

A NEW MATERIAL DEVELOPED FOR METAL OXIDE VARISTORS APPLIED IN ELECTRONICS AND TELECOMMUNICATION

Flaviu M. Frigura-Iliasa¹, Liliana Matiu-Iovan², Mihaela Frigura-Iliasa³ and Doru Vatau¹

¹ Faculty of Electrical and Power Engineering, POLITEHNICA University of Timisoara, Romania

² Faculty of Electronic and Telecommunication Engineering, POLITEHNICA University of Timisoara, Romania

³ Faculty of Chemical and Environmental Engineering, POLITEHNICA University of Timisoara, Romania. E-mail:^{1,2,3} flaviu.frigura@et.upt.ro

Abstract

Metal oxide varistors (also known as ZnO based varistors) are today used for making state of the art surge arresters for all voltage levels, but they are less used for telecommunication lines. Essentially they are “n” semi-conductor ceramics made of ZnO (more than 90%) and many other oxides having different roles. This paper presents a new manufacturing technology based on 2 additional oxides Cr₂O₃ and MnO₂. This varistor material has a smaller electrical capacity, suitable for telecommunication applications. Started from chemical measurements, and finished by electrical tests, the experimental part of this paper is an Interdisciplinary research.

Key words: metal oxide varistors, telecommunications

1. INTRODUCTION

It is well known that Metal Oxide Varistors (also named ZnO varistors, due to their most important component) are today used for making state of the art surge arresters for all voltage levels, from domestic low voltage to high voltage transport lines. Their main goal is to protect any piece of electrical equipment against any type of over voltage which occurs on the power supplying network (technical incident, induced voltages or lightning stroke) [2]. They are applied in modern technologies due to some important advantages such as: a high level of non-linearity for the current-voltage characteristic, a high energy absorption capacity and an excellent response time. They are essentially ceramic poly-crystalline n – semiconductors. They are made from a mixture of metal oxides such ZnO (more than 90 %), Sb₂O₃, MnO₂, Bi₂O₃, Cr₂O₃, Co₃O₄ and many others [1]. But, for different purposes, not all the ingredients are necessary. This paper intends to demonstrate this. Varistors were invented at the beginning of the sixties, by Russian scientists, in order to protect military telecommunication lines against the overvoltage effects caused by the Nuclear Power Pulse. But this first application was rapidly forgotten.

ZnO in his natural state is an excellent semiconductor. Generally it is more likely to find more Zn²⁺ ions inside his structure. By introducing other metal oxides, Zn²⁺ ions are substituted inside the crystal structure only by bivalent metal ones. The others will be placed between the ZnO fragments and work like a supplementary potential barrier.

Figure 1 shows us the microstructure of a metal oxide varistor, as observed on the electronic microscope. We notice the large ZnO crystal grains and the inter-granular layer of other oxides, which, in fact, gives the varistance effect by introducing a supplementary potential barrier. This micro-structure looks like a stone-wall having ZnO grains as stones and other oxides acting as cement [1].

The varistance effect consists in a non-linear (non-ohmic) relation between the crossing current (the crossing current density) and the voltage (the field intensity applied to the material). In fact, at low

voltage, the varistor acts as an insulator and at higher voltages, it acts like a conductor. So, it is ideal for any protective devices made for voltage suppression [4].

Cr_2O_3 and MnO_2 are used in order to obtain different structure phases during the elaboration process. It's obviously that the amount of Cr_2O_3 and MnO_2 used during manufacturing has a highly influence over all electrical proprieties of that varistor [1]. The main purpose of this paper is to determine the influence of Cr_2O_3 and MnO_2 concentration over the electrical capacity of that varistor. The opening voltage of a certain varistor V_N is the DC voltage measured between the faces of the varistor, conventionally, when a 1 mA DC current is established through that varistor [1].



Figure 1. Micro-structure of a Metal Oxide Varistor

All phases of the varistor manufacturing process are shortly described bellow:

First, all metal oxide powders are carefully weighed. After weighing, all components are mixed and grinded by using pure water and organic solvents for a few hours. Water and organic solvents are removed by slowly heating that mixture. Another grinding operation is necessary after removing those solvents. The resulting powder mixture is sifted to avoid formation of large pieces. The resulting powder is put into moulds and carefully exposed to higher pressure (hundred of barrs). After pressing, the resulting piece is gradually submitted to extreme heating (at temperatures higher than 1000 °C) for a few hours. Next, the varistor is naturally cooled down. When the varistor is cooled at the environmental temperature, a small layer of Ag is applied to both ends, as electrodes. The Ag based compound is a semi liquid paste which has to be dried before any other action could be performed (by slowly heating again). Then, the final phase of the technological process consists in submerging the heated piece into an epoxy resin powder in order to obtain the rapid polymerization of that organic insulator [1].

2. THE CHEMICAL COMPOSITION AND THE MANUFACTURING OF THE VARISTORS

Generally, all physical and electrical proprieties are depending of the chemical composition. Weighing all ingredients (after establishing a correct composition) is an important operation. This operation is made by using a standard METTLER electronic balance for weights more than 0.1 mg. This operation is relatively simple, because all the ingredients are delivered as powders, having a very uniform and well determined granulation.

The initial chemical composition of a standard varistor having 5 additional oxides is shown in table 1 [1], according to a technology developed by the Génie Electrique Laboratory in Toulouse, France (now it is called the Laplace Laboratory). All masses are reported to 500 g of mixture. The role of each component is different. There are many oxides inside this material, but the role of the last 4 oxides is not very important, because they are used only for grain growth [2].

The authors developed, during their stages at the Génie Electrique Laboratory from the PAUL SABATIER University of Toulouse, France, another varistor material which could be used for telecommunication applications, due to its reduced electrical capacity. It is based only to no more than 2 additive oxides (having a reduced electrical capacity). This initial chemical composition is shown in Table 2 (all masses are reported to 500 g of mixture [3]). By comparing to the initial composition, we notice that only the Sb_2O_3 amount has been modified.

Table 1 - The initial chemical composition of a varistor (with 5 additive oxides)

Substance	Percentage [%]	Mass [g] for 500 g mixture
ZnO	82.25	411.28
MnO ₂	0.75	3.75
Cr ₂ O ₃	1.32	6.601
Co ₃ O ₄	2.09	10.457
NiO	0.648	3.244
Bi ₂ O ₃	4.047	20.235
Sb ₂ O ₃	8.862	44.345
B ₂ O ₃	0.0756	0.378
MgO	0.0438	0.219
Al(NO ₃) ₉	0.0260	0.130

Table 2 - The initial chemical composition of a varistor (with 2 additive oxides)

Substance	Percentage [%]	Mass [g] for 500 g mixture
ZnO	87.45	437.25
MnO ₂	1.843	9.215
Cr ₂ O ₃	1.515	7.575
Sb ₂ O ₃	9.0466	45.233
B ₂ O ₃	0.0756	0.378
MgO	0.0438	0.219
Al(NO ₃) ₉	0.0260	0.130

We insist that this is only the initial chemical composition. It will be changed after passing all the phases of the manufacturing process, due to the vaporization and decomposition of many supplementary oxides. Practically, only the first two useful oxides will remain inside the electrical material [4].

For the two remaining oxides we can say that their roles are:

- Cr₂O₃ is used mostly for grain growth limitation;
- MnO₂ is used as a doping element.

After weighing, all ingredients have to be carefully mixed by using the mixing ball machine shown in Figure 2. The mixing procedure can last for more than 30 hours, in order to obtain a homogeneous powder, which could be pressed after.

As we mentioned before, the rest of the oxides will be decomposed after passing through all the phases of the manufacturing process.

The resulting piece of semiconductor equipment will be carefully put to electrical measurements in order to determine all its parameters

A 7 mm varistor made according to this technology, during all phases of the manufacturing process, is shown in Figure 2.

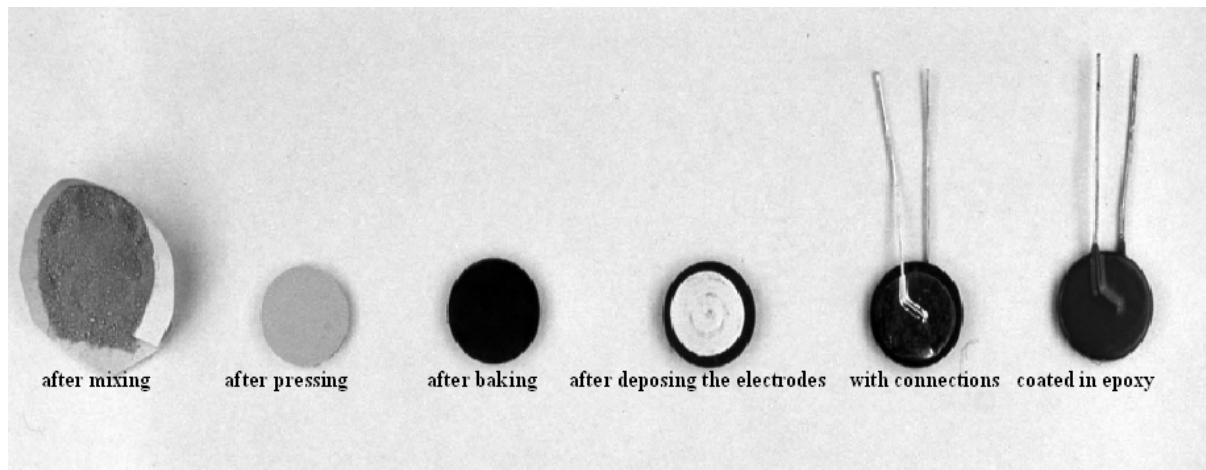


Figure 2. The results for the main phases of the manufacturing process

Figure 3 shows as some of the equipment used in laboratory for varistor manufacturing. It may be different from the industrial one, but in principle, it is the same.

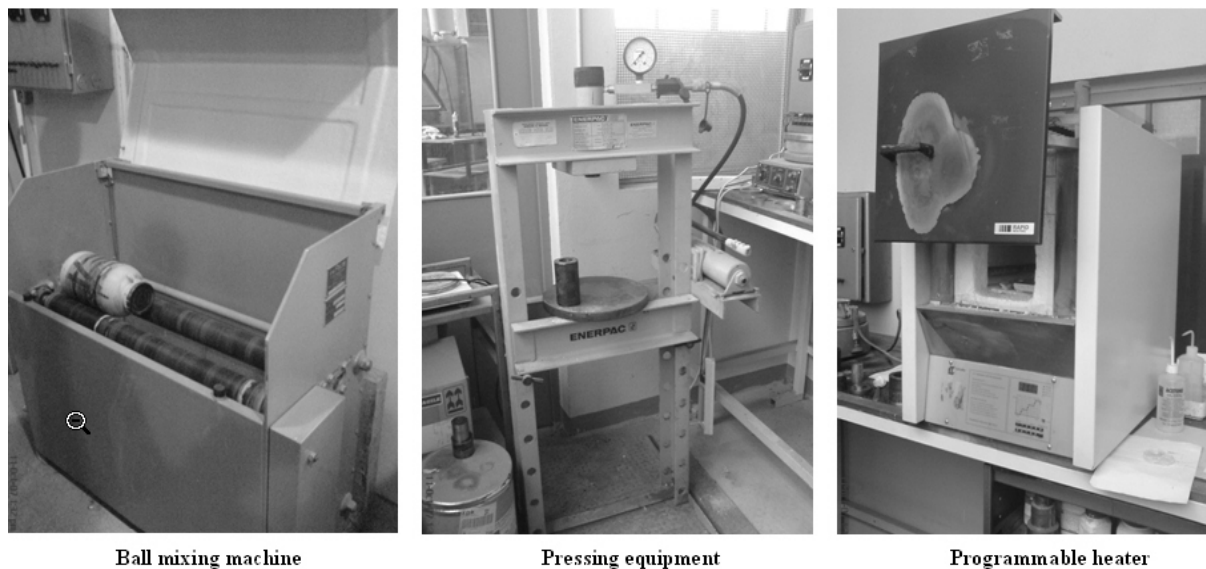


Figure 3. Laboratory equipment for varistor manufacturing process

This equipment is used for making all type of varistors, starting from low voltage ones to medium and high voltage series.

3. EXPERIMENTAL PROCEDURE AND RESULTS

For telecommunication equipment (such as digital phone centers), supplied from the low voltage power network, it is necessary to measure the electrical capacity of the varistor at 50 Hz. There is an original, simple and efficient method, described below, which could be applied by using a simple digital oscilloscope.

This method is based on the fact that the varistor is a non-linear electric device, having, at this frequency, an important capacity.

The varistor is equivalent to a parallel electrical schema having a capacity C_V and a resistance R_V (variable with the applied voltage, but constant for a certain voltage). This schema, together with the principle schema for carrying out measurements is presented in Figure 4. A SEFRAM 5064DC two channel digital oscilloscope was used. The PC is recommended, but not absolutely necessary.

One channel is reserved to the varistor voltage and another is reserved for observing, by using the R_d resistance, the current passing through the varistor. The varistor was connected to 250 V_{ef} (U_{MCOV} , the maximum RMS voltage value in normal conditions). If the supplying voltage is higher, the varistor is a conductor and the resistive part of the current is higher. If the voltage is lower, that varistor acts like an insulator, and the capacitive component is higher than the resistive one. All measurements made at 50 Hz AC were performed at the Faculty of Electrical Engineering in Timisoara.

In principle, we can separate the two current components, I_r the resistive one, in phase with the main voltage, and I_c , the capacitive one, with a 90 degrees delay.

We have to measure the maximum capacitive current $I_{c_{max}}$, obtained, obviously, to the maximum 90 degrees distance, when the main voltage reaches 0.

By knowing this value, we can write this relation for the varistor capacity C_V :

$$C_V = I_{c_{max}} / (V_{max} \cdot \omega) \quad (1)$$

We know that $V_{max} = 250 \cdot 1.41 = 352$ V, $\omega = 314$ rad/s

After obtaining the C_V capacity at 50 Hz, we can measure its relative permittivity, ϵ_r for this 250 V_{ef} voltage and 50 Hz frequency. The computing relation is:

$$\epsilon_r = (4 \cdot h \cdot C_V) / (\epsilon_0 \cdot \pi \cdot d^2) \quad (2)$$

where:

$h = 2.8$ mm (for the 230 V_{ef} –RMS classic varistors);

d is the diameter;

$\epsilon_0 = 8.854 \cdot 10^{-12}$ F/m (the absolute air permittivity).

All results are shown in Table 3:

Table 3 - AC measurements at 250 Vef, 50 Hz

Type of the classic 230Vef Varistor (diameter)	$I_{c_{max}}$ [A]	C_V [nF]	ϵ_r
7 mm	$1.32 \cdot 10^{-5}$	0.12	1044
20 mm	$1.13 \cdot 10^{-4}$	1.03	1038
30 mm	$2.57 \cdot 10^{-4}$	2.33	1046

From Table 3, we notice that the average value for ϵ_r is around 1040, for a material having 5 additive oxides, used in common AC applications.

Using the new material, applied to telecommunication lines, with 2 additional oxides, only varistors for 48 Vdc were made. They have reduced ϵ_r . The maximum RMS value of the voltage (in AC regime) is about 0.65 from the opening voltage (aprox. 40 Vef, not 38.9).

We considered $V_{max} = 0.65 \cdot 59 \cdot 1.41 = \text{aprox. } 56.4 \text{ V}$, $\omega = 314 \text{ rad/s}$

Relations (1) and (2) are applied by knowing:

- $h = 0.9 \text{ mm}$ (the 48 Vcc varistor height);
- $d = 7 \text{ mm}$;

All results are shown in Table 4.

Table 4 - AC measurements at 40 V, 50 Hz

Type of the new 48 Vdc Varistor (d)	$I_{c_{max}}$ [A]	C_V [nF]	ϵ_r
7 mm	$3.01 \cdot 10^{-6}$	0.17	468

The measurements were carried out at an environmental temperature of 20 °C.

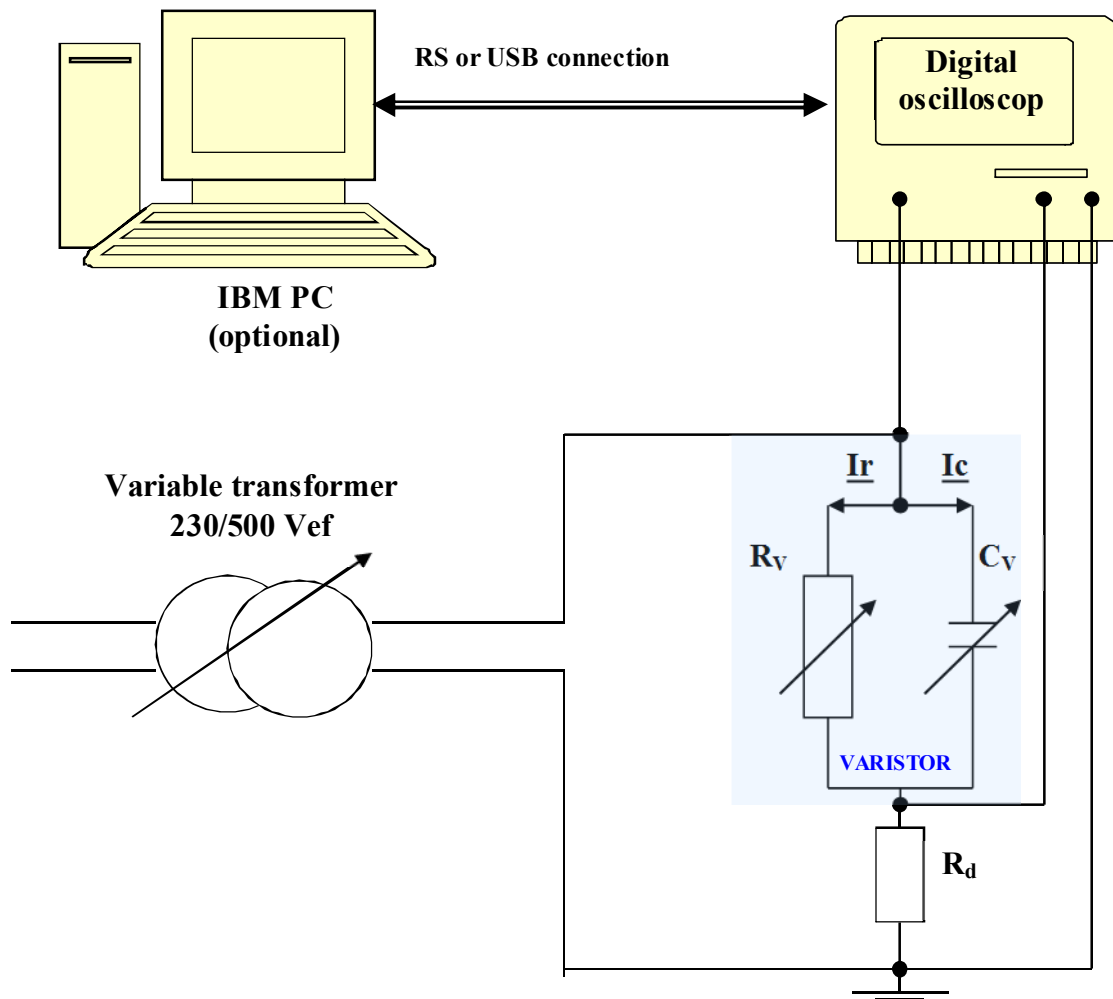


Figure 4. The electrical schema for alternative measurements

From Table 4, we notice that the average value for ϵ_r is around 470, for a new material having 2 additive oxides, which could be used in common telecommunication applications. It gives a reduced electrical capacity and a higher capacitive reactance for the useful signals.

4. CONCLUSIONS

The new material developed by the authors is easy to make and easy to use. It is suitable for protecting all telecommunication equipment, having a lower electrical capacity. Test were carried out by using a new, simple and efficient method for varistor testing.

This method is simple, easy to use, with equipment available in any electrical engineering laboratory, by medium qualified persons. It gives information about the performances of all those materials involved and gives also suggestion for their application domain.

The results obtained by using this method are simple and they are confirmed by obtaining an ϵ_r which is 2.2 times lower for the 2 oxides material by comparing with the 5 oxides one, which has a 2.11 higher granulation. They are also confirmed with the close range of values obtained for 230 Vef varistors. Generally, on literature, for this classic material, only values of 1000-1500 are shown.

REFERENCES

1. Frigura-Iliasa F.M. (2002) *Stabilitatea termica a varistoarelor pe baza de ZnO. Aplicatii la joasa tensiune*, « Orizonturi Universitare » Publishing House, Timisoara, Romania
2. Hassanzadeh, M., Bui, A., Dorlance, O., Loubierre, A. (1995) “*Propriétés électriques des varistances à oxyde de zinc en couches épaisses*”, Journal of Applied Physics, 25
3. Nguyen, H.T., Bui, A., Loubierre, A. (1994) *Role of Additives in the High-field ZnO based Varistors*, International Conference on Electronic Ceramics, Aachen, Germany
4. Vasilievici A., Andea P., Frigura-Iliasa F.M. (2002) *Aparate si Echipamente Electrice. Aplicatii*, « Orizonturi Universitare » Publishing House, Timisoara, Romania