$: m = 38.80 mg; E: m = 26.10 mg; $D_{200°C/1h}$: m = 40.20 mg.
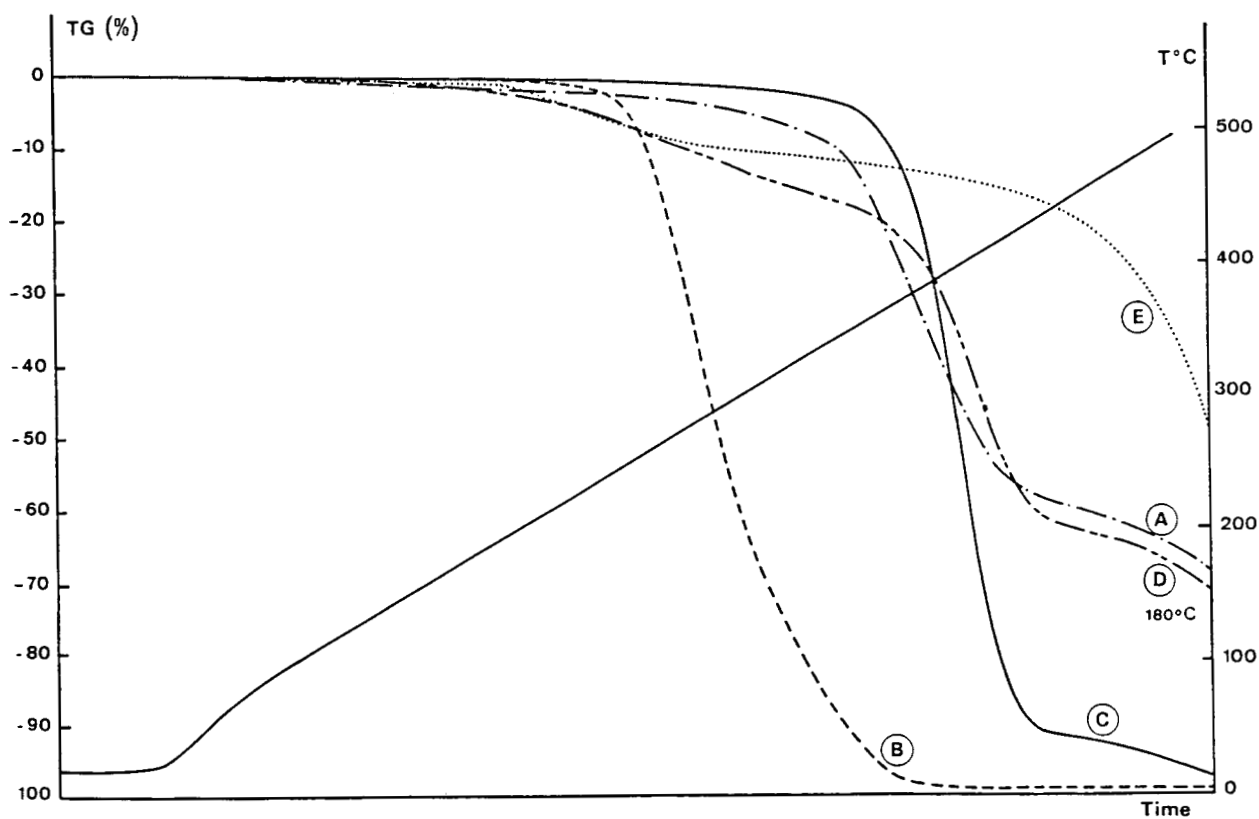

Figure 7 A–E extracted resin (without silver flakes) TGA thermograms after curing.
TGA heat rate: 5°C/mn. $A_{170°C/1h}$: m = 11.30 mg; B: m = 17.60 mg; C: m = 21.70 mg; $D_{180°C/1h}$: m = 7.50 mg; E: m = 5.20 mg.
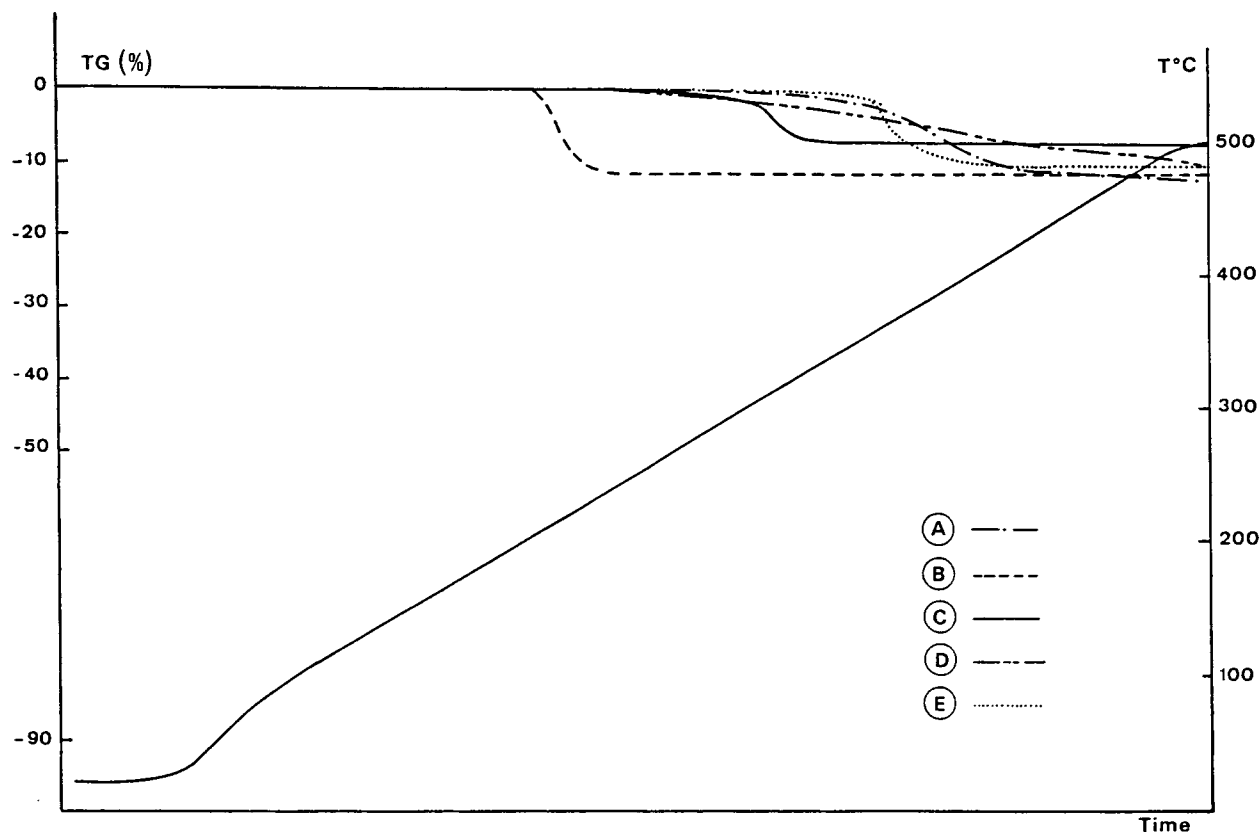
Figure 8   A–E silver-coating TGA thermograms after curing. TGA heat rate: 10°C/mn. $A_{170°C/1h}$: m = 101.70 mg; B: m = 79.70 mg; C: m = 37.10 mg; $D_{180°C/1h}$: m = 63.00 mg; E: m = 25.01 mg.

contained. We noted that, except for the D sample, the differences between the T_g of the silver coatings and their extracted resins are small. In the case of resin D, the presence of metal fillers induce an increasing of the polymerization due to a better thermal conduction. Sample D contains an epoxy resin and a latent curing agent. Even after 1 h at 200°C, its polymerization is not achieved yet. The T_g^{max} measured, after 6 h at the same temperature, is 132°C. Also, we can observe a large difference, after

Table VI   Glass Transition Temperature of the Five Silver Coatings With and Without Silver Flakes After Curing

	Glass Transition Temperature (T_g) (°C)	
Silver Coatings	Without Silver Flakes	With Silver Flakes
A	69	70
B	124	118
C	64	Not observed
D 180°C/1 h	50	68
D 200°C/1 h	53	106
E	198	200

Table VII   Thermal Degradation Temperature With and Without Silver Flakes After Cure Cycles

	Thermal Degradation Temperature (°C)	
Silver Coatings	Without Silver Flakes	With Silver Flakes
A	320	300
B	240	200
C	330	300
D 180°C/1 h	350	320
D 200°C/1 h	350	320
E	410	340

Table VIII   Silver Coating Weight Loss (in Percentage) vs Time at 260°C and After Curing Cycles

Time (mn)	Weight Loss					
	B	C	E	D 180°C/1 h	D 200°C/1 h	A
0	0.00	0.00	0.00	0.00	0.00	0.00
0.5	−0.06	−0.08	−0.01	−0.07	−0.01	−0.05
1	−0.10	−0.13	−0.08	−0.12	−0.06	−0.12
1.5	−0.38	−0.24	−0.17	−0.22	−0.10	−0.23
2	−1.44	−0.42	−0.26	−0.37	−0.14	−0.34
5	−8.60	−0.82	−0.39	−1.17	−0.75	−0.75
10	−10.94	−1.04	−0.45	−1.69	−1.25	−1.55
15	−12.19	−1.17	−0.49	−1.91	−1.49	−1.47

curing, between the T_g for sample D with and without silver. At the same temperature, the polymerization will be accelerated and the epoxy network will be stronger.

Except for the polyimid resin E, all the T_g values are less than 150°C. But, at the present time, 150°C is the temperature into the holes of the molders used to encapsulate the anodes of the capacitors. So, it seems impossible to have a good mechanical resistance at 150°C with the other resins (A → D).

Thermal Degradation

We defined the temperature of thermal degradation as the extreme temperature beyond which the poly-

mer has lost its plastic properties (DSC thermogram profiles change after a first passage over this temperature).

The results of our observations are summarized in Table VII:

1. The PMMA containing the B resin is the less thermal-resistant. The thermal degradation processes are now well known: After 240°C, PMMA is transformed into its own monomer, MMA, which is sublimed over 300°C.[12]
2. The most thermal resistant is the polyimid containing the E resin. It resists at temperatures above 400°C. All the other resins sup-
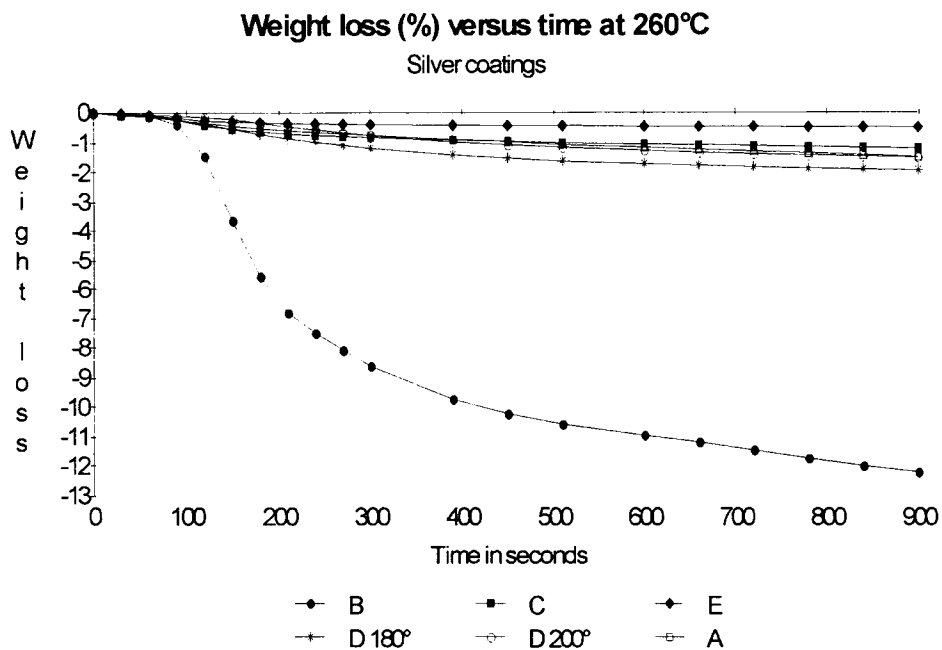

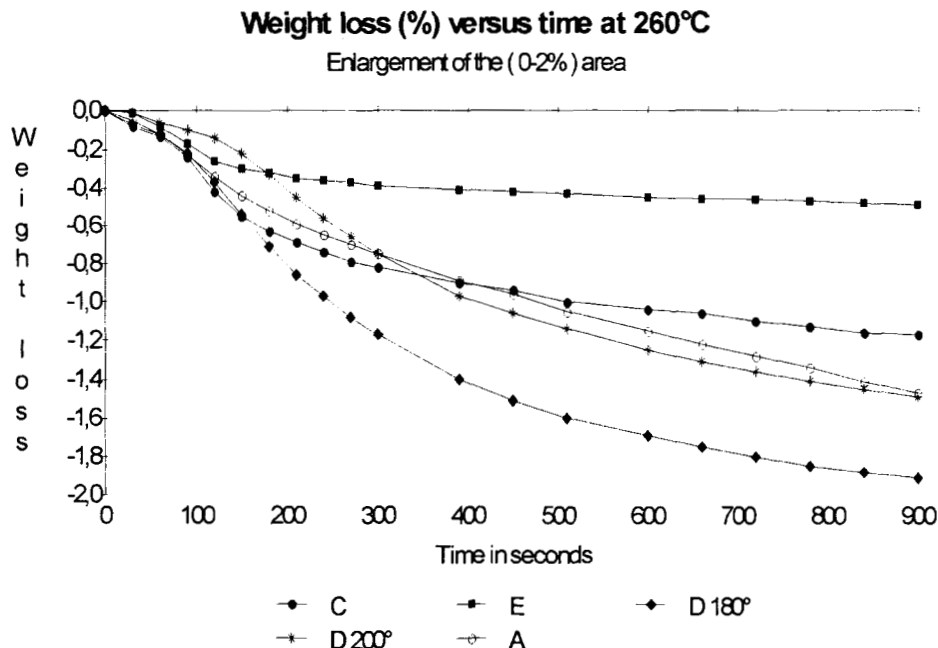**Figure 9**   Silver-coating weight loss after curing vs. time at 260°C.

Weight loss (%) versus time at 260°C

Enlargement of the (0-2%) area

Figure 10   Silver-coating weight loss vs. time at 260°C. Enlargement of 0-2% zone.

port temperatures ranging between 320 and 350°C.

3. When the resins are mixed to silver flakes, the thermal degradation temperature decreases. We observed a difference of between 20 and 70°C, the greatest difference concerning the polyimid one. The presence of metal bits induces always a decrease of the thermal resistance, due probably to thermal conduction and change in the bulk at the interface silver/polymer, as seen for mechanical toughness.[13] However, the silver containing the E sample, although submitting the largest temperature decrease, remains the most thermal-resistant.

Weight Loss at 260°C

The temperature of 260°C is the temperature defined in the RTSH test used in the electronic industry. It consists of putting the capacitor in the same conditions as used during the reflow soldering operation. The chip is dipped into a 260°C tin–lead bath for 10 s. Using thermogravimetry, we observed the weight loss, at 260°C, of our five silver coatings after drying/curing. The results are summarized in Table VIII. Figure 9 exhibits the low thermal resistance of the PMMA resin at 260°C. We see that, after 1 min, the weight loss is greater for the PMMA resin than for any other resin, whereas Figure 10 shows

that the weight losses during the first 30 s are very similar, due probably to the experimental conditions (introduction of the sample into the TGA furnace). Then, after 1 min, some differences appear: Coatings containing epoxy resin lose more than 1% in weight after 10 mn and are the less stable. At the same time, those containing polyester resin (C) or polyimid resin (E) are losing, respectively, 1.04 and 0.45% of their initial weight.

N.B.: We can remark that during the short time of the test (RTSH) the quality of the different resin may not be affected by the heat (260°C).

CONCLUSION

The thermal degradation of the PMMA resin starts over 240°C, whereas the polyimid resists to 410°C. For the other resins, the temperature is between 300 and 350°C. The incorporation of metal bits (here silver) to the mix leads to a thermal degradation temperature decrease of between 20 and 70°C.

Indeed, the quality of the PMMA may not be affected by the heat (260°C) during the short time of the test (10 s). We estimate that it will be better to use another material. In the future, the test will be certainly modified and the new conditions will be more aggressive (300°C during 1 mn).

This study establishes that the most thermal-resistant silver coatings are those containing polyester (C) and polyimid (E) binders. The E resin is certainly better, but its cost is, at the present time, too high and its use reserved for special applications.

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