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Development of new series of aluminium solid capacitors with organic semiconductive electrolyte (OS-CON)

Shinichi Niwa, Yutaka Taketani

Saga Sanyo Industry Co., Ltd., 217 Omachi-cho, Saga, Japan

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Abstract

We have researched tetrecyanoquinodimethane (TCNQ) complex salts, developed a new series of organic semiconductive electrolytes (OS-CONs) such as chip-type OS-CONs, and improved our original facilities for mass-production of OS-CONs during the ten years since mass-production was begun. Results of this research and development are presented in this paper. Various new applications of OS-CONs have been developed which fully utilize their properties. This paper also introduces some of these new applications.

Keywords: Organic semiconductors; Tetracyanoquinodemethane; Electrolytic capacitors; Chips; TCNQ

1. Introduction

1.1. Electrolytic capacitors

All types of electrolytic capacitors which were mass-produced in the past as well as today are listed in Table 1 as a fundamental background information for the properly understanding the organic semiconductive electrolytes (OS-CONs).

The most important material in an electrolytic capacitor in relation to its electrical characteristics is an electrolyte in which the element of the capacitor is immersed, or with which the element is impregnated. An organic semiconductive crystal is used as the electrolyte in the OS-CON, while an electrolytic solution comprised of solvent and solute or manganese dioxide have been used in past capacitors.

1.2. Capacitors and organic semiconductors

7,7,8,8-tetracyanoquinodimethane (TCNQ) complex salt, a kind of organic semiconductor, is used to form a cathode in the OS-CON. The following is a history of the development of the capacitors in relation to organic semiconductors or a history of the OS-CONs development.

1948, an organic substance which can conduct electric current was discovered [1].

1960, a TCNQ complex salt which had high conductivity was composed [2].

1961, Ross, a US manufacturer, researched the use of TCNQ complex salts in capacitors [3].

1968, Japanese manufacturers started the developing of capacitors (immersion in solution and other methods).

1981, a TCNQ complex salt, which can be melted was composed and a capacitor using melted and liquidized organic semiconductors (OS-CONs), was developed [4].

1981, the mass-production of the OS-CON started.

1991, a TCQN complex salt for the chip-type OS-CONs (SMD) was developed, leading to the mass-production of the chip-type OS-CONs [5].

Organic semiconductors were difficult to apply for practical use because they are, generally speaking, not heat stable

Table 1
History of electrolytic capacitors

Generation	Type	Electrolyte	Developed	Company
1st	Aluminium electrolytic capacitor	Liquid electrolyte	1908	G.E
2nd	Tantalum solid capacitor	MnO_2	1953	W.E, Sprague
3rd	Aluminium solid capacitor	TCNQ complex salt	1982	SANYO
4th	Conductive polymer capacitor	Polypyrrole	1988	N, JPN

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and difficult to process though the molecule design, such as composition of various derivatives, is flexible. The OS-CON is the first example of a mass-produced component in which an organic semiconductor is used on a full scale [6].

1.3. Qualities of a semiconductor used in electrolytic capacitors

A semiconductor or solid electrolyte needs to have the following qualities to be adopted in a solid electrolytic capacitor:
1. high conductivity;
2. processability to impregnate elements of capacitors;
3. solid adhesion to dielectric films;
4. heat-resistance and a long life;
5. causing no reaction from metals used as dielectric films, or not causing deterioration of the voltage-proof;
6. ability to restore dielectric films, and highly voltage-proof, and
7. stable temperature characteristics.

The development of a semiconductor that satisfies all these conditions is very difficult and only three semiconductors listed in Table 1 have been obtained.

2. Theory and experimental

2.1. Organic semiconductors for the OS-CON

2.1.1. TCNQ complex salt for lead-type OS-CONs

TCNQ, first composed by Du Pont, USA in 1960, is an excellent electron acceptor. It can be connected with various electron donors to form conductive complex salts. It was generally considered that organic semiconductors such as TCNQ complex salts were not heat stable.

It was believed that when heated they decomposed or, without respect to whether they could be melted or not, lost conductivity.

Some TCNQ complex salts having nitrogen heterocyclic components in which *N*-positions are substituted by e.g. alkyl groups, show, in a certain range of temperature, high conductivity even after being melted, if they are cooled and solidified within a certain time after melting.

An example of such a substance is *N*-*n*-butyl isoquinoline $(TCNQ)_2$ (nBIQ), see Fig. 1.

This semiconductor has a conductivity of 0.29 S/cm which is higher by a order of magnitude or two than that of the usual electrolytes used in electrolytic capacitors, such as electrolytic solutions or manganese dioxide. The substance is used in the lead-type OS-CONs, even today. The stable high conductivity in a wide temperature range of −55 °C through +105 °C and, particularly in sealed-up conditions, stable heat-resistance of this semiconductor contributes to the excellent high frequency, temperature, and life characteristics of the OS-CONs.

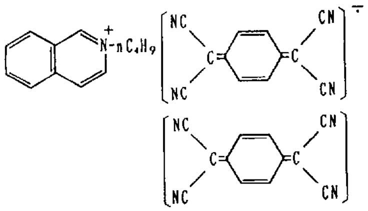

Fig. 1. *N*-*n*-butyl isoquinoline $(TCNQ)_2$.

2.1.2. TCNQ complex salt for chip-type OS-CONs

The nBIQ as used in the lead-type OS-CON has a melting point of about 210 °C. The heat resistance is sufficient if it is used in lead-type components. The conductivity of nBIQ, however, falls by degrees at temperatures higher than about 200 °C because pyrolysis will occur. In addition, the nBIQ melts at a reflow-soldering temperature of 230 °C. The melted nBIQs well out from joints between the seal resin and outer case because its volume increases when the phase changes from solid to liquid. As a result, the nBIQ cannot be used as a material for chip-type components.

The development of a semiconductor having melting point higher than 240 °C was therefore needed to realize the chip-type OS-CON. It went without saying that the semiconductor had to be melted to be processed in a liquid condition and maintain high conductivity after processing.

We have composed and examined qualities of many types of TCNQ complex salts using various types of donors such as pyridine, quinoline and other derivatives as well as various kinds of *N*-position-substituent such as alkyl, phenyl, methylene and other groups, and discovered the following.

Many TCNQ complex salts, when heated, do not melt but are decomposed. Those which can be melted lose conductivity after they are cooled and solidified. Those with melting points higher than 240°C have conductivity after the melting process are obtained, but the conductivity is generally much lower than that of nBIQ as to be insufficient for capacitors.

There is no TCNQ complex salt which can be melted and has a higher conductivity than nBIQ. Some TCNQ complex salts of the same type of isoquinoline have about the same level as nBIQ, but their melting points are also at the same level as nBIQ and therefore cannot be adopted as the material for chip-type OS-CONs.

Fig. 2 shows melting points and conductivity data of typical TCNQ complex salts which can be melted and processed.

Fig. 3 shows melting points and liquid continuation time, during which the salts remain liquid after melting, before foaming and decomposition occur. When the liquid continuation time is longer, element impregnation can be achieved more sufficiently and more easily. On the other hand, when the melting point is higher, the liquid continuation time of the salt is shorter. These figures mean that the maunfacturing of a chip OS-CON is difficult.

As a result of further research, however, we discovered that the conductivity rises extremely, though the melting point decreases a little, by mixing and melting two types of

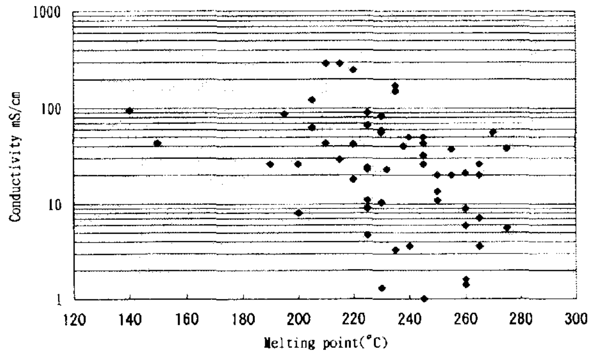

Fig. 2. Melting point and conductivity data of typical TCNQ complex salts after melting and processing.

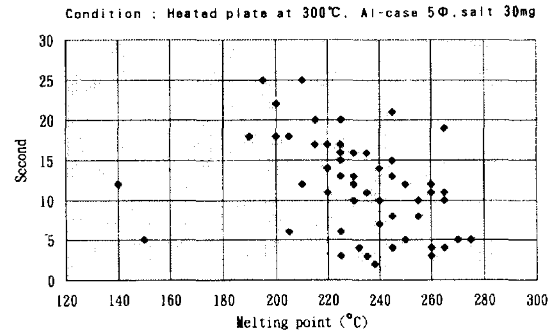

Fig. 3. Melting point and liquid continuation time after melting before decomposition of typical TCNQ complex salts.

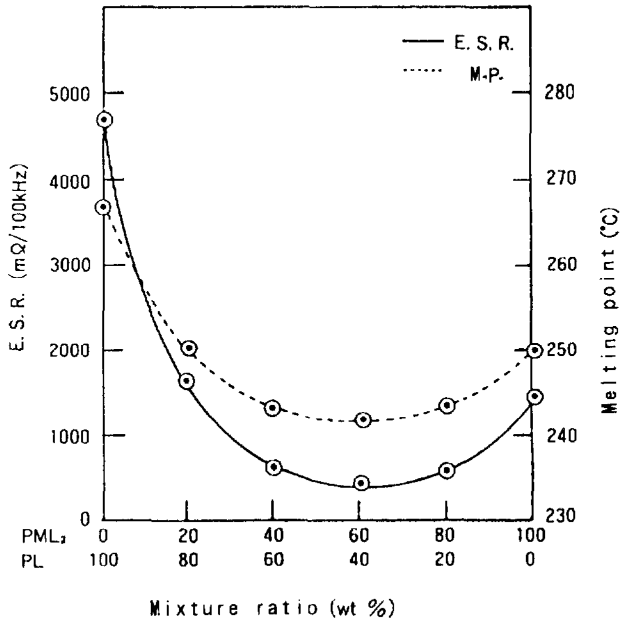

Fig. 4. Mixture ratio vs. ESR and melting point. PML_2: *N*-*N'*-pentamethylenedilutidine $(TCNQ)_4$, and PL: *N*-phenethyldilutidine $(TCNQ)_2$.

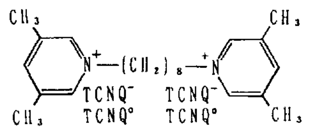

Fig. 5. *N*-*N'*-octametylenedilutidine $(TCNQ)_4$.

particular TCNQ complex salt, having high melting points, of which donors and *N*-position-substituting alkyls differ.

Fig. 4 shows the relationship between ratios of mixing, equivalent series resistance (ESR) when a capacitor is impregnated with the salts, and melting points of the salts. In this case, the conductivity of the mixed salts is 0.11 S/cm, which is comparatively near that of nBIQ; the melting point is raised by about 30 °C through 40 °C when the weight ratio of mixing is 1:1. Such a mixed compound of particular TCNQ complex salts having high melting points is used in chip-type OS-CONs.

2.1.3. Highly voltage-proof TCNQ complex salts versus 30 V [7]

Today, it is easy to make electrolytic capacitors using electrolytic solutions which withstand high voltage, e.g. 450 V. On the other hand, it is difficult to make solid electrolytic capacitors that can withstand high voltages.

Though some tantalum solid electrolytic capacitors can withstand as high as 50 V, actual use is usually restricted to a voltage reduced by 50% to guarantee reliability.

As polypyrrole-type capacitors and OS-CONs can withstand a voltage as high as 16 and 25 V, respectively, 25 V is the highest voltage which solid electrolytic capacitors can withstand.

Application of voltage higher than 25 V to an OS-CON impregnated with nBIQ inevitably raises the short-circuit generation rate, which means that designing an OS-CON that can withstand voltage higher than 25 V is impossible.

We have researched fundamental characteristics, such as melting points, conductivity, possibility of processing in melting condition, etc., of various types of TCNQ complex salt, together with the highest voltage which they can withstand. As a result, a TCNQ complex salt which permits design of an OS-CON that can withstand 30 V has been discovered, though its conductivity is 0.09 S/cm, which is a little lower than that of nBIQ. This TCNQ complex salt is *N*,*N*-octamethylene(3,5-lutidine)2TCNQ4, shown in Fig. 5 and called OS-L8 hereafter. Design of OS-CONs that can withstand 30 V has now been realized, which has made it possible to use the OS-CONs on a 24 V power supply line.

The reasons why OS-L8 can withstand higher voltage than nBIQ and occurrence of short circuits is reduced are briefly described here.

The electric characteristics, in particular leakage current, of an OS-CON impregnated with OS-L8 is more stable than one impregnated with nBIQ in relation to both heat and time. As a result, the increase in leakage current on loading is rare and the occurrence of short circuits is prevented.

3. Other developed products

Some of the other products we have developed in the new line-up of OS-CONs are as follows:

1. large capacity OS-CONs (2200 μF); the previous capacity did not exceed 220 μF;
2. long life OS-CONs; 105 °C × 5000 H is guaranteed while only 105 °C × 1000 H was previously guaranteed, and
3. the use of OS-CONs in audio equipment.

4. Results

4.1. OS-CON construction and manufacturing process

Electrolytic solution in aluminium electrolytic capacitors is replaced by semiconductive electrolyte in OS-CONs. The rubber seal is also changed to a resin seal. These are two essential differences between aluminium electrolytic capacitors and OS-CONs.

The chip-type OS-CON is constructed by, after lead forming of the lead-type OS-CON, being encased into a resin container for horizontal-type chips, putting each lead through a corresponding hole on the bottom of the container, and fixing the ends of the leads at the holes.

Fig. 6 is a flow chart illustrating the manufacturing processes of lead- and chip-type OS-CONs. The processes are characterized by the steps of carbonization, filling of containers with semiconductive electrolyte, and impregnation and assembly.

Carbonization aids easy impregnation with the semiconductive electrolyte by carbonizing separator papers. This step is effective in reducing the ESR.

As the pot life of the semiconductive electrolyte is short after the TCNQ complex salts are melted, each aluminium case must be filled with a predetermined quantity of the semiconductive electrolyte.

Impregnation and assembly is the important step which determines the characteristics of the OS-CON. The performance of an impregnating and assembling machine has a large influence on the characteristics.

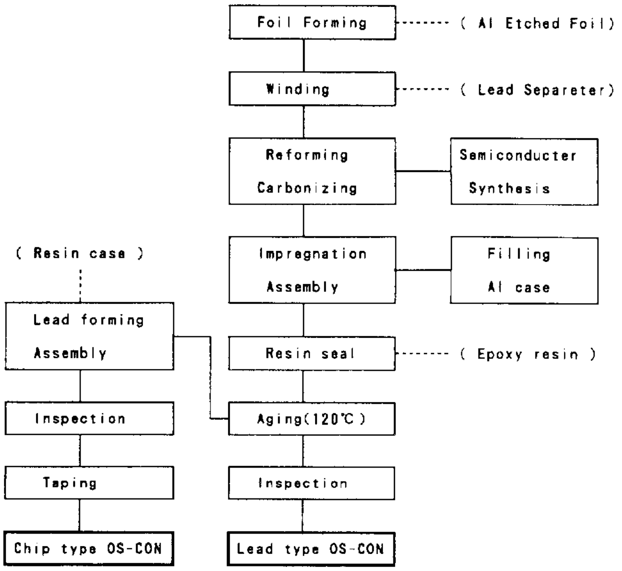

Fig. 6. Flow chart of manufacturing process.

The impregnating process seems simple and easy, but the process is in fact troublesome to perform continuously and automatically with a mass-production machine. As various restrictions existed regarding time and temperature, know-how concerning management of temperature, adjustment of timing, material of the machine and jigs, and method of maintenance had to be accumulated through trial and error. We have finally adopted a batch-processing system in which scores of elements are impregnated at one time.

To manufacture the chips, an automatic machine now performs all the steps of lead-forming encasing, inspection, sealing, and taping.

4.2. OS-CON ratings and measurements

Ranges of the rate voltage and rated static capacitance of the OS-CON have been expanded. We are now manufacturing OS-CONs with the following ratings and measurements:

Temperature range	−55 to +105 °C
Guaranteed life	+105 °C × 1000 H through 5000 H
a) *Lead-type OS-CON*, see Fig. 7:	
Rated voltage	6.3 to 30 V
Rated capacitance	0.1 to 2200 μF
Case measurements (mm)	diameter/length, 3/5 to 16/25
b) *Chip-type OS-CON*, see Fig. 8:	
Rated voltage	6.3 to 20 V
Rated capacitance	1.0 to 150 μF
Measurements of the smallest chip (mm)	4.6 W × 4.6 H × 7.3 L
Measurements of the largest chip (mm)	8.8 W × 8.8 H × 13.0 L

4.3. OS-CON electrical characteristics

Figs. 9–11 show a high frequency characteristic, a temperature characteristic and a characteristic in a high temperature load test, which are special features of the OS-CON.

4.3.1. High frequency characteristics

ESRs of a capacitor distinctively represent the quality of the high frequency characteristic of the capacitor. The quality of the OS-CON is represented by means of the ESR at 100 kHz and guaranteed.

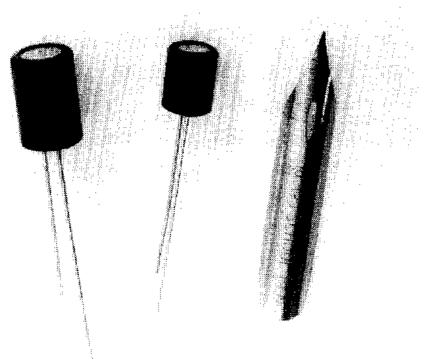

Fig. 7. General view of the lead-type OS-CONs.

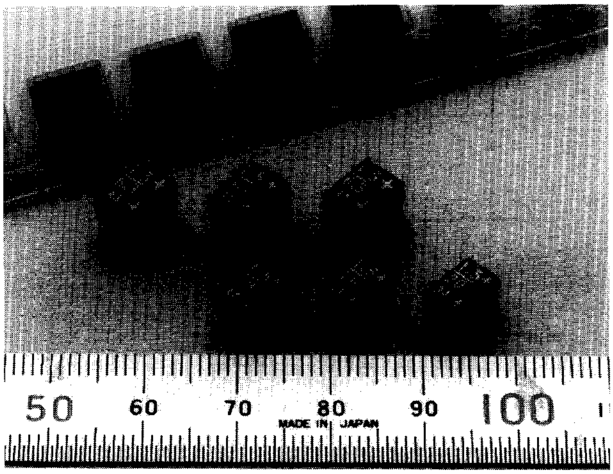

Fig. 8. General view of the chip-type OS-CONs.

The standard ESR at 100 kHz of an OS-CON of 25 V 4.7 μF for example is smaller than 150 mΩ. The real average value is 65 mΩ, which is about 1/10 to 1/100 of an aluminium electrolytic capacitors.

4.3.2. Temperature characteristics

The change rate of impedance of the OS-CON is $Z(-55$ to $+105\,°C)/Z(+20\,°C)=0.75$ to 1.25 at 100 kHz, which can practically be regarded as invariable in relation to temperature.

4.3.3. Characteristics in a high temperature load test

The semiconductive electrolyte of the OS-CON deteriorates by degrees at high temperatures as illustrated in Fig. 8, since it does not have the strong heat resistance such as inorganic semiconductors. However, since it is solid, the deterioration is not so sharp as capacitors using electrolytic solutions; it has a comparatively long life.

4.3.4. Reliability

800 million OS-CONs have been mounted in various equipment since their development. Though we have experienced many kinds of problems such as tube damage and adherence of resin to leads, a serious problem that could thoroughly destroy confidence in the quality of the OS-CON has not occurred. It is said that short circuits are apt to occur in solid electrolytic capacitors. The OS-CON has the ability to restore dielectric film when voltage is applied, though it is weaker than that of electrolytic solutions.

It is considered that this reason is as follows: (i) the OS-CON has the large leakage current and high resistance heat (I^2R) in the part of damaged dielectric film when OS-CON is charged; (ii) the restoring ability is stronger when temperature is higher; (iii) the TCNQ salt is insulated at an extremely high temperature. (iv) this restoring phenomenon is due to the deterioration and insulation of TCNQ salt contacting directly the damaged dielectric film, and (v) this ability is considered to be effective in the prevention of short circuits and maintains high reliability.

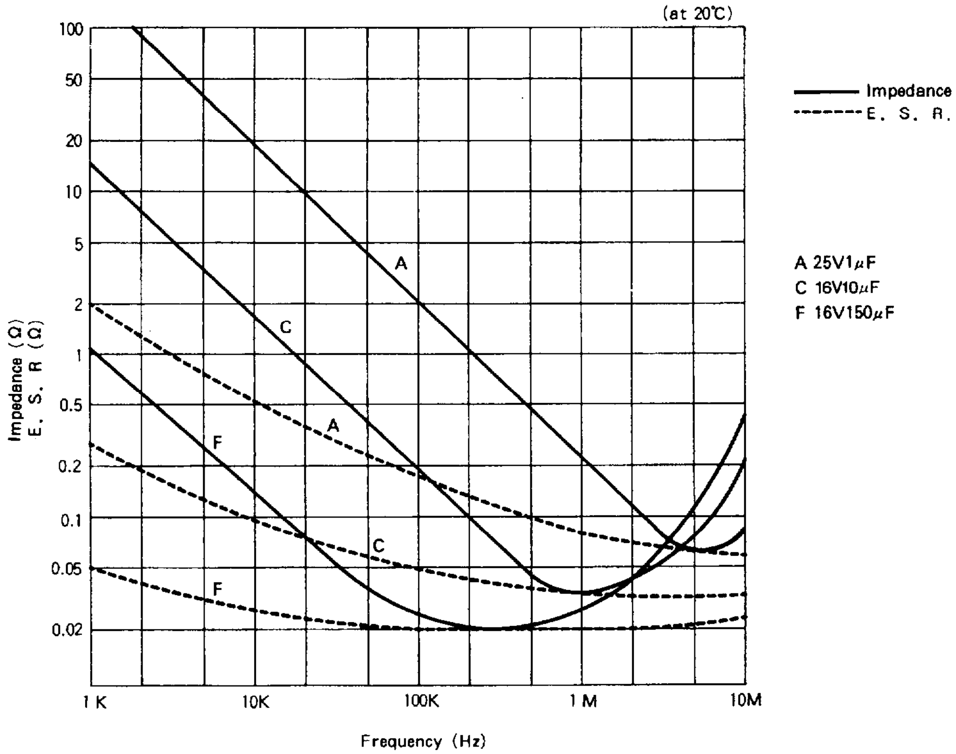

Fig. 9. Frequency characteristics.

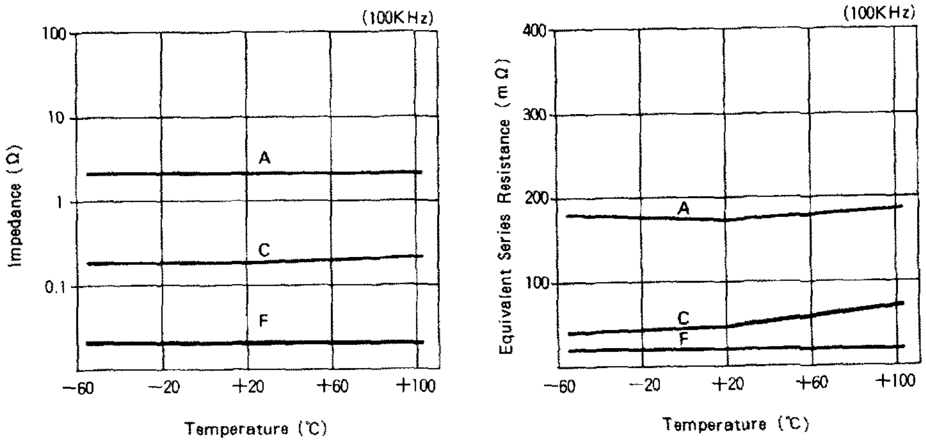

Fig. 10. Temperature characteristics.

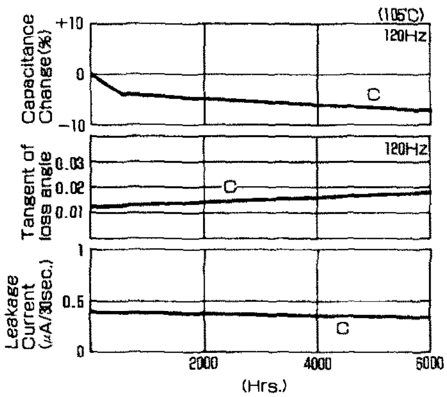

Fig. 11. Deterioration characteristics on loading.

4.4. *OS-CON applications* [8]

The OS-CON can satisfy various needs as reducing the size of products, reducing the noise, guaranteeing of low temperature performance, high ripple, improving of the picture or sound quality, increasing product life, improving of reliability and safety, reducing cost, etc. Typical examples of products and circuits in which the OS-CON has been adopted are as follows:

- In 8 m/m and VHS-C camcorders: to smooth input to or output from a DC/DC converter, for the filter of a power supply in view finder
- In television sets (general TVs and HDTVs): in digital circuits, in noise filters in power supply lines of Y/C separation circuits
- In digital audio equipment (CDs, DATs, MDs and DCCs): to improve the quality of sound in D/A converters, in power supply noise filters
- In video cassette recorders: to smooth output from a switching power supply, in pre-amplifiers, and in LC filter in Y/C separation circuits
- In computers (lap-top type, notebook type and palm-top type): to smooth input to or output from a switching power supply, in noise filters to remove clocks
- In telephone public and private branch-exchangers: to smooth distributed power supplies, for bypassing ICs in DAC
- In digital portable telephones or personal handyphone systems: in battery chargers for portable telephones, in unit power supplies in base stations

5. Conclusions

Development of a new series of OS-CONs, such as chip-type ones or voltage-proof ones that can withstand voltage as high as 30 V, has been achieved by improving TCNQ complex salts with which elements of the OS-CONs are impregnated. Production of OS-CONs with a long life or capacitance as large as 2200 μF has been realized by improving facilities for mass-production and promotion of automation.

Usage of the OS-CONs has widely been expanded due to the success in its development, which has resulted in the today's production of 15 million per month and aggregate production and sales of about 800 million.

Acknowledgements

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