ABSTRACT

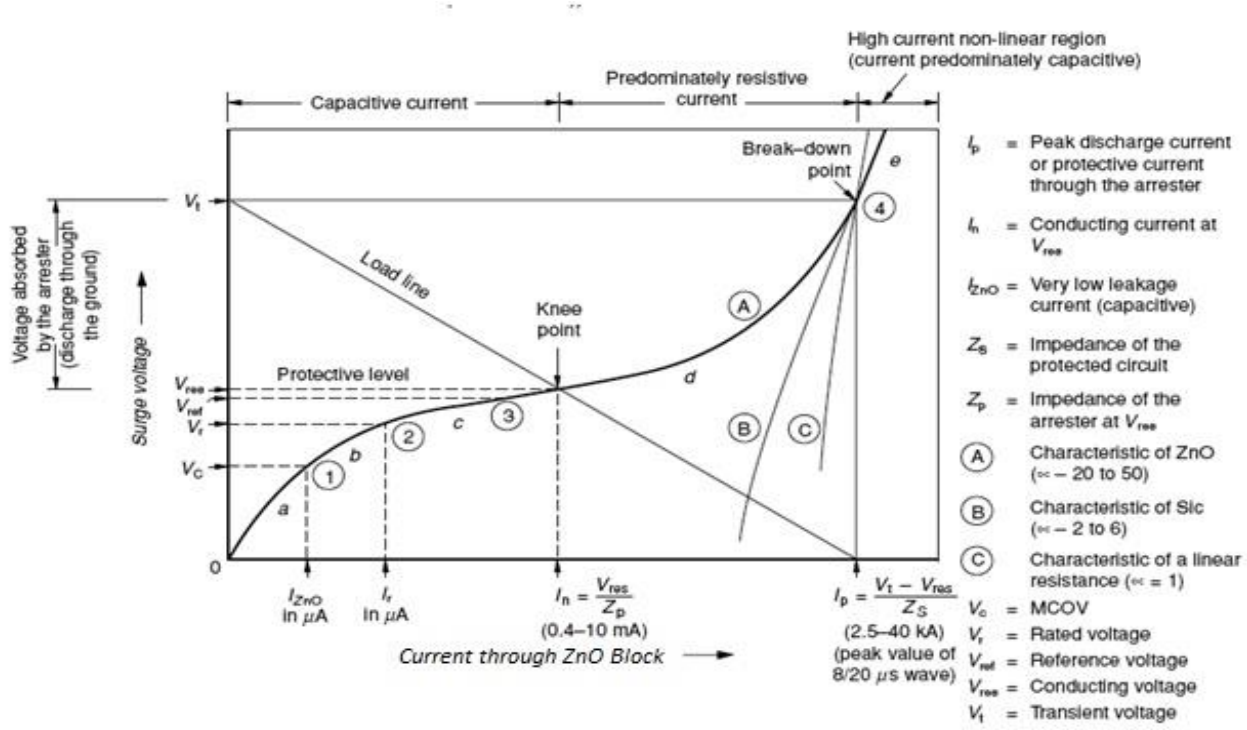
When surge protection is considered for a system or for equipment, surge/lightning arresters are installed on or near the equipment being protected. This is a device that limits the high TVs (transient voltages) generated during a system disturbance by diverting the excessive part of it to the ground and reducing the amplitude of the transient voltage wave across the equipment to a permissible safe value less than the impulse withstand level of the equipment. As on there are lot of books and papers for selection & importance of a lightning/Surge arrester. But I want to evaporate this book on process how it is manufactured.

The heart of the arrester is ZnO [Zinc oxide] block. It is a combination of different metal oxides which has good electrical properties, like {Zn, Bismuth, Cobalt, Antimony, Manganese, Chromium, Nickel etc.}.These materials are polarized and mixed with proposition of weight converted into powder later to solid blocks. These blocks are sintered up to a temperature 1200◦C later lapped, insulated, and metal coated. This is a big process and need a highly controlled environment to obtain good results.

Zinc oxide varistors are electronic ceramic devices processed through conventional ceramic technique. Energy absorption capability of the varistor is highly beneficial either in increasing the reliability of the device and of the system or in reducing its volume providing the same level of protection.

So, I want to explain the different stages of manufacturing zinc oxide varistors. How a chemical product is converted into an electrical product by sintering process and there effects on products related to electrical characteristics.

Zinc oxide (ZnO) blocks characteristics



ZnO varistors are formed by mixing ZnO powder with the powder of other oxides such as those of Bismuth, Cobalt, Antimony, Manganese, Chromium, Nickel etc. and subjecting the powder to conventional ceramic processing. After the sintering operation, the resultant product is a polycrystalline ceramic with a unique grain-boundary property that contributes to the well-known non-linear I-V characteristics of the device.

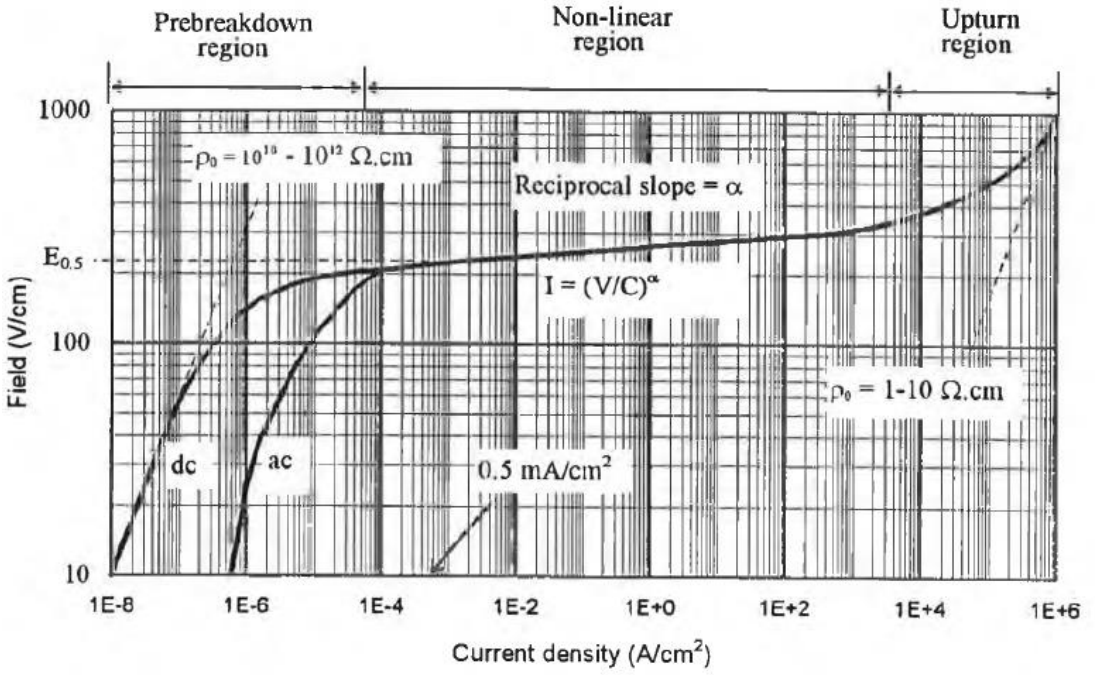
$$I = (V/C)^{\alpha}$$

I = Current in Amps.

V = Voltage in Volts.

C = Material and Geometry dependent constant.

α = Non-linear exponent.



Typical current-voltage characteristics of ZnO varistor plotted

Basically the ZnO characteristics can be divided into three regions, they are:

Pre-Break down (or) Low Current Region:

The I-V characteristic is ohmic in this region and is defined as the pre-breakdown region. This region determines the leakage current and consequently the watt loss under normal steady state voltage. There is a need to balance the values of operating voltage and leakage current. In this region the current flowing through it will be <800 micro-amps

Intermediate Non-linear Region:

The non-linear region of the intermediate current is the heart of the ZnO varistor, wherein the device conducts an increasingly large amount of current for a small increase in voltage. It is this large non-linearity over a wide range of current densities that makes the ZnO varistor distinctly different from any other non-linear resistor and thus makes it useful for a variety of applications. The degree of non-linearity is determined by the flatness of the non-linear region, the flatter the I-V curve in this region, the better is the device. The controlling parameters for this important region are only qualitatively understood. The addition of Bi203 has been found to be essential for forming

the non-ohmic behavior. Some oxide dopants are found to enhance the non-linearity.

High Current Upturn Region:

In the high current region, the I-V characteristic is again linear, similar to that in the low-current region, the voltage rising faster with current than in the non-linear region. This is also known as the upturn region. This region is controlled by the impedance of the grain in the ZnO microstructure.

To characterize a ZnO device, it is desirable to determine the I-V curve for all the three regions. However, due to the wide range of currents involved, different measurement techniques are adopted for different regions.

i) Usually I-V characteristics below 100 mA/cm2 are measured by 1mA direct current or 50/60 Hz alternating current and
ii) Those above 1 A/cm2 are measured by the impulse current method (DC impulse).

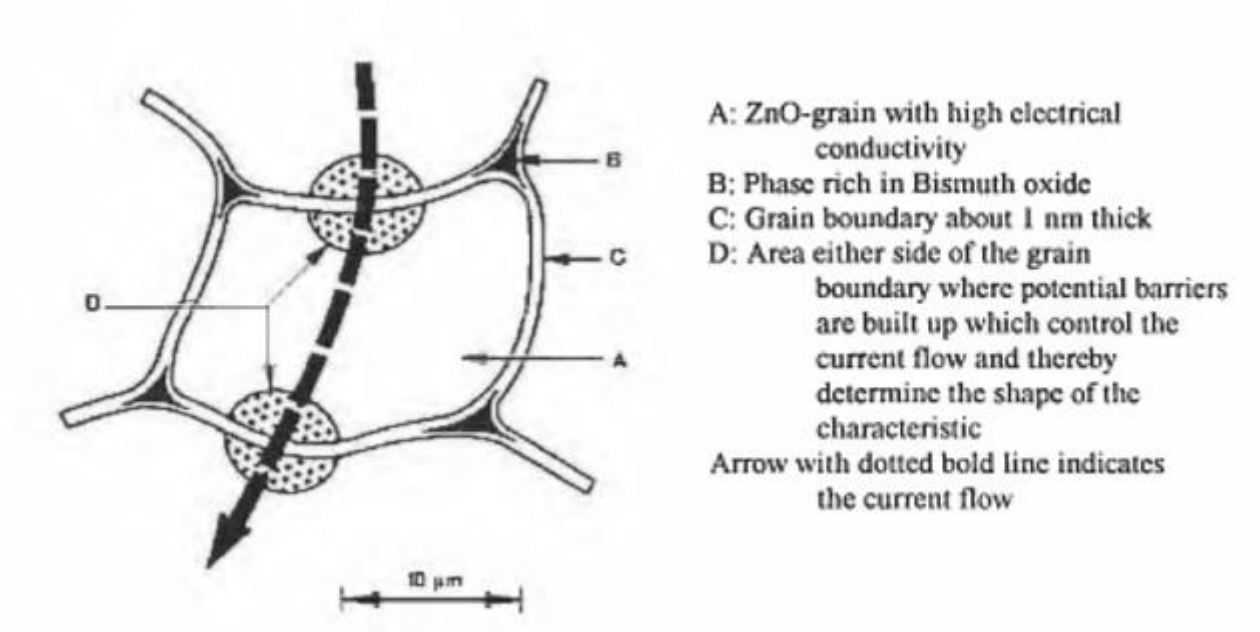
Parameters of ZnO varistors:

Varistor take the advantage of all the regions of the I-V curve.

a) The low current region determines the watt loss and, hence, the operating voltage during the steady application of an external voltage.
b) The non-linear region determines the clamping voltage upon application of a transient surge.
c) The high current region presents the limiting condition for protection from high current surges such as those found in lightning. Devices where the upturn occurs at increasingly higher current density are, therefore, most desirable for applications involving high magnitudes of currents, since the voltage rise can be minimized with such devices.

zinc oxide varistor is selected on the basis of some critical parameters such as non-linear coefficient, nominal voltage, leakage current, and energy absorption capability etc. These parameters are directly depends on The material and processing parameters like the density of the green and the fired body, homogeneity, grain size, porosity, varistor chemistry, and sintering parameters. These are identified to affect of energy handling capability.

Basic structure of ZnO varistor



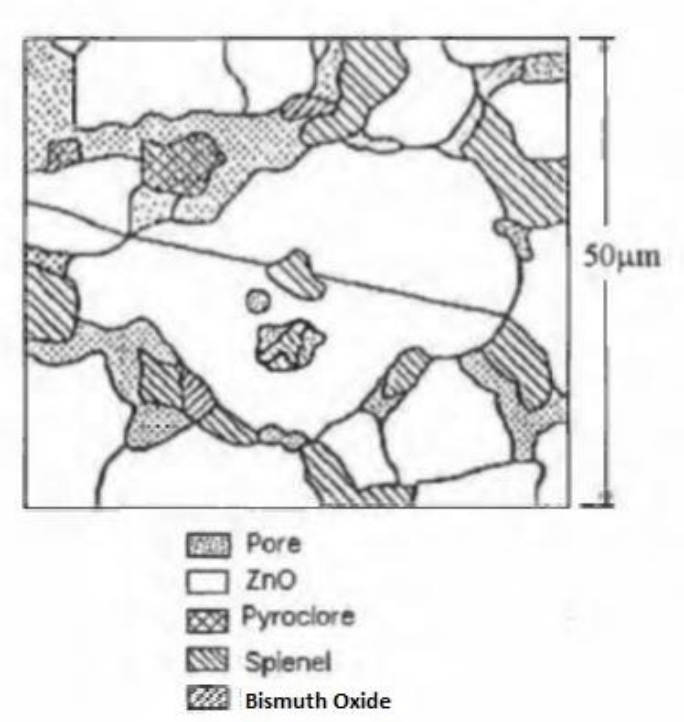
The formation of the microstructure of the varistor is dependent on the sintering time, temperature and environment. Pure zinc oxide is n-type semiconductor with linear I-V characteristics. The addition of Bi203 is essential to form a non-linear region. However, multiple dopants (additives) such as a combination of Bi203, Sb203, Mn02, Si02, Cr2O3 and C03O4 etc. are added to produce greater non-linearity than a single dopant.

The high current non-linearity can be enhanced by decreasing the grain boundary resistivity which is usually achieved by doping with aluminium or gallium oxide. Transition metal oxide C03O4 and Mn02 are used to improve the non-ohmic property and NiO, Cr203, or a small amount of glass frit are included to improve the reliability and peak pulse stability.

Zinc oxide and additives react with each other during the sintering process, forming intermediate compounds such as pyrchlore and spinel phases. Low temperature is favourable for the formation of pyrochlore phase, whereas, high temperature is for the spinel phase.

pyrchlore = $Bi_2(Zn_{4/3}\,Sb_{2/3})0_6$

spinel = $Zn_7Sb_20_{12}$


50μm
Pore
ZnO
Pyroclore
Spienel
Bismuth Oxide

Weighing, Milling, Mixing of ZnO powder

The basic material used to manufacture metal-oxide varistors are pulverized, very finely grained ZnO with particle sizes of about 1μm, and 10 or more doping elements are added in the form of fine oxide powders. Its actual composition differs from manufacturer to manufacturer. The proportion by weight of all additives together is about 100 percentages in weight. The purity and fineness of the metal-oxide powders and the homogeneity of the mixture are, therefore, of immense importance for the quality of the end product.

Basically the ZnO blocks contains additives as, Bismuth Trioxide (Bi_2O_3), Antimony trioxide (Sb_2O_3), Manganese Dioxide (Mno_2), Cobalt oxide (Co_3O_4), Chromium Oxide (Cr_2O_3), Silicon Dioxide (Sio_2) & Tin oxide (SnO). These oxides are mixed with a proportion weight. While collecting the oxides homogeneity is very important and need accuracy in weighing.

There are different kind of compositions depends on productivity and quality. But while preparing composition basic material characteristics (Physical, Thermal, Mechanical & Electrical) should be known well.

But as on to my experience I divided the material as follows in proposition by weights that can be used.

a) Main Component (n type material) :

Zinc Oxide –	ZnO	(86-90%)

b) Dopents or additives :

Antimony trioxide -	Sb_2O_3	(3-5.5%)
Bismuth trioxide -	Bi_2O_3	(3-6.5%)
Cobalt oxide-	Co_3O_4	(1-1.5%)
Manganese dioxide-	Mno_2	(0.8-0.9%)
Chromium oxide-	Cr_2O_3	(0.8-0.9%)
Nickle oxide-	NiO	(0.5-0.55%)
Tin oxide-	SnO	(0.5-0.55%)
Silicon Dioxide-	Sio_2	(0.1-0.2%)

c) For Oxidation & Cold conduction :

Aluminum nitrate-	$Al(NO_3)_3$	(0.01-0.012%) or <100gms.

d) Binders :

PVA (Polyvinyl alcohol)-	$[CH_2CH(OH)]_n$
Gum Arabic -	$C_{26}H_{34}N_2O_{13}$
PEG(Polyethylene glycol)-	$C_{2n}H_{4n+2}O_{n+1}$

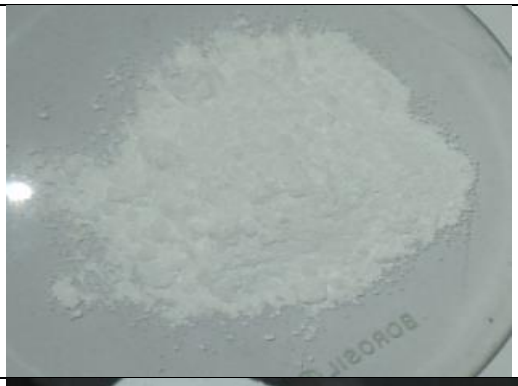
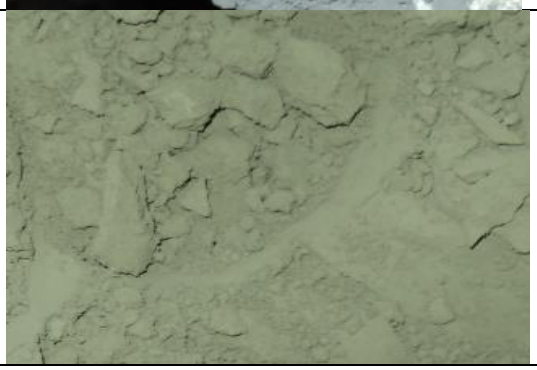
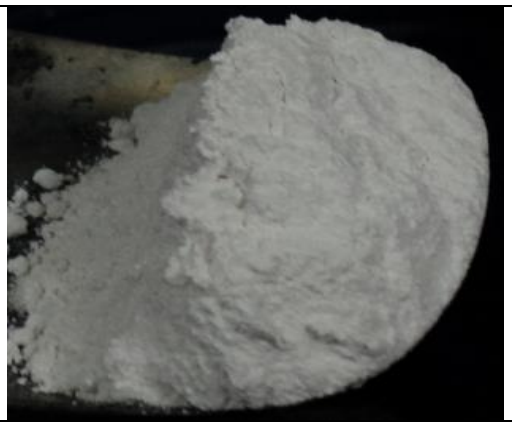
e) Pressing lubricant:
Zinc stearate- C36H70O4Zn

Note: ZnO is the main component. And from the remaining dopants & binders all need not to use, it depends on the properties of the material which we need the quality of the final material and cost implications are also considered. Any one of the binders mentioned above can be used but it differs in change in weight of usage.

Ceramic material properties

Before going to further studies, the basic material properties should be well known.

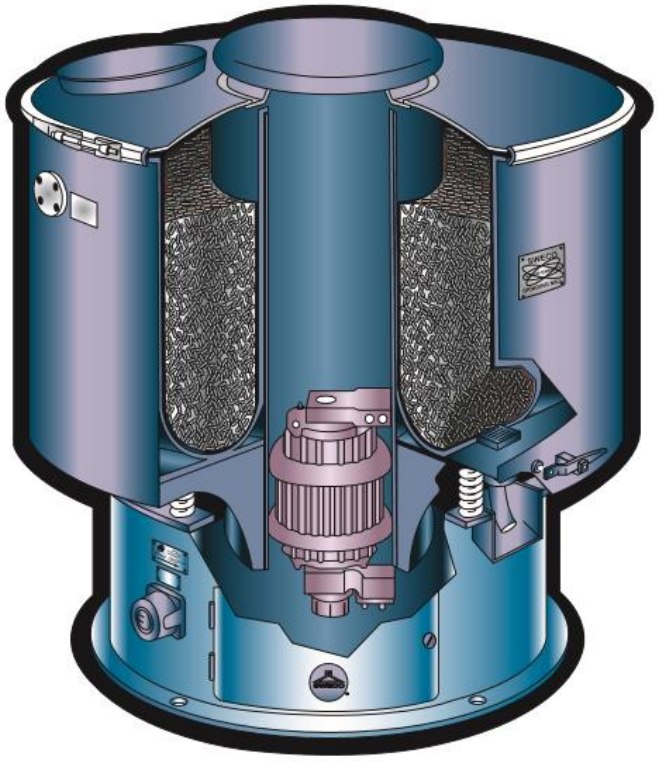
1	Zinc Oxide(ZnO) : a) Colour - White b) Grain size - 0.7-1µm c) Density - 5.606 g/cm^3 d) Melting point - 1975^OC	
2	Bismuth Trioxide (Bi2O3) : a) Colour - Yellow b) Grain size - 3.8-6.3µm c) Density - 8.90 g/cm^3 d) Melting point - 817^OC	
3	Cobalt oxide (Co3O4) : a) Colour - Black b) Grain size - 0.3-3µm c) Density - 6.11 g/cm^3 d) Melting point - 895^OC	

4	Antimony trioxide (Sb_2O_3) : a) Colour - White b) Grain size - 0.4-3µm c) Density - 5.20 g/cm^3 d) Melting point - 656^{O}C	
5	Manganese Dioxide (Mno_2) : a) Colour - Grey b) Grain size - 0.4-4µm c) Density - 5.026 g/cm^3 d) Melting point - 535^{O}C	
6	Nickle oxide (NiO) : a) Colour - Green b) Grain size - 1-10µm c) Density - 6.67 g/cm^3 d) Melting point - 1955^{O}C	
7	Chromium Oxide (Cr_2O_3) : a) Colour - Green b) Grain size - 0.8-12µm c) Density - 5.22 g/cm^3 d) Melting point - 2435^{O}C	Same as nickel
8	Tin Oxide (SnO_2) a) Colour - White b) Grain size - 0.4-4µm c) Density - 6.95 g/cm^3 d) Melting point - 1630^{O}C	
9	Silicon Dioxide (Sio_2) : a) Colour - White b) Grain size - 0.4-4µm c) Density - 2.64 g/cm^3 d) Melting point - 1713^{O}C	Same as Tin Oxide

Milling:

But here is the question, does all the material will be in same size, which favors in sintering for equal distribution of particle?

From the above question, I want to confirm that the zinc oxide will be less size compared to others. i.e ZnO will be 0.7 to 1µm but remaining dopants will be >5µm that which doesn't give a proper compaction of particles. So, except ZnO remaining oxides/dopants are milled/Pulverized in a vibro energy mill or ball mill for 8-12 hours that which brings to size similar to ZnO. The dopants are mixed with DM water (Demineralised water around 450ml/kg) and milled.



As a grinding zirconia balls (ZrO2) media is used with 10:1 ratio (media:dopants). The small amount of aluminium nitrate is also added. After the total process the particle size should be <2-1µ.

Mixing:

Later to this milled dopant fined powder, ZnO powder was mixed with a high speed mixer for 5-8 hours, into this mixer PVA (PVA dissolved with hot water with a continuous rotating motor) is added with a small amount for number of times, or else the mixer will get solid.

But here an another question, if all the materials are mixed; do the particles joint together, which results in high particle size?

Yes obviously, the particle size of the slurry will be very high that which resulting in lumps. So, to avoid this DISPEX A4040 is added to mixing tank keep particles individual, identical and to avoid waterborne.

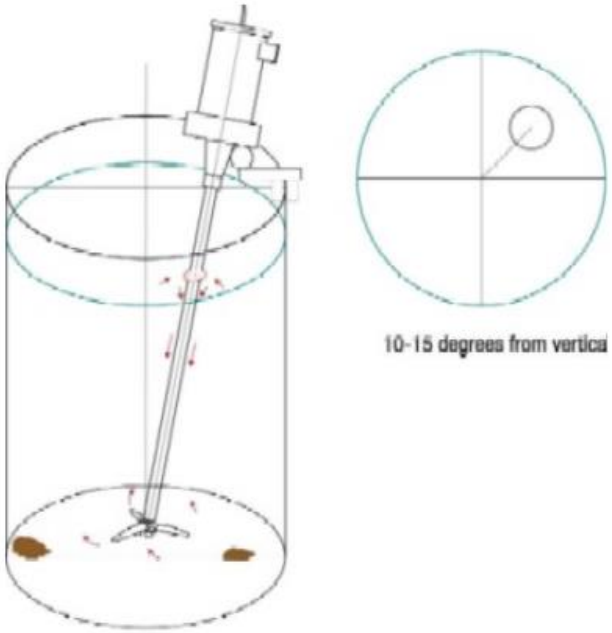
Dispex® AA 4040 is a derivative of a family of highly effective, low viscosity dispersing agents for water-based coating systems, especially suitable for the dispersion of inorganic pigments

To this powder Zinc stearate is added as a lubricant while pressing of blocks. But while going detailed study it suggests that the zinc stearate should not mix into powder, that which affect the uneven surface of pressed block. It should be used as powder only while pressing, mean a small amount of zinc stearate was poured into die that which works a lubricant and minimizes the stress of the machine.

But the controversy with the practical application says that adding the zinc stearate into slurry gives better results. Study has to go on this matter.

And finally Aluminum nitrate was added to this slurry, because a very small amount of powder was added which is less than 100grams.

Finally this powder is spray dried to convert into powder, which can be pressed. But this powder was transferred to a small tank which is having a high speed mixer (Slurry tank), to avoid gravitational force on particles (heavy density particles flows to bottom of the tank influence to uneven spray drying of particles.) basic slurry specific gravity of the slurry is very important that which should be 2.3 to 3.3. if the slurry is less than <2.3 the spray dryer chamber temperature should increase because the water content will be more if the slurry is >3.3 the liquid can’t be spray dried.



Later this slurry is spray dried to get a fine powder.

Spray Drying:

Spray drying is one of the most efficient ways to convert ceramic slurries into a free-flowing powder. It has been used for decades to process clays for whitewares manufacturing, as well as to produce oxide ceramics such as aluminas, ferrites, steatites and titanates.

The most common application of spray drying is in producing powders that will subsequently be pressed and fired, where the unique properties of spray dried products—namely, a narrow particle size distribution and spherical particle shape—result in excellent flow characteristics. For this reason, spray drying has been widely adopted for the manufacture of advanced ceramics, such as carbides, nitrides and borides. Other applications include powders for plasma spray and slip casting, as well as ferrites for toners and magnetic tapes.

However, for a spray drying application to be successful, it is important that users understand both the benefits and the limitations of the spray drying process. It is also important that users choose the right system based on the requirements of the application.

Spray drying is a method of producing a dry powder from a liquid or slurry by rapidly drying with a hot gas. This is the preferred method of drying of many thermally-sensitive materials such as foods, pharmaceuticals & ceramic processed items.

The basic spray drying process consists of three processing steps:

a) Atomization of the feed slurry into tiny droplets. This is accomplished using rotary or nozzle atomizers.

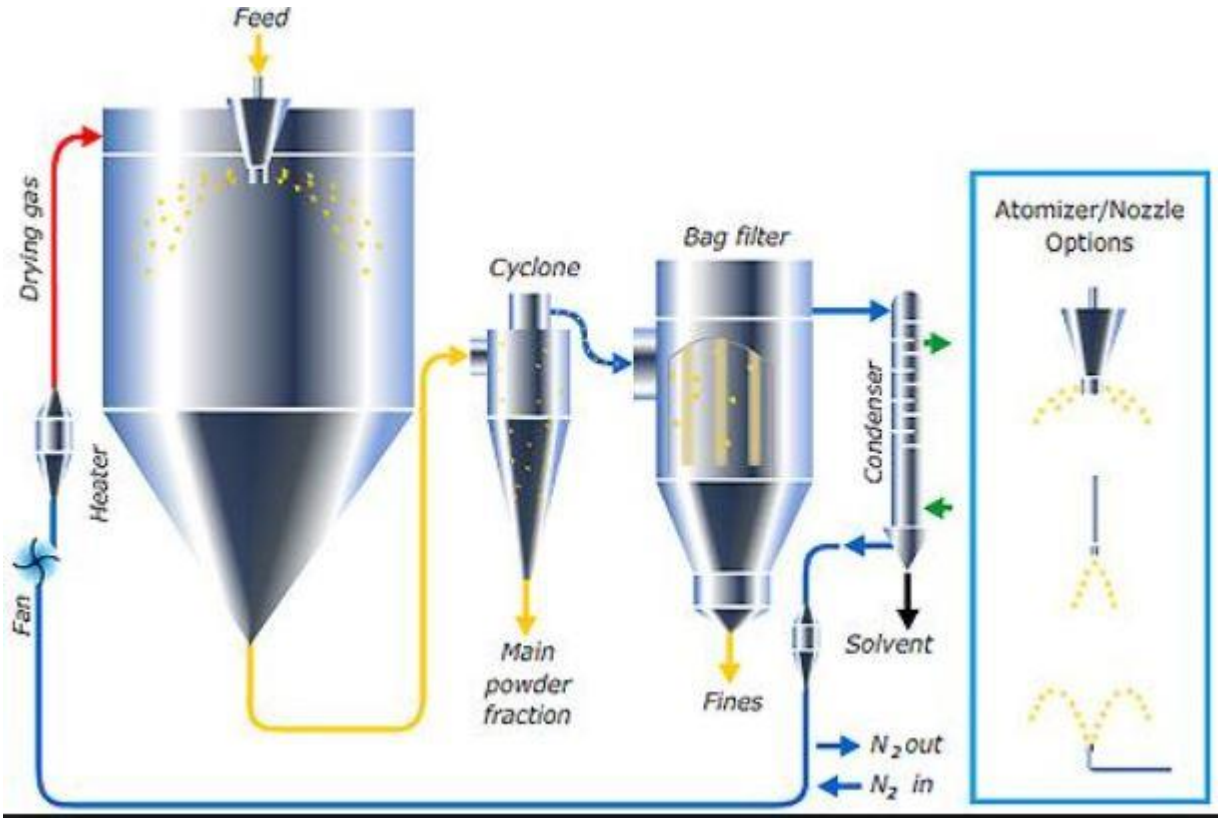
b) Mixing of the atomized spray with the hot drying gas, typically air, and drying of the individual droplets into solid particles. This is carried out inside the drying chamber, and it is important that the particles are dry (at least on the surface) before they contact the internal surfaces of the drying chamber.

c) Recovery of the dried product. This can be done partly from the base of the drying chamber and partly from separation equipment for the spent drying air.

A spray dryer takes a liquid stream and separates the solute or suspension as a solid and the solvent into a vapor. The solid is usually collected in a drum or cyclone. The liquid input stream is sprayed through a nozzle into a hot vapor stream and vaporised. Solids form as moisture quickly leaves the droplets. A nozzle is usually used to make the droplets as small as possible, maximising heat transfer and the rate of water vaporisation. Droplet sizes can range from 75 to 180 μm depending on the nozzle.

Using a pressure nozzle, a very narrow particle size distribution can be obtained with a typical yield of 85-95%, depending on the specific gravity of the spray-dried ceramic. However, if the feed rate to the spray dryer is low (less than 100 lbs/hr), the orifice in the pressure nozzle becomes so small that plugging is inevitable. In such cases, a two-fluid nozzle is used, and the expected yield is reduced to 75-85%. (Yield in this context is defined as the fraction of product discharged from the drying chamber; the rest is conveyed with the spent drying air to the cyclone and bag filter.)

Basic spray drier will be as follows:



The liquid slurry was spray with a high pressure through 1mm nozzle in vertical direction and the powder was collected in three types of sizes:

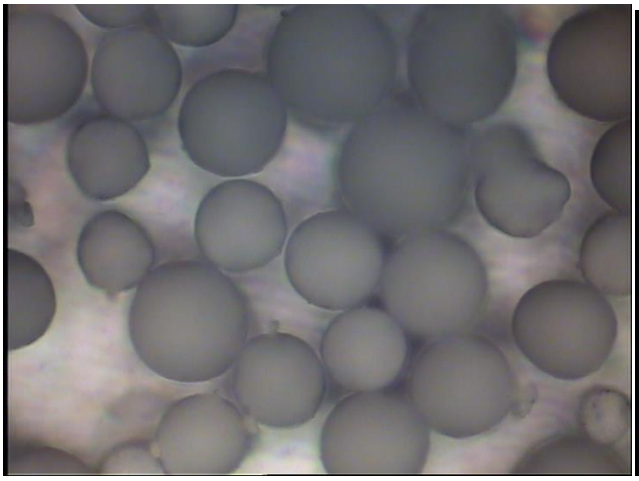
1) Less than 150μ (Cyclone)
2) 150-160μ (Regular use)
3) Greater than 150μ (Again reprocess)
4) Fines (Waste)

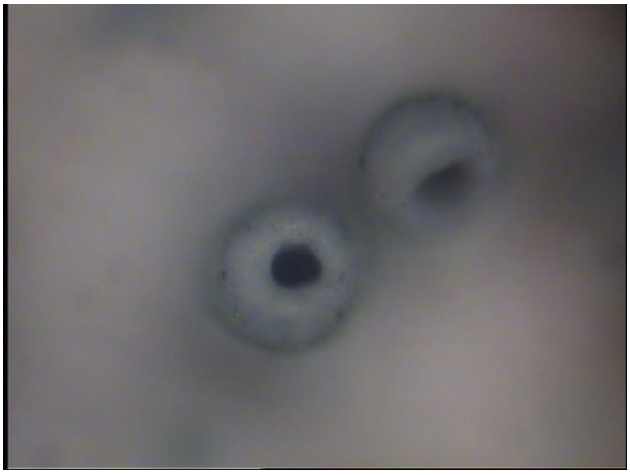
Less than 150μ can't be used in fabrication of ZnO blocks that which causes for non-uniformity growth of grain and causes low insulation resistance and poor non-linear characteristics.

Greater than 150μ causes low breakdown voltages so, this powder is collected and again reprocessed from milling process.

Fines are collected which having very low density and travels with air and cause to air pollution, so this is collected to avoid pollution. This powder can be used in paints.

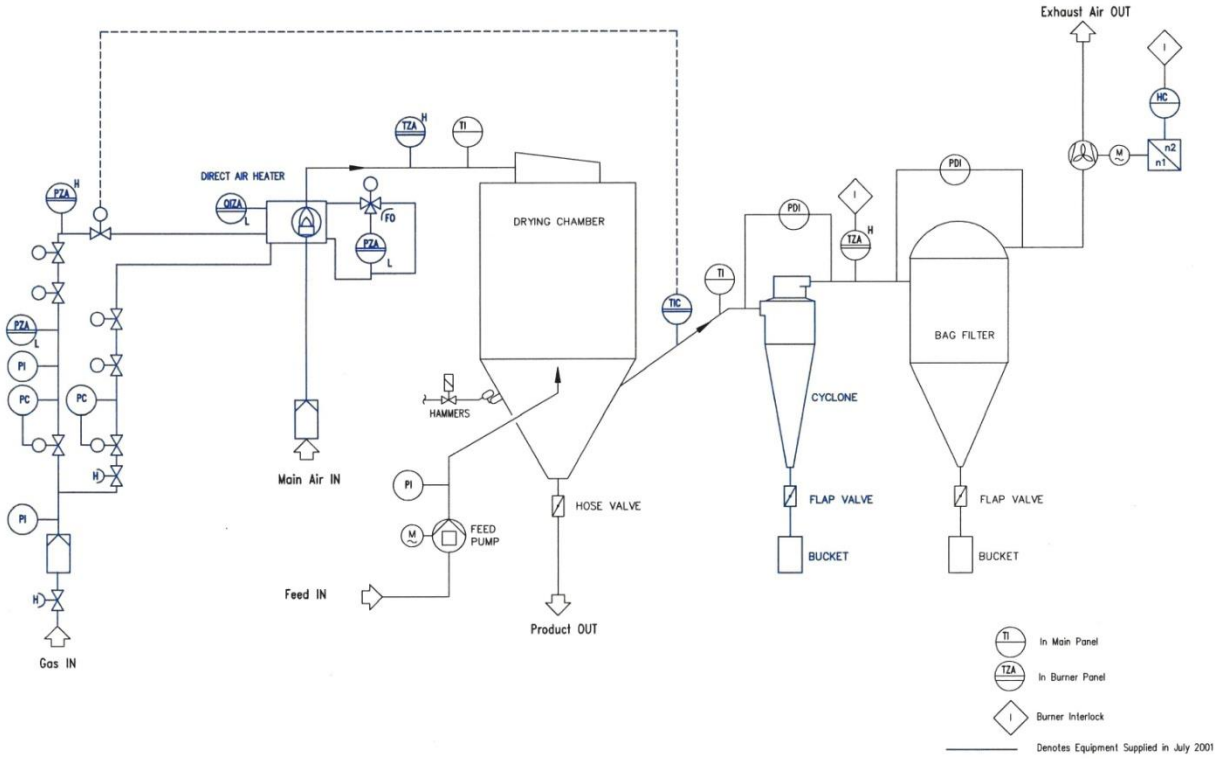
The proper collected 150-160μ is further moved to pressing stage. The microscopic view of collected powder looks like below.





Later this powder is gone for a pressing/ compaction process.

For my application we developed the below schematic spray :

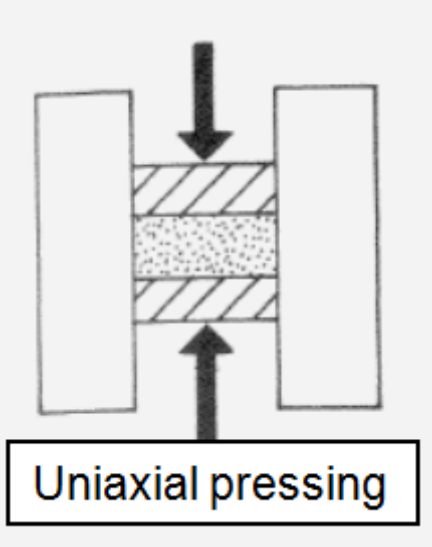


Hot air generator to be used for process of metal oxide powder, no LPG to be used; where carbon content is not good for this process.

INLET Temperature	:	400 centigrade.
OUTLET Temperature	:	110 centigrade.
Particle size	:	150 microns.
Nozzle Diameter	:	1mm

PRESSING/COMPACTING OF BLOCKS

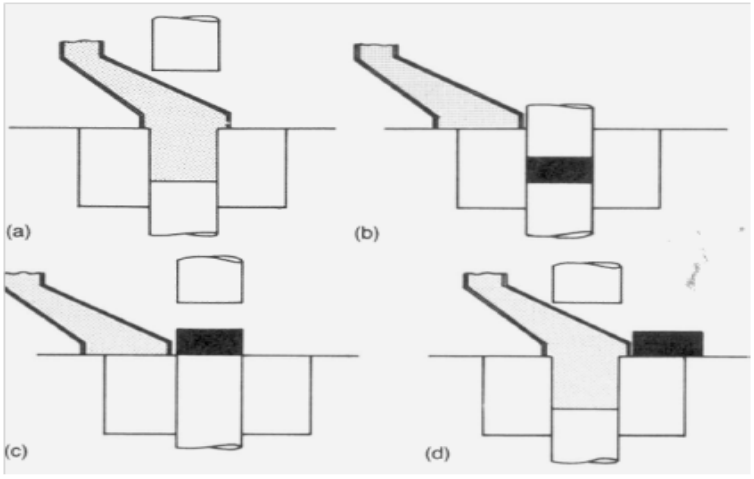
The spray dried powder in the form of granulates are compressed into disc-shaped blocks with approximately 55 to 65 percent of their theoretical density. The pressing is performed by uniaxial double action compaction technique. Compaction is the process of applying pressure and simultaneously giving a desired shape on a powder material confined in a rigid die or in a flexible mould.



The process depends on an external source of pressure for deforming the powders into a high density mass with required shape and dimensional accuracy. Powder feed is usually in the form of controlled granules containing pressing additives produced by spray drying. The means of compaction, the mechanical constraints and the rate of pressurization are the significant process parameters which play a vital role in the resulting properties of the green body. Main concern with properties of the green as well as of the fired body dictates that high densities with minimum gradient be achieved following compaction operation.

So compaction is undoubtedly a very important step in the manufacturing process of arrester discs.

Compaction process passes through different phases of material deformation. Three distinct stages can be identified in the compaction cycle. At the initial stage the loose array of powder particles is compressed to a closer packing. Then the particle- to-particle point contact deforms as pressure increases. Finally the particles undergo extensive plastic deformation.



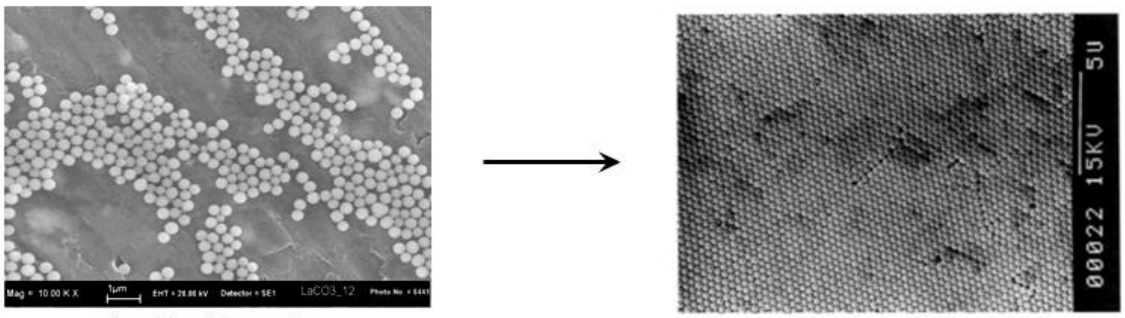
The stages of dry pressing

At the beginning of the compaction cycle, the powder has a density approximately equal to the apparent density. The highest obtainable density at this stage is only the tap density. As pressure is applied, the first response is observed in the form of rearrangement of particles, giving a higher packing co-ordination.

The compact ability of dics depends on mainly four factors:

(i) Powder characteristics: Particle size and distribution, Flow ability of powder & Surface condition.
(ii) Organic systems: Binder & Lubricant.
(iii) Pressing/ Compaction technique: Die filling, pressing rate, dwell time, maximum force, die-wall friction.
(iv) Geometry of compact body: Height, Diameter & Shape of body.

Particle packing and granulation



"perfect" powder

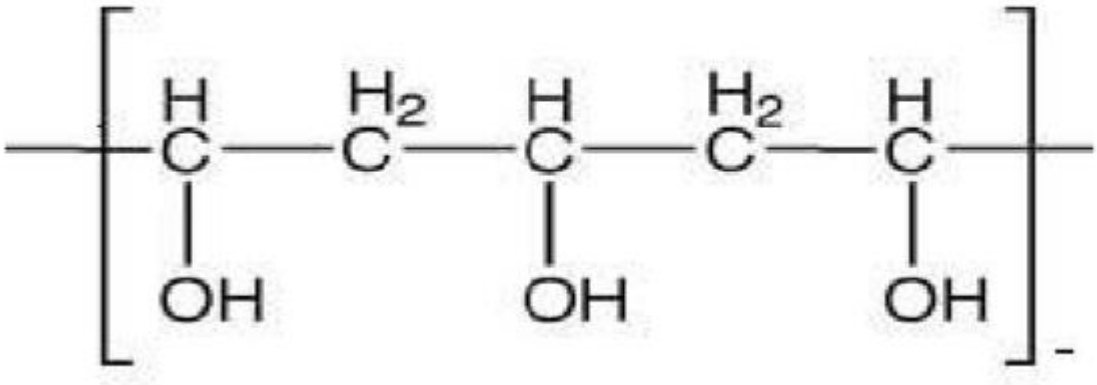
Maximum packing

As from the above it was clear that for a better packing and to avoid moisture content, and for more productivity PVA is used as a binder.

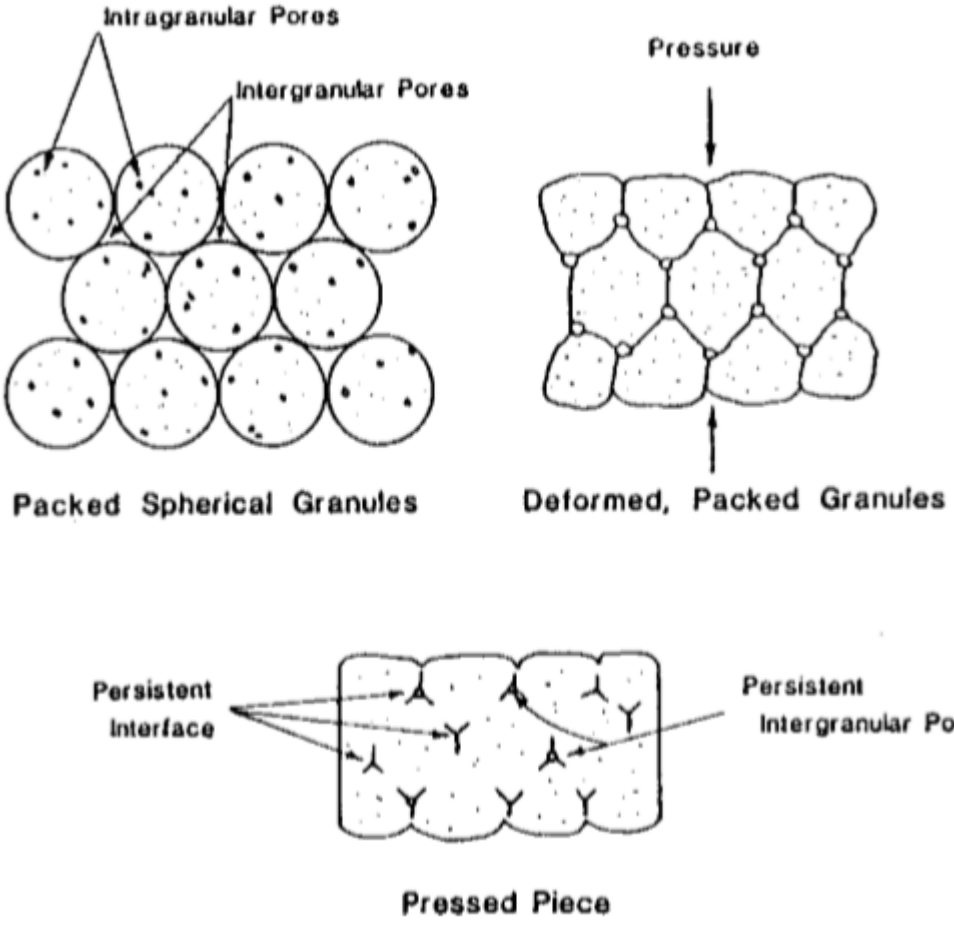
Role of Binder: Binders have a variety of roles depending upon the forming process being used for shape forming of green ceramics. The major role of

binders is to bind the granules together. This means that the binders improve the green strength of the products and help in handling of products before sintering. They can also act as plasticizers to provide plasticity to the system and also help to control the flow properties of the slurry. As a wetting agent, they help to improve the packing density in granules. Organic binders are less expensive and therefore widely used. They provide better burnout at low temperatures and are efficient due to the absence of inorganic impurities. Widely used binders are Vinyl Binder(PVA), Dextrin, Polyethylene glycol binder, Film-forming binder & Starch.

But PVA was a good characteristic for binding. Poly Vinyl Alcohol is a water soluble binder and is manufactured by hydrolysis of Poly Vinyl acetate in presence of a catalyst. Fully hydrolyzed PVA contains less than 2% residual acetate and dissolves in hot water. It has C-C linkage and the -OH groups provide initial wetting and adhesion properties. PVA has strong affinity for adsorption on oxide particles dispersed in water. PVA is largely used as a binder in dry pressed ceramics as it provides better mechanical strength to green bodies.



Dry Pressing is a very important fabrication process used to produce products of relatively high density. Proper formulation and controlling of feed material is a prerequisite for every pressing operation. The feed material commonly used is a granulated powder and the binder that is added to the system gives better flow ability and packing density increases.



The important thing should be considered is when the powder is compacted in a die pressure machine it causes a heavy friction between granules to granules and between granules to die, which causes un proper compaction of green density block and cracks, even where powder acts as a spring while pressing. So to avoid this, lubricant is used between the die and the powder. The lubricant used is ZINC STEARATE.

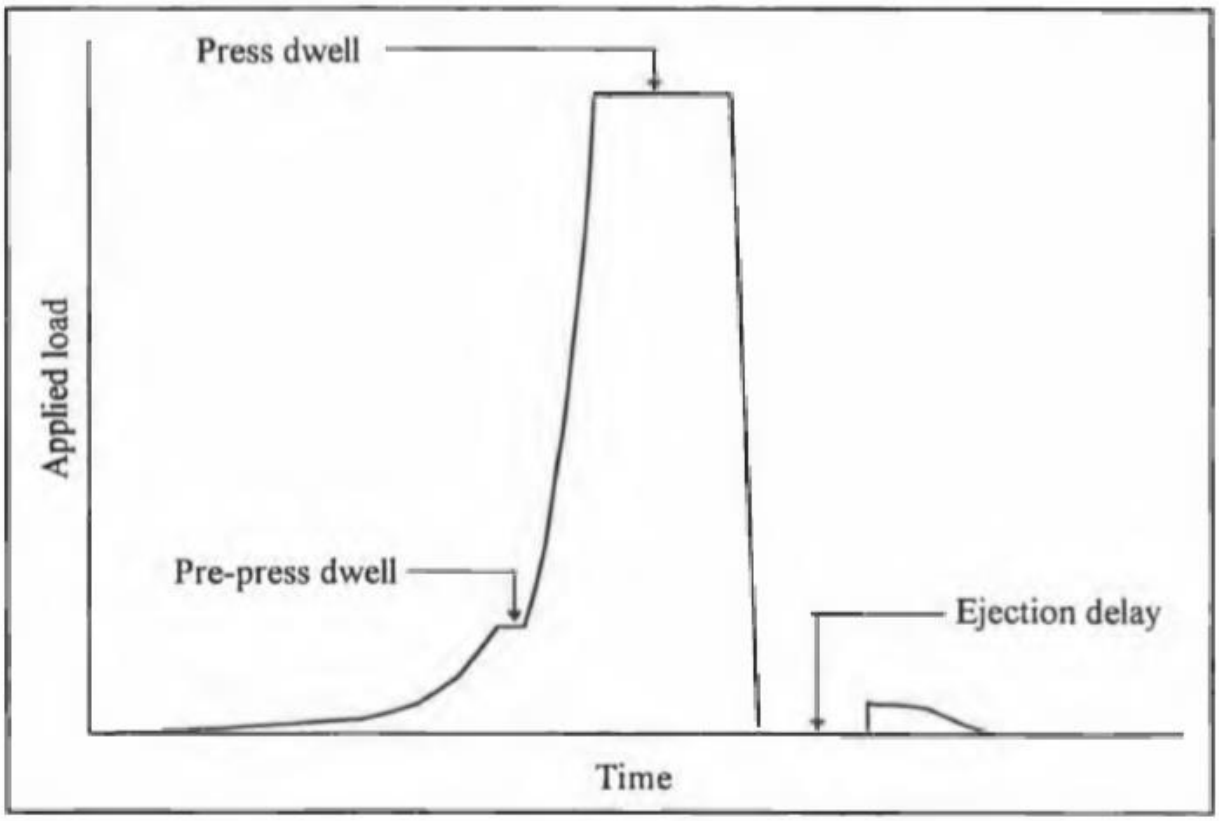
Zinc Stearate ($C_{36}H_{70}O_4Zn$), a soft and white powder is widely used as a release agent for the production of many kinds of objects rubber, polyurethane, polyester processing system, powder metallurgy. These applications exploit its "non-stick" properties. In cosmetics, zinc stearate is a lubricant and thickening to improve texture.

The compacting machine, Hydramet (Model HC 75 EC) used for pressing the arrester blocks is equipped with special features having precise and reliable controls. The pressing cycle consists of three main steps - filling, pressing and ejecting. Filling of the die with powder is facilitated by 8 joggs. After reaching a low pressing load (approximately 10 tons for three compacts of 49 mm in diameter, equivalent to about 18 MPa), a pre-press dwell time of 0.5 second is maintained followed by a higher load of 60-100 tons at which

the compacts are held for 2-3 second as press dwell. On releasing the load but keeping the disc inside the die an ejection delay for 2.0 seconds is provided. The compact is ejected by the lower punch but keeping it in contact with the upper punch. A delay of one second is adopted to detach the upper punch from the compact. Thus the operation is completed by a total cycle time of 28-30 seconds. A target green density is maintained within a range of 3.30 - 3.50 gm/cc.

Machine used: The Hydramet press (model HC-75 EC) though is equipped with the same basic compaction features of FILL - PRESS - EJECT. The machine is programmed by a combination of electrical, hydraulic, and mechanical controls and motions, which having a variable pressure control from 50Tonne to 100Tonne press. The die cylinders were made of SS which is having a little carbon which gives good strength.

Pressing Cycle: The pressing cycle consists of a number of steps beginning from filling the die with powder and ending with the ejection of the green body. Rise of pressure during compaction follows the pattern of a typical compressibility curve. The pressure increases at a lower rate in the initial stage and then with a rapidly higher rate in the final stage.

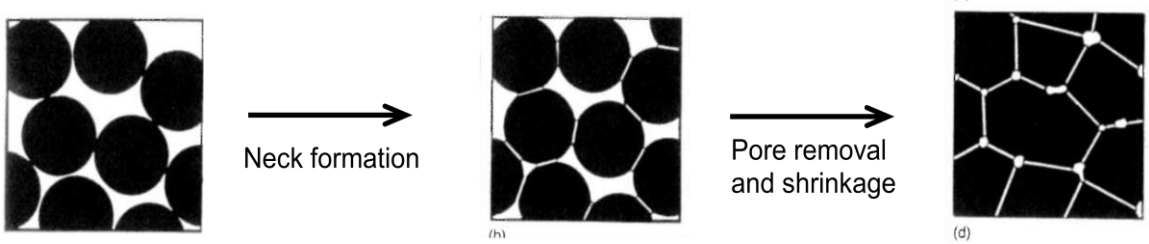


General pressing will be as follow:

	pressed block						
	Dia (mm)	**Hei (mm)**	**Wt (grm)**	**Radi (mm)**	**Area (mm2)**	**Volume (mm3)**	**density**
30-30	34.2	35.82	99.52	17.1	919.0029	32918.68	3.023207
60-30	71.8	37.27	476.3	35.9	4050.546	150963.8	3.15506
100-21	123.3	29.54	1021.1	61.65	11945.13	352859.1	2.89379

SINTERING OF ZnO BLOCKS

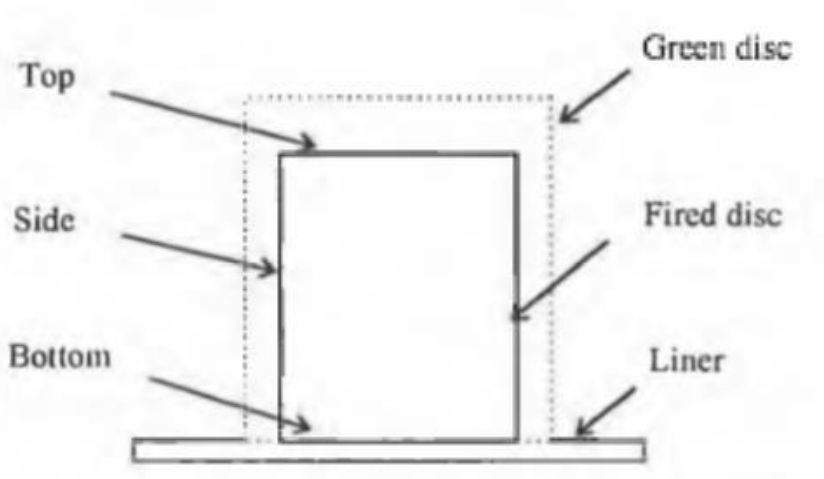
Sintering is the process of compacting and forming a solid mass of material by heat and/or pressure without melting it to the point of liquefaction. Sintering happens naturally in mineral deposits or as a manufacturing process used with metals, ceramics, plastics, and other materials. The atoms in the materials diffuse across the boundaries of the particles, fusing the particles together and creating one solid piece, because the sintering temperature does not have to reach the melting point of the material. Sintering is effective when the process reduces the porosity and enhances properties such as strength, electrical conductivity, translucency and thermal conductivity. During the firing process, atomic diffusion drives powder surface elimination in different stages, starting from the formation of necks between powders to final elimination of small pores at the end of the process. The sintering process passes through two different stages: 1) an early stage with local bonding (neck formation) between adjacent particles, and 2) a late stage with pore-rounding and pore shrinkage. In both stages, the bulk volume of the sintering particles shrinks – in the early stage, the center distance between adjacent particles decreases, in the late stage, the total pore volume shrinks.



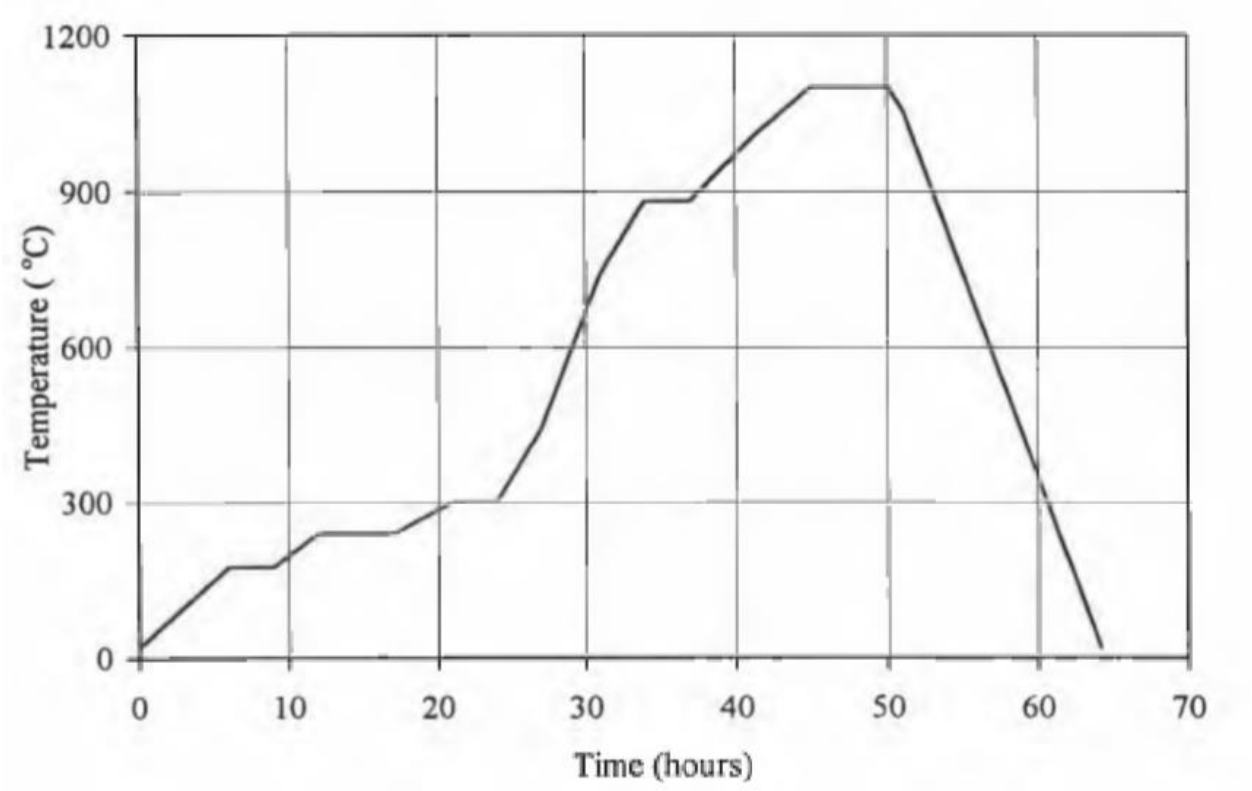
During sintering process the following process take place:

a) The binder burns out at 350°C to 400°C duration about 3-4 hours.
b) ZnO particles weld together and form bigger particles through nech growth.
c) The additives melt and form a more or less continous layer around the ZnO particles.
d) Some of the additives penetrate the ZnO particles through diffusion.

The sintering process of the zinc oxide arrester blocks or discs is commonly carried out in the electric kilns with controlled temperature profile. The sintering of the discs is performed by a conventional sintering profile with a peak temperature of 1125 °C and a total sintering cycle time of about 70 hours. The sintered ceramic body takes the shape of a rigid cylinder with a theoretical density usually more than 95 percent. In the sintering process the adjacent powder particles are united by means of diffusion, and subsequently grow into large grains.

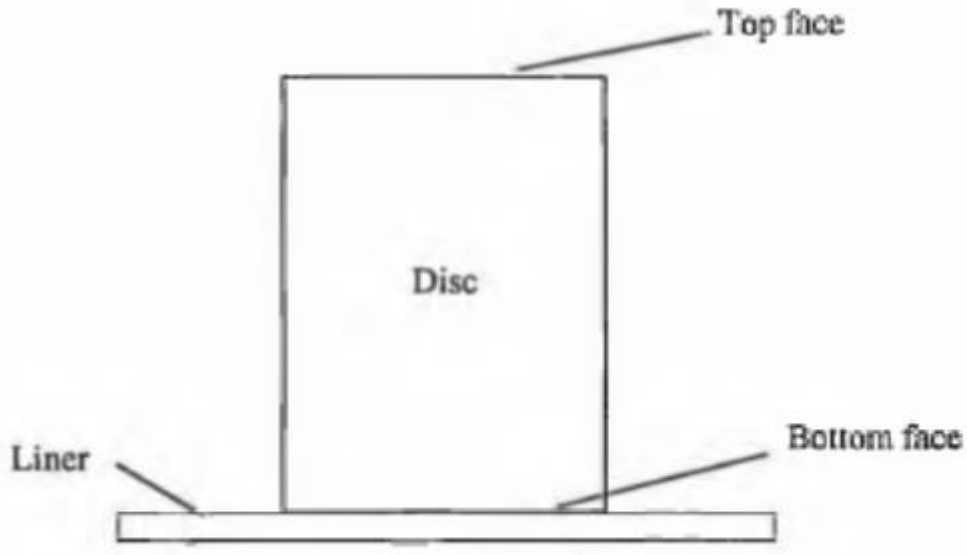


Zinc oxide varistors undergo a liquid phase sintering process. During this process the bismuth oxide melts to form the liquid phase which dissolves, at least in part, the other doping substances and promotes their uniform distribution. The liquid phase also favours the grain growth and dense sintering. The spinel precipitates, on the other hand, inhibit grain growth and generates a uniform distribution of the ZnO grain size. However, it is known that there are temperature differences from location to location inside the overhead large capacity (8000-10,000 discs in a single charge) kiln.



Like all other ceramic products, this operation requires the green compact bodies of varistor to be placed upon some sort of supports or saggers. To prevent the contamination from the direct contact of the repeatedly used sagger material the discs are kept physically separated from them by a liner material either in the form of a fine powder or a solid plate.

The orientation of the cylindrical arrester discs or blocks during sintering is shown in below figure. The face of the disc remaining in contact with the liner material (bottom face) is not physically as good as the top face. As a result this face needs more material to be ground off from this face.



The zinc oxide varistor discs are conventionally sintered in a vertical position resting on a liner material in the form of ZnO powder or ceramic flat plate. It is known that a varistor disc undergoes a process of considerable shrinkage during sintering. However, due to the density gradient in the green compact the fired diameter at the middle height of the disc is found to be the lowest. Apart from the scope of contamination, the bottom part of the disc passes a phase of sliding against the supporting liner material during shrinking. The frictional effects due to sliding with the liner material cause the diameter at the bottom face to become greater than that at the top.

So, from above it was clear that the blocks can't be kept on the saggers directly which effects the uneven sinckage at the bottom surface so the blocks are kept on a layer of zinc.

While sintering, at the given temperature in the block can be much higher during shorter periods. This leads to inter granular cracks, which start at the inside and are clearly visible after sintering because they will get opened. Therefore it is clear that the BBO (Binder Burn Out).

Binder burnout can be defined as the region of sintering where there is removal of binders, plasticizers, pore formers, dispersants and lubricants. They are removed by sintering at a temperature 350^{o}C to 400^{o}C for 3-4 hours which gives bind out the PVA and lubricants used in pressing.

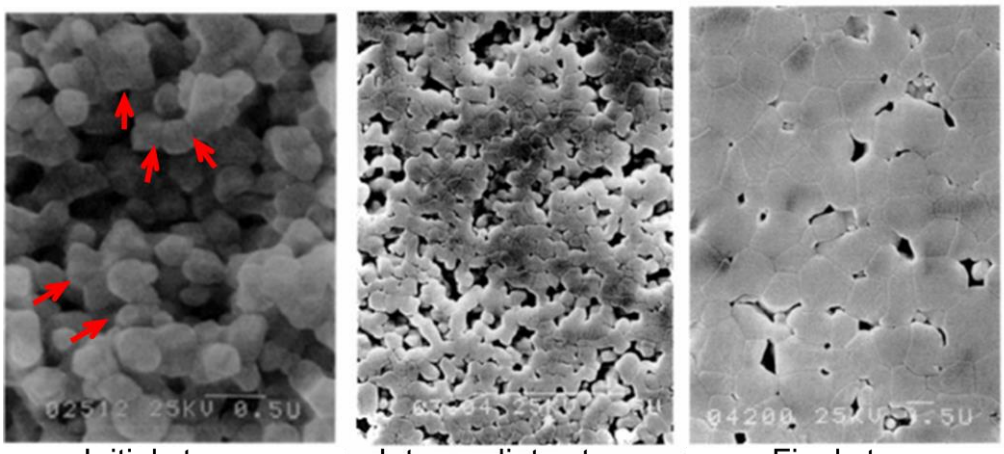
The binder has to be completely removed from the products during the high temperature processes. In the event of incomplete removal of binders, the sintered bodies will have defects like- black coring, sealed pores and bloating. This may lead to variation in pore size and shapes and the distribution of pores. Bubble formation in green bodies during binder decomposition can also lead to several defects within a fired body

There are different Stages of sintering:

a) Initial stage sintering: Formation of strong bonds and necks between particles at the contact points. Moderate decrease of porosity (initial 40-50%) from particle rearrangement.

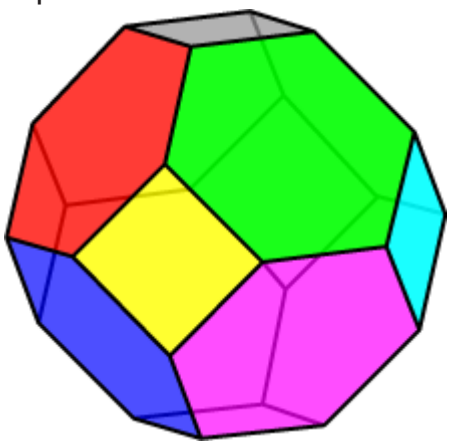
(b) Intermediate stage sintering: The size of the necks increases and the amount of porosity decreases. The sample shrinks (the centers of the grains move towards each other. The grains transforms from spheres to truncated octahedral*. This stage continues until pores are closed (r.d. 90%).

(c) Final stage sintering: Pores are slowly eliminated and major grain growth can occur.



Initial stage Intermediate stage Final stage

Arrow mark indicates the ZnO particles



*Truncated octahedral Shape

The increase of sintering time or temperature leads to an increase in grain size and results in fewer grain boundaries & low breakdown voltages. The typical grain size of a commercial zinc oxide varistor is between 15-20 μm.

While sintering the following reaction takes place in chemicals:

1) ZnO starts backing and the grain start growing.
2) Al gives donors in the ZnO, particularly enhancing cold conduction.
3) Al enhances α indirectly.
4) Bi promotes sintering and reduces the amount of pores.
5) Bi promotes distribution of the second phase and homogeneity provided that no Ti is present.
6) Bi promotes the presence of short circuit barriers.
7) Bi promotes length of active part of grain boundary.
8) Bi promotes (Together with Ti) grain growth.
9) Bi Determines for the greater part the value of α.
10) Bi gives acceptors in the grain boundary.

11) Bi (without Ti) limits grain growth.
12) Bi stabilizes he grain growth acceptor layer by introducing donors.
13) Ti (Together with Bi) promotes exaggerated grain growth.
14) Ti enhances grain growth.
15) Ti leads to degradation.
16) Ti decreases crack resistance.
17) Ti decreases max. energy impulse load.
18) Ti decreases breakdown voltages.
19) Mn gives donors in the ZnO, enhancing general conduction.
20) Mn enhances conduction of ZnO.
21) Al enhances α indirectly.
22) Co gives donors in the ZnO, enhancing general conduction.
23) Co enhances α indirectly.
24) Cr gives donor in the grain growth.
25) Cr acting as a donor in the grain boundary limits the acceptor conduction in the grain boundary due to Bi.
26) Si promotes distribution of the second phase and homogeneity.
27) Si limits grain growth.
28) Si decreases break-down voltage due to decrease in grain size.
29) Sb promotes distribution of the second phase and homogeneity.
30) Sb limits grain growth.
31) Sb decreases break-down voltage due to decrease in grain size.

Note: 1) In place of chromium oxide, nickel oxide can be replaced & silicon dioxide, tin oxide can be replaced.

The below are the major electrical & mechanical properties that involves in their properties

1) A smaller width of the active part of the grain boundary decreases insulation resistance.
2) A better distribution of the second phase and homogeneity decrease degradation.
3) A better distribution of the second phase and homogeneity improves max. energy impulse load.
4) More short circuit barriers improve insulation resistance (Max. Energy impulse load).
5) More pores increases degradation.
6) More and more elongated pores decreases crack resistance.
7) Exaggerated grain growth, increases degradation.
8) Exaggerated grain growth, decreases insulation resistance.
9) Exaggerated grain growth, lower crack resistance.

10) Exaggerated grain growth, is negative for the max. energy impulse load.
11) Donors in ZnO leads to better conductivity, thus lower insulation resistance.
12) The amount of acceptors in the grain boundary determine α.
13) The smaller the grain size, the higher the break-down voltage per unit length.

After sintering the blocks dimensions will changes which results in change of density. The blocks after sintering will changes as follows.

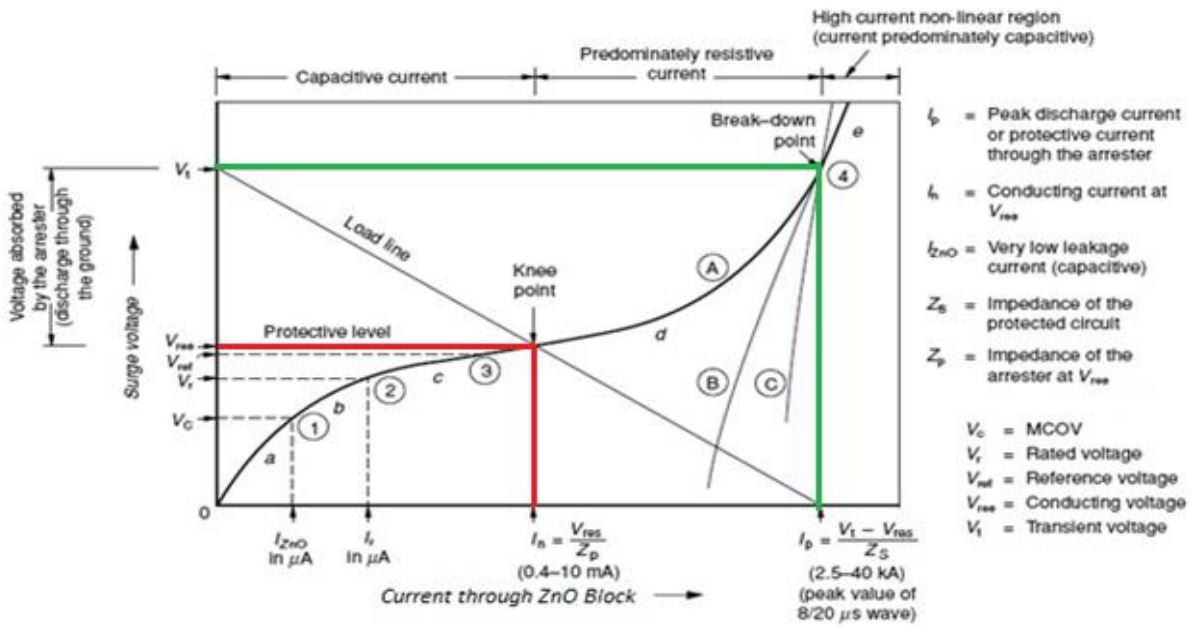
	fired block						
	Dia (mm)	**Hei (mm)**	**Wt (Grms)**	**Radi (mm)**	**Area (mm2)**	**Volume (mm3)**	**density**
30-30	28	29.43	100.01	14	616	18128.88	5.516612
60-30	59.5	31.28	473.31	29.75	2781.625	87009.23	5.439768
100-21	99.5	24.29	996.3	49.75	7778.768	188946.3	5.272928

Technical descriptions:

(A) The α can be defined from below formula

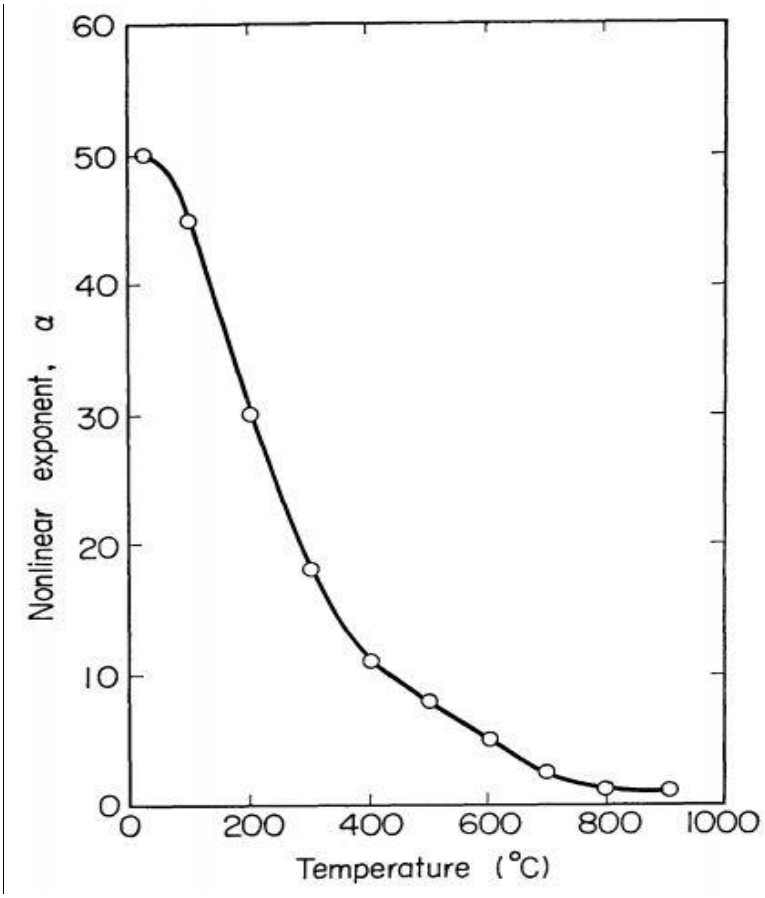
$$\frac{\log(b)-\log(a)}{\log(d)-\log(c)}$$

From the below graph

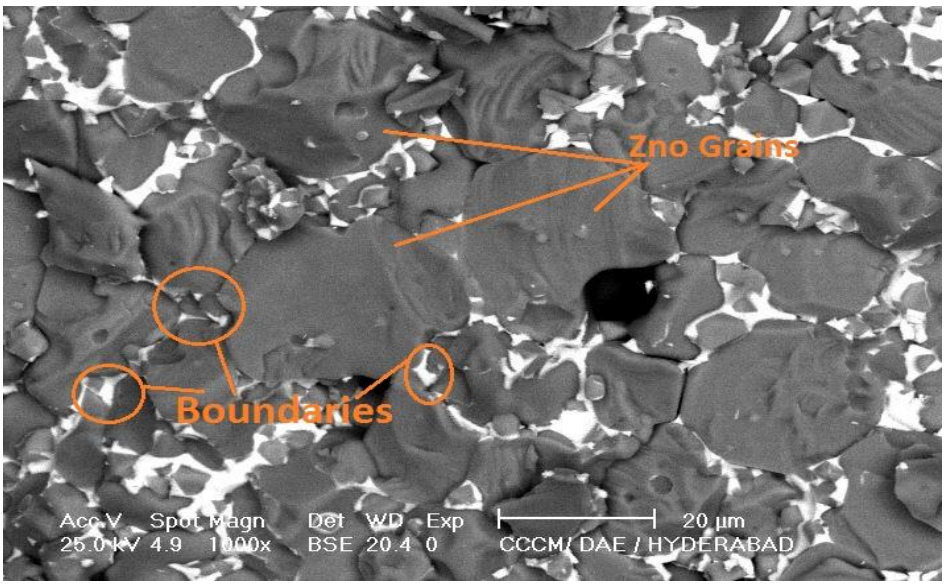


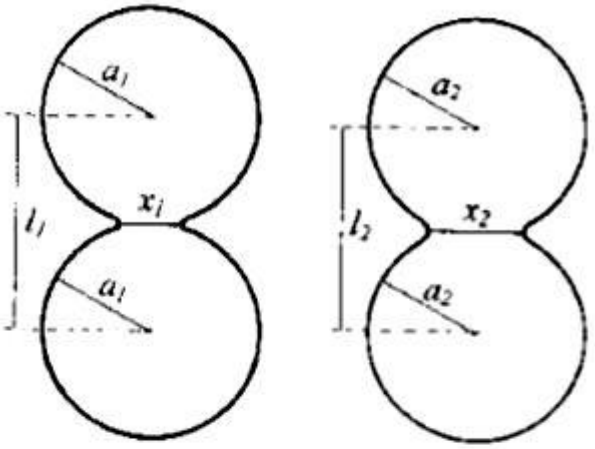
a= current density at In = Amp/area of ZnO block in cm2.
{Current will be in 1mA to 5mA}
b= current density at Ip = Amp/area of ZnO block in cm2.
{Current will be from 1.5kA to 30kA}
c= field density at Vres = voltage in volts/ height in cm.
d= field density at Vt = voltage in volts/ height in cm.

(B) α value depends upon the sintered temperature which inversely proportional to the increase in the temperature.

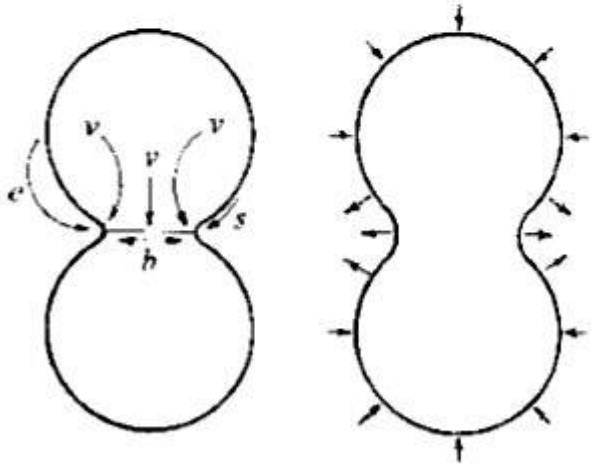


(C) While sintering the diffusion process takes place as below figure





$x_2 > x_1$, $l_2 < l_1 < 2a_1$, $a_2 \leq a_1$



v - volume diffusion.b - grain boundary diffusion
s - surface diffusion.e - evaporation/condensation
← ↓ = forces from surface tension (viscous flow)

(D) Shrinkage:

The theoretical density of ZnO material is 5.68 gm/cc. Since more than 90 percent of the constituent materials of a varistor is zinc oxide, this value can be conveniently considered to be the theoretical density of varistor material. The green compact density commonly lies between 55 - 65 percent of the theoretical density and the sintered density of the varistor is usually more than 95 percent. Since during sintering the loss in weight is very small- only about 2 percent, it is easily conceivable that a significant level of volume shrinkage occurs during this process. The overall volume shrinkage has been evaluated from the below equation as the ratio of the change in volume to the original green disc volume.

$$\frac{Vg - Vf}{Vg}$$

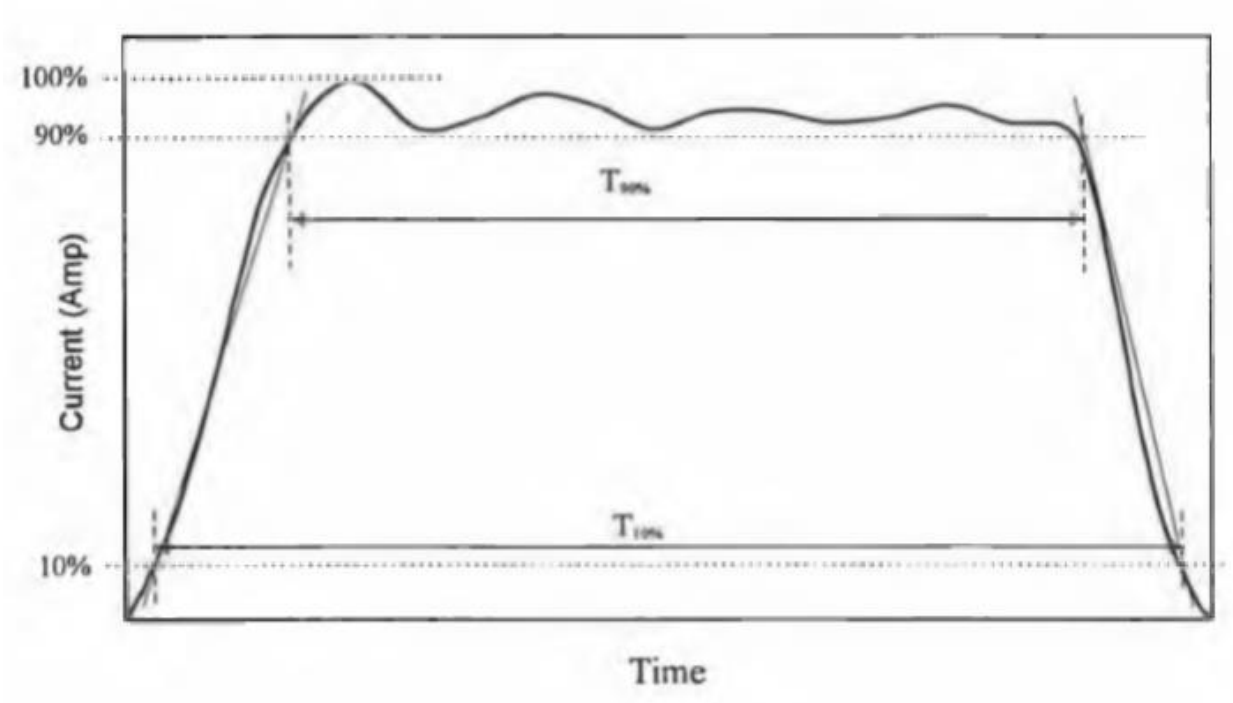
Vg = Volume of green body; Vf = Volume of fired body.

(E) Energy absorption capability:

This is a very important property for a varistor. A higher value of energy absorption capability can allow a reduction in the volume of the disc or the same disc can be used for more demanding applications. The average energy absorption capability of present day varistors should be more than 400 J.cm3. Discs pressed with lower compacting stress look poor in the context of withstanding capability in the higher level of energy. The discs pressed with maximum load also did not show the best results whereas those pressed with medium pressure exhibited best performance.

E = Voltage X current x time

Voltage = Voltage built up across the Zno Block when energy was applied
Current = Currrent flowing through the block as shown in below figure.
Time = time taken by the current to flow through the block (T90%)



(G) Temperature profiles:

The maximum temperature or the total time of sintering time depends upon the volume of the furnace or weight of the furnace. The main profile should be like below.

BBU out ----- soaking time ------- peak time

Some of the temperature profiles based on volume of the block are described below as of my experience and practice:

32 X 31 Size **TOTAL TIME: 94 Hours**

Initial Temp	Final Temp	Temp / hr	Time Required	Total Time (hrs)
50	175	30	4	4
175	180	2	2.5	6.5
180	210	3.3	9	15.5
210	240	4	7.5	23
240	295	6.5	8.5	31.5
295	305	5	2	33.5
305	450	35	4	37.5
450	450	Soaking	5	42.5
450	750	75	4	46.5
750	870	16	7.5	54
870	890	6.66	3	57
890	1070	23	8	65
1070	1070	Soaking	5	70
		Cooling	24	94

Size: 120X21 **TOTAL TIME: 136 Hours**

Initial Temp	Final Temp	Temp / hr	Time Required	Total Time (hrs)
50	175	20.8	6.01	6.01
175	180	0.83	6.02	12.03
180	190	1.25	8.00	20.03
190	210	1.53	13.07	33.11
210	240	2.3	13.04	46.15
240	295	4.23	13.00	59.15
295	305	3.33	3.00	62.15
305	450	24.16	6.00	68.16
450	450	Soaking	5.00	73.16
450	750	50	6.00	79.16
750	870	12	10.00	89.16
870	890	2	10.00	99.16
890	1040	20	7.50	106.66
1040	1040	Soaking	5.00	111.66
1040	700	83.75	4.06	115.72
700	30	Coaling	20.0	135.72