Technical Note

Electrical Characteristics of a Highly Hydrated Battery Grade Manganese Dioxide Powder

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Summary

The manganese dioxide powder under study, called Permanox is a by-product of saccharin manufacture. It contains about 10% by weight of water and 7.5% KOH. The electric conductivity is highly dependent on pressure, water content, temperature and not least, the measuring procedure. Conductivity rises considerably in transverse electric fields. From Argand diagrams, the apparent powder resistivity can be split into two parts. To a first approximation, the first part belongs to the grain cores, the second to intergranular contacts.

Überblick

Der hier untersuchte Braunstein "Permanox" wird bei der Herstellung von Saccharin gewonnen. Er enthält rund 10 Gew.-% Wasser und rund 7,5% KOH. Seine elektrische Leitfähigkeit hängt stark vom Druck, vom Wassergehalt, von der Temperatur und nicht zuletzt vom Messverfahren ab. Im elektrischen Querfeld nimmt seine Leitfähigkeit zu. Mit Hilfe von Ortskurven kann man den Widerstand in zwei Anteile aufspalten, von denen einer in erster Näherung dem Innern der Körner, der andere den Kontakten zwischen den Körnern zugeordnet wird.

Introduction

In the manufacture of the sweetening material saccharin (Fig. 1) o-toluene sulphonamide is oxidized with $KMnO_4$ in alkaline medium to the o-sulphonamide of benzoic acid, and a highly hydrated manganese dioxide, the saccharin sludge, is precipitated. This is carefully washed, gently dried

CH₃ — SO₃H   o-toluenesulfonic acid

+ PCl₅ and NH₄ salt

CH₃ — SO₂NH₂   o-toluenesulfonamide

+ KMnO₄

COOH — SO₂NH₂   o-benzoic acid sulphonamide

Mn O₂ precipitated

water extracted by evaporation or treatment

with acid thus giving benzoic sulfimide
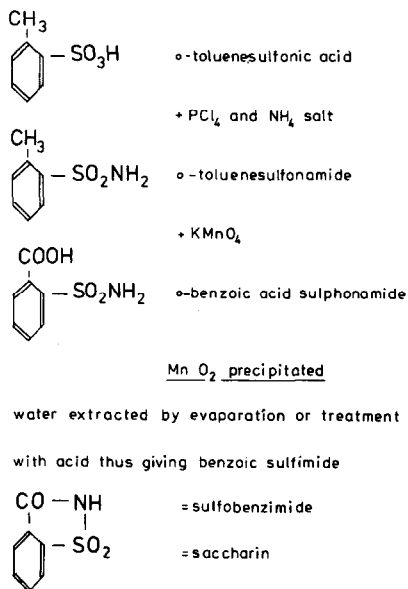
CO — NH / — SO₂   = sulfobenzimide = saccharin

Fig. 1. Manufacture of saccharin.

and carefully disintegrated by a sieving procedure. A light, readily reactive, synthetic manganese dioxide is then obtained (Table 1). We have had two samples of this at our disposal. Sample A was received in 1960 and sample B in 1977.

Poerscke [1] appears to have been the first to use this or a similar material in dry batteries. Meantime a whole group of synthetic manganese dioxides suitable for battery use has appeared on the market. These are known as chemical or artificial manganese dioxides (CMD or AMD). They are characterized by a high degree of reactivity and by their high potential, which is 250 to 300 mV above that of natural material (Table 1).

Manganese dioxide is formed from permanganate with practically any oxidizable material [2 - 5]; often this happens almost spontaneously. Apparently different products are thus formed which can be greatly altered by further mild treatment. Thus apparent densities from 0.7 to 1.1 g/cm^3, oxidation values from $MnO_{1.85}$ to $MnO_{1.99}$, water contents between 5 and 18% and alkali contents, as KOH, between 4 and 12% are found. The Permanox which we have investigated is therefore only one out of the family of permanganate manganese dioxides. It has a series of interesting electrical properties which we have investigated. The two samples A and B differed essentially in their water contents. The earlier sample A had 15 wt% (dried for 1 h at 110 °C), the more recent sample B 11 wt% water (dried for 1 h at 105 °C). Meanwhile it has been shown that the more recent sample of Permanox takes up exactly 18 wt% of water at high humidities.

TABLE 1

Properties of Permanox powder. Sample B (if not otherwise indicated)
Manufacturer: Perstorp Austria GmbH, A 1211 Vienna, P.O. Box 97

Composition:

manganese dioxide	MnO_2	79 wt.%
lower oxides as	Mn_2O_3	2
water, dried 1 h at 105 °C		11
alkali, as KOH		7.5
iron as Fe		0.4
Cu, Pb, Ni, Co		traces

Grain size: 100% pass DIN sieve 100

BET surface area: Sample A

with nitrogen	~ 30 m^2/g
with water vapour	~ 150 m^2/g

Grain shape: Agglomerates of 20 to 40 μm diameter formed from round primary particles 1 to 2 μm in diameter

Density:

X-ray density [7]	3.55 to 3.63 g/cm^3
pycnometer density	~ 2.4
shake density, DIN 51057	~ 0.8
rammed density	~ 1.25

Compressed density (g/cm^3):

Pressure, bar	as delivered	dried
50	1.01	1.13
150	1.15	1.24
250	1.30	1.37
350	1.44	1.48
450	1.59	1.61

Potential vs. saturated calomel electrode in battery electrolyte (210 g NH_4Cl and 90 g $ZnCl_2$ in 700 g water, density 1.14 g/cm^3, pH value 4.3).

Sample A	+807 ± 20 mV
For comparison in the same solution	
Zinc	−1010 ± 10 mV
West African natural ore	+535 ± 15 mV
Electrolytic γ-MnO_2	+620 to 615 mV
Oxygen (reversible) at pH 3.3	+790

Shaken with 30 cm^3 electrolyte 3 g Permanox gave a solution with a pH value of 3.3 ± 0.1

Structure

Figure 2 shows a photograph of Permanox powder in the scanning electron microscope. The powder has cauliflower-like grains, agglomerates of round primary particles of 1 to 2 μm diameter. The X-ray diagrams show only weak reflections. We have therefore, instead of goniometric diagrams,
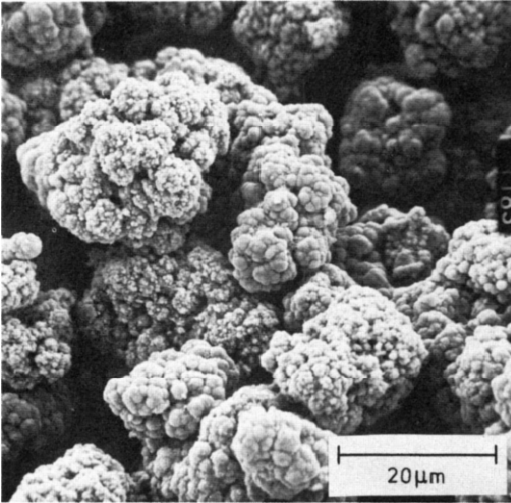
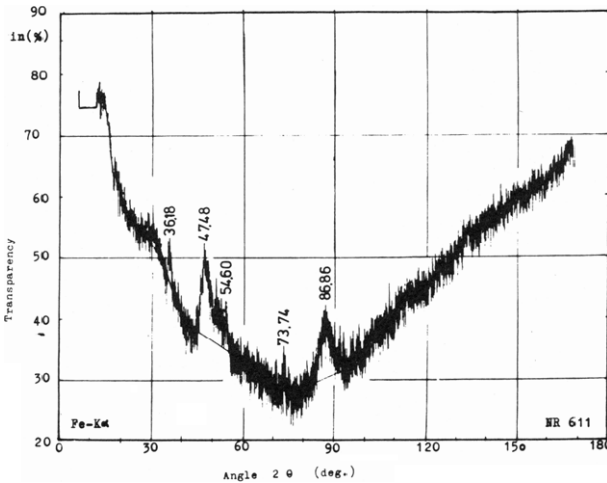Fig. 2. Electron scanning microscope photograph of Permanox powder.

Fig. 3. Photometric lines from a Debye–Scherrer photograph of Permanox powder using FeKα radiation.

preferred to take classical Debye photographs which, because of their sharper definition, show the reflections more clearly. Figure 3 shows the variations in film transmission obtained by the use of a recording photometer. Two broad unsymmetrical reflections can be recognized at $2\Theta =$ 47.5° and 87.5° and also two weak reflections at 36° and 73° and a form of step at 29°. The interpretation of X-ray diagrams of nearly amorphous materials is always to some extent arbitrary. This applies to the large number of modifications and sub-types which are known generally as "Braunstein". With some caution then the following can be stated for Permanox.

The reflections fit [6], "a synthetic, poorly defined manganese dioxide lacking in lines" which is related to ramsdellite or γ-MnO_2. However, they can equally well be equated with the δ-MnO_2 modification [2, 3]. This, in fact, is more probable [4]. The observed reflections [4] coincide apparently exactly with a preparation that is precipitated at 70 °C from $KMnO_4$ solution with hydrogen peroxide, filtered, washed and dried, after which it is treated with nitric acid. The δ-MnO_2 is thereby changed via α-MnO_2 (with potassium) into β-MnO_2. Permanox is to be found in this series. However, the reflections are very weak, their recorded strength really does not go beyond the description "quasi-amorphous". Bode [7] has proposed a layer lattice of the brucite type with water rich layers between hexagonal MnO_2 layers, constants $a = 2.4$ and $c = 6.9$ Å. The high water content (up to 18 wt.%) can, however, hardly be contained within the layers. Therefore it is probable that some water is contained in cation defects in the lattice. The apparently essential potassium content also indicates an obvious close relationship with cryptomelane, α-MnO_2 with potassium in the lattice. Similarly significant is the finding by differential thermal analysis of a weak exothermic reaction at 550 °C. This [4] is characteristic of δ-MnO_2, while the α- and γ-modifications give an endothermic reaction at about the same temperature (570 °C).

Water content

The Permanox powder which has been investigated contains about 7.5 wt.% alkali, as KOH, and 11 wt.% water. From this composition by stoichiometric calculation the following empirical formula is obtained:

$$MnO_{1.987}(H_2O)_{0.65}(KOH)_{0.143}$$
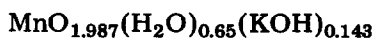
The alkali content corresponds to approximately 1/7 mol KOH to 1 mol MnO_2, rather higher than in α-MnO_2 in which the molar ratio is about 8:1. The water content corresponds to 2 mol of water to 3 mol of manganese, similar to the structure proposed by Bode for δ-MnO_2 [7]. There are, however, quite similar manganese dioxides with considerably higher water contents. In general the water content is not unambiguous. Permanox is slightly hygroscopic and takes up water in the course of time.

Figure 4 shows a drying curve. The different drying, water determination experiments give slightly different values. By storage in high relative humidities, 98% r.h. at 60 °C, the water content can be raised to 18 wt.%. There are no steps in the drying curve which indicate definite hydrates. There is also no loss of oxygen at 110 °C nor at 60 °C and 98% r.h.

Electrical resistivity of the powder under pressure

Here we have three independent series of investigations: sample A, measured in a cylindrical pressure tool at 500 Hz using a hydraulic hand-
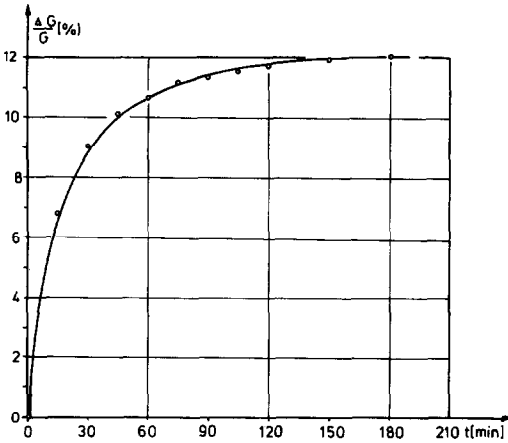
Drying curve

Fig. 4. Drying curve for Permanox powder sample B. Initial weight 8.5 g. Drying carried out with air circulation at 105 °C; there is no oxygen loss at this temperature. $\Delta G/G$ = weight loss %.
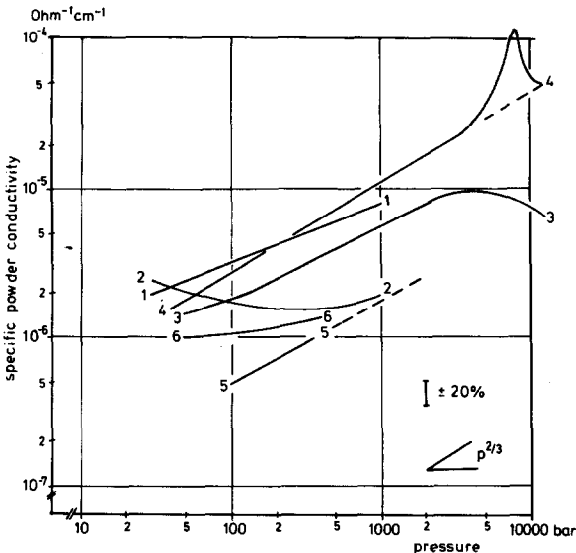

Fig. 5. Pressure dependence of the conductivity of Permanox powder. 1, Sample A, dried for 1 h at 110 °C, measured at 22 °C [8]; 2, sample A, as delivered, 15 wt.% water content, at 22 °C [8]; 3, sample B, dried for 3 h at 105 °C, measured at 20 °C [9]; 4, sample B, as delivered, 12 wt.% water content, at 20 °C [9]; 5, sample B, dried for 2 h at 110 °C, measured at 31 °C [10]; 6, sample B, as delivered, 12 wt.% water content, at 31 °C [10].

lever press (Euler [8]), curves 1 and 2 of Fig. 5. Sample B, also measured in a cylindrical pressure tool but at 50 Hz using a precision screw press (Kirchhof [9]), curves 3 and 4. Sample B, measured in a rectangular pressure

tool at 5 kHz using a hydraulic press (Mueller-Helsa [10]), curves 5 and 6. Curves 2, 4 and 6 were determined on the samples as delivered, curves 1, 3 and 5 on dried samples. The results of these three investigations differ considerably as can be seen from Fig. 5, but the following generalizations can be made.

From experience it is known that with poorly conducting, finely powdered MnO_2 powders a reproducibility of ±20% in the apparent conductivity may be expected; this means that for example curves 1 and 3 can be considered to be in agreement. The measuring frequencies of 50 and 500 Hz are so low that contact capacity is of no importance. On the contrary, as has been subsequently determined, 5 kHz is already excessively high, the measured resistance too low and so curves 5 and 6 are too high. Similarly for temperature, but the curves 5 and 6 should not be lowered but raised. In rectangular pressure tools the pressure distribution is always problematic. Unequal pressure distribution always has the effect of an apparent reduction in cross-section, so that the value of conductivity determined is low. Therefore the measurements made by Kirchhof under the best conditions are considered to be the most reliable. Whether the hump at the top right of curve 4 is genuine has still to be proved. From these measurements it follows that: dry samples have a lower conductivity than those containing water; to a rough approximation dried samples show an exponential dependence of conductivity on pressure with an exponent of 2/3. The very anomalous curve 2 in Fig. 5 was obtained with a sample with a particularly high water content.

From this it can be inferred that an appreciable part of the electrical conductivity results from the water (or electrolyte) content. The water probably forms a film between the grains which is squeezed out in the lower pressure range, up to 300 bar. The value of 0.66 for the exponent implies that the elementary theory of powder conductivity previously proposed [11] applies also to Permanox powder, but only if it is dry.

From Fig. 6 it can be seen that the electrical conductivity is strongly dependent on temperature. The range investigated only extended to 60 °C
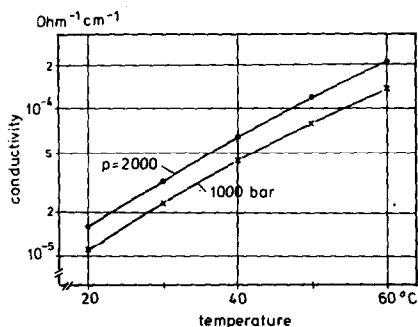

Fig. 6. Temperature dependence of the conductivity of Permanox powder as delivered [9].

but nevertheless, from the Schottky lines, a value for the activation energy has been calculated in the usual way:

$$-U = R \ d(\ln \kappa)/d(1/T)$$

where κ = conductivity and R = gas constant. Then taking into account all uncertainties, a value of 12 kcal/mol (51 kW/mol), that is 0.53 eV, is obtained. This is a very steep temperature dependence and probably the highest in the whole range of activation energies measured for MnO_2 [5]. Hall effect measurements have not yet been carried out. It can, however, be stated that dried Permanox powder is an n-type conductor. In the as-delivered condition the water content is responsible for a considerable amount of ionic conductivity. The average carrier density of compressed samples in this pressure range (100 - 2000 bar) is approximately 10^{19} cm^{-3} and the mobility probably of the order of magnitude of 1 cm^2/V.

Change of resistance in a transverse electric field

Mueller-Helsa has found [10] that the electrical conductivity of this manganese dioxide increases in a transverse electric field. Figure 7 is a schematic drawing of the pressure tool which has been used and Fig. 8 shows the sample geometry. The conductivity was measured between contacts 4 in Fig. 7 at 5 kHz in the same direction as the applied pressure. A transverse electric field, which could be raised to 240 V/cm, was applied perpendicularly to this, this was unearthed (floating) and obtained from the 50 Hz mains supply. The measuring circuit and driving circuit were carefully
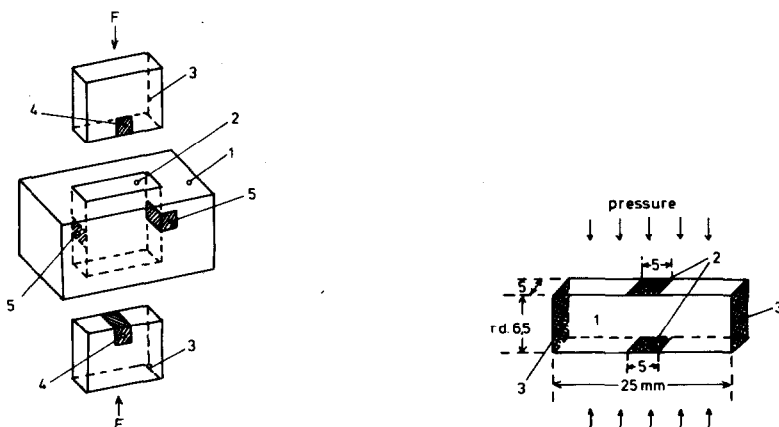

Fig. 7. Pressure tool made from insulating material [10]. 1, Matrix with cavity for sample 2; 3, pressure piston with contacts 4; 5, side contacts.

Fig. 8. Sample geometry and measurements. 1, Compressed powder sample; 2, contacts parallel to the direction of pressure; 3, contacts perpendicular to the direction of pressure.
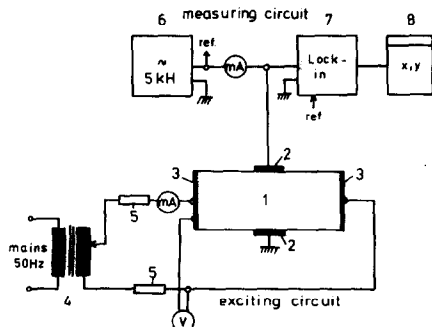
Fig. 9. Change of resistance in a transverse electric field. Circuit diagram of the measuring arrangements. The resistance parallel to the direction of pressure was measured at 5 kHz with a lock-in amplifier. Field strength, 0 to 240 V/cm (effective). 1, Sample; 2, contacts parallel to the direction of the pressure; 3, field contacts; 4, isolating and control transformer; 5, protective resistances; 6, RC generator; 7, lock-in amplifier; 8, recorder.

TABLE 2

Electrical conductivity of Permanox powder in the direction of the pressure. Sample B, dried for 2 h at 110 °C, measured at 5 kHz.
The conductivity is increased by a transverse electric field. Results corrected to the initial temperature [10]. L is the percentage increase in conductivity at 240 V/cm over the value with no field.

Transverse field 50 Hz (V/cm)	Conductivity (ohm^{-1} cm^{-1} × 10^{-6}) at a pressure of		
	100 bar	200 bar	400 bar
0	0.47	0.73	1.05
40	0.49	0.76	1.06
80	0.51	0.73	1.12
160	0.52	0.86	1.13
240	0.50	0.86	1.26
	L: 9%	17%	19%

decoupled (Fig. 9). The results of these measurements are given in Table 2. As can be seen, with a transverse field of 240 V/cm the order of magnitude of the effect is 20%; it increases with pressure. The increase in conductivity takes place rather slowly and it is possible that it could be a thermal effect.

However, according to Fig. 6 the thermal explanation of the increase in conductivity requires a temperature rise of about 2.5 °C. This cannot be completely excluded; it is, however, relatively unlikely. At 400 bar and 240 V/cm the electrical power dissipated is of the order of 0.3 W/cm^3. From the dimensions and specific heat of the matrix material this power will give a maximum temperature rise of 0.5 °C. Probably therefore the electrical transverse effect has other causes. We assume that in the compressed powder the single current paths follow a zigzag course. Therefore some sections of

them will be in the same direction as the transverse electrical field. The high transverse field can moreover bring about a marked sintering effect [11] which in this case will take a transverse course and only influence the corresponding parts of the current paths.

Specific heat

If the undried Permanox powder heated to 100 °C is mixed with water at 20 °C so that a final temperature of about 30 °C results, a value of about 1.3 ± 0.1 W/gK (0.31 cal/gK) can be evaluated for the specific heat. This is higher than the value of about 0.67 W/gK generally given in the Tables for MnO_2. The water-rich powder which has been investigated can well have a noticeably higher specific heat on account of its water content. In this connection consideration should also be given to the lower oxides of manganese, not only Mn_2O_3 but also hausmannite, Mn_3O_4, or the water-containing hydrohausmannite, the specific heats of all of which are quite high, about 1.58 W/gK for water-free hausmannite. The presence of any of these will obviously raise the measured specific heat. The possibility of water being driven off during the warming of the powder and taken up again on mixing with the liberation of heat of hydration has also to be considered.

Argand diagrams of the resistance of the powder

According to Braun [12] a compressed powder can be considered as a three element RC circuit, as shown in Fig. 10. The quantities ρ_1, ρ_2, and c refer to unit surface of 1 cm^2 and unit thickness of 1 cm. Their units are therefore ohm.cm and μF/cm. ρ_1 is to the first approximation the resistance of the core of the grains, therefore it is similar to the resistance of the solid material from which the grains are formed. ρ_2 is essentially the contact resistance between the grains, by-passed by the contact capacity c. The three quantities are the macroscopic, apparent specific quantities measurable on the powder, that is specific resistances and a specific capacitance.
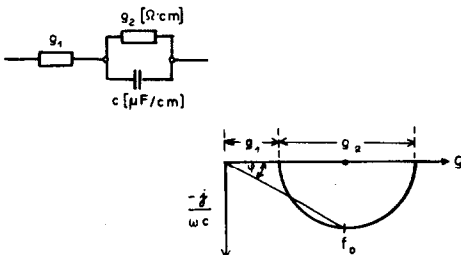

Fig. 10. Equivalent circuit and Argand diagram of a conducting powder in the resistance mode (schematic representation) [12].
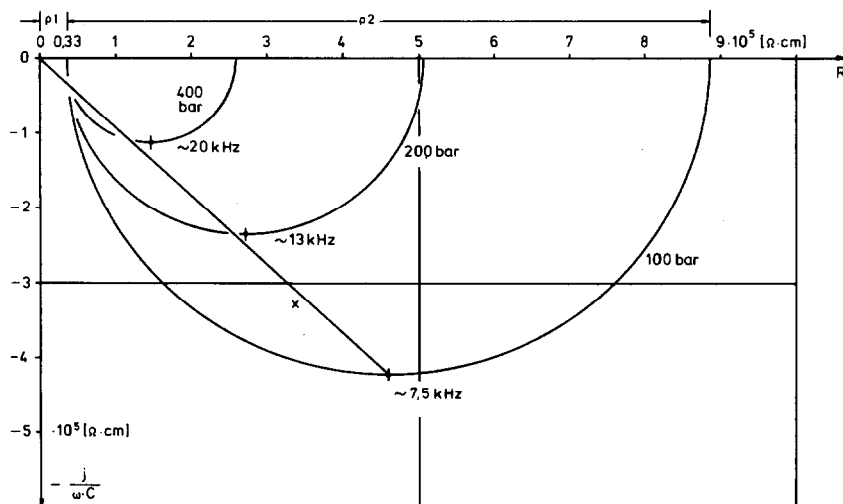
Fig. 11. Argand diagram of the resistance of Permanox powder under pressure. Sample B after drying for 2 h at 105 °C, measurements made at 20 °C and 100, 200 and 400 bar. Values of ρ_1, ρ_2 and c are shown in Table 3.

TABLE 3

"Solid" portion ρ_1 and contact portion ρ_2 of the resistance, contact capacity c and summit frequency f_o of Permanox powder determined from the Argand diagram. Sample B, dried at 105 °C for 2 h.

	In direction of the pressure at			Perpendicular to the pressure		
	100 bar	200 bar	400 bar	100 bar	200 bar	400 bar
ρ_1 (ohm.cm)	5.6×10^4	5.6×10^4	5.6×10^4	3.3×10^4	3.3×10^4	3.3×10^4
ρ_2 (ohm.cm)	2.5×10^6	1.4×10^6	0.87×10^6	8.5×10^5	4.4×10^5	2.2×10^5
c (μF/cm)	1.1×10^{-5}	1.0×10^{-5}	0.92×10^{-5}	2.5×10^{-5}	2.8×10^{-5}	3.6×10^{-5}
f_o (kHz)	6	11	20	7.5	13	20

Figure 11 shows an example of the Argand diagram. The pressure tool shown in Fig. 7 was used, between contacts 4 the approximate conductivity parallel to the pressure is measured and between contacts 5 the conductivity perpendicular to the direction of the pressure. The values obtained are a little too large because the current paths in the sample are curved. The results are shown in Fig. 11 and Table 3. The core part of the specific resistance is relatively small and is not very dependent on pressure. On the other hand, the specific contact resistance decreases considerably with increase in pressure.

The contact capacity is around some 10^{-5} μF/cm. Conclusions on the dielectric constant of the powder are hardly possible; for this other methods

or considerably higher pressures must be used. It can, however, be remarked that the relative dielectric constant of the powder which has been studied is probably less than 10, and so is not comparable with the high value of (ferroelectric) β-MnO_2.

The simple interpretation of the Argand diagrams in terms of grain core and contact resistances is probably too great a simplification, as Braun [12] has already pointed out. In the present case, for example, the values for ρ_1 parallel and vertical to the pressure should be approximately the same, if they truly correspond to the pure core resistance of the grains. Actually the two values differ by a factor of about 1.7. The fact that the contact resistance ρ_2 is considerably lower in value perpendicular to the pressure than parallel to it, in the present case by a factor of about 3, is in general a well known experience, although it must be admitted that an anisotropy of this magnitude has not been previously observed. Naturally the contact capacitance behaves similarly, it is also higher perpendicularly to the direction of the pressure than parallel to it by a factor of about 3.

Conclusions

The artificial manganese dioxide Permanox has a cauliflower-like structure formed of agglomerates of particles of 1 to 2 μm diameter. It is quasi-amorphous, probably an extremely poorly crystalline form of δ-MnO_2. On the drying curve no steps are apparent. A considerable part of its conductivity is due to its water content. The conductivity is strongly dependent on temperature, with an activation energy of about 0.5 eV. Hall effect measurements have not yet been made. The conductivity increases in a transverse electrical field. By means of Argand diagrams the apparent specific resistance of the powder can be separated into two parts which can, as a first approximation, be considered as representing grain core and grain contact resistances respectively. The resistance parallel to the direction of the applied pressure is considerably higher than the value perpendicular to it.

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