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**A PROCESS FOR MAKING AN IMPROVED TANTALUM POWDER AND HIGH
CAPACITANCE LOW LEAKAGE ELECTRODE MADE THEREFROM**

Field of the Invention

This invention relates to a process for producing capacitor
5 grade powder from a base material selected from Group V-B of
the Periodic Table which has been reacted with nitrogen and
oxygen; the powder produced therefrom; and a solid electrode
fabricated from the powder and anodized at voltages of 100
volts and higher. Improved electrical leakage characteristics
10 are obtained through a range of specific charge of up to
25,000 $\mu\text{FV/g}$.

BACKGROUND OF THE INVENTION

The performance characteristics of capacitors or
15 electrodes formed from capacitor grade powders are expressed
in terms of specific charge and electrical current leakage.
The specific charge, normally expressed in $\mu\text{FV/g}$, is a measure
of electrical charge capacity of the capacitor and is usually
proportional to the surface area of the powder as a sintered
20 and anodized pellet. The electrical leakage, normally
expressed in units of $\text{nA}/\mu\text{FV}$ or $10^{-3} \text{ uA}/\mu\text{FV}$, is an indication
of how well the capacitor holds the specific charge.
Capacitors with improved electrical leakage characteristics
are recognized as having higher reliability.

25 It is well known that the performance characteristics of
finished capacitors are affected by the chemical and physical
characteristics of the powder employed to make the capacitors.
Base powders having greater than 3000 ppm by weight of oxygen
30 often develop crystalline like flaws in the dielectric film
during sintering and anodic oxidation. The flaws allow
current to pass through the dielectric, producing parts which
exhibit excessive electrical leakage and premature failure.
The likelihood of flaw formation increases for high
35 reliability capacitors where anodization voltages of 100 volts
or higher are used.

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leakage or the effect of such doping on the electrical characteristics for anodization voltages above 100 volts. Furthermore, the percentage reduction in electrical leakage is relatively low for anodization voltages above 200 volts, suggesting that the role of the dopants employed is to modify the dielectric material rather than to reduce dielectric defects during formation.

In Japanese Kokai No.: 53[1978] -49, 254, a method for forming a uniform tantalum nitride film is disclosed. In one embodiment, tantalum powder is subjected to ammonia gas and mixtures of nitrogen or ammonia with an inert gas such as argon. Alternately, tantalum powder may be exposed to a salt bath consisting of NaCN, NaCO₃, BaCl₂, and KCl. The powder is then pressed into anodes and sintered.

In Japanese Kokai No.: 63[1988]-86,509, a process for reducing electrical leakage is disclosed. Tantalum powder which was pressed into an anode and sintered was subject to an ammonia gas atmosphere at a temperature of 1,100°C. Reacted oxygen was held below 3000ppm. No disclosure is made however, of the significance of doping with both oxygen and nitrogen in the critical range claimed by the present invention.

Only marginal improvements in electrical leakage have been observed for capacitors utilized in high reliability applications. Typically these rugged capacitors are anodized at voltages above 200 volts and operate in a specific charge range of between 5,000 and 24,000 uFV/g and more particularly between 5,000 and 15,000 uFV/g.

One object of the present invention therefore is to reduce electrical leakage in solid electrolytic capacitors at formation voltages of 100 volts or higher, while maintaining specific charges above 5,000 uFV/g;

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BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more readily understood from the following description and from the accompanying non-limiting Figures:

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Figure 1 illustrates the synergistic effect of reacting tantalum base material with oxygen and nitrogen together as compared with reacting the material with oxygen and nitrogen separately. Percent reduction in electrical leakage is illustrated over a range of formation voltages.

10

The lower curve of Figure 1 was prepared from data obtained by the evaluation of electrodes anodized at voltages of 150 volts and 200 volts, and was prepared in accordance with Examples 1 and 3, and 2 and 4 discussed below. The percent reduction in electrical leakage was calculated by taking the average leakage from Examples 3 and 4 over a sintering range of from about 1400°C to 1700°C, and subtracting the value from the average leakage from control Examples 1 and 2. The percentage reduction in the average electrical leakage from the control was then calculated. The reduction is approximately 35% at 100 volt anodization, 55% at 150 volts, 60% at 200 volts, and over 80% at 400 volts.

15

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The middle curve of Figure 1 was prepared from electrodes anodized at 100, 150, 200, and 400 volts. Comparison data was obtained from electrodes prepared in accordance with Examples 9 and 8, 2 and 1, 4 and 3, 12 and 11, and 14 and 13.

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Figures 2 and 3 illustrate an improvement in specific charge over a range of sintering temperatures between about 1400°C and 1600°C. Tantalum base materials were doped with oxygen and nitrogen in accordance with the process of Examples 1-4 and 8-10 respectively, and tested for specific charge. The results were compared with the results obtained from control samples prepared in accordance with the steps of

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The base materials employed in one embodiment of the present invention were agglomerated by heat treatment while being subject to a vacuum or an inert gas environment. Temperatures in the range of 1200°C to 1600°C, and preferably
5 in the range of 1400°C to 1500°C were used. The heat treatment process may be repeated to achieve a desired degree of agglomeration. Those skilled in the art will recognize the thermal conditions and heating times necessary to achieve a desired level of agglomeration of the selected powder.

10 After agglomeration, the base material was subjected to size reduction to a screen size smaller than 40 mesh. Various traditional methods for reduction are contemplated by the present invention including the use of jaw crushing.

It is also within the scope of the present invention to
15 prepare electrodes from powders which have not been subject to agglomeration heat treatment.

The inventor has discovered that by reacting a range of nitrogen and oxygen with the base material, capacitors produced from the treated powder demonstrated improved
20 electrical leakage characteristics. While a range of about 500 to 7000 ppm by weight of nitrogen and of about 700 to 3000 ppm by weight of oxygen is contemplated by the present invention, a range of 1400 to 4500 ppm nitrogen and 1100 to 2900 ppm of oxygen is preferred. At anodization voltages of greater than
25 200 volts, ranges of 1400 to 2600 ppm nitrogen and 950 to 2900 ppm oxygen are preferred. Where the quantity of nitrogen and oxygen fall either below or above the cited range, desired reduction levels of electrical leakage and increases in specific charge are not achieved.

30 It is also contemplated by the present invention that nitrogen and oxygen can be added to the base material at different points during the process. For example, the dopants may be added during any heat cycle after the powder is pressed



Those skilled in the art will recognize that the values of x, y, and z will depend on the level of oxygen and nitrogen present in the tantalum base material. In accordance with Examples 6 and 7, between about 2050 and 2900 ppm of oxygen by weight remained after the powder was purified of magnesium oxide. A reduction in electrical leakage of between 75 and 84% and a specific charge range of 9,800 to about 15,350 was obtained for an anodization voltage of 150 to 200 volts. Desired quantities of both oxygen and nitrogen were reacted with base metal in the same step.

Where at least a stoichiometric amount of magnesium is used and appropriate temperatures and residence times known to those skilled in the art are employed, oxygen in the tantalum metal lattice can be completely removed. Tantalum rapidly forms tantalum oxide as a surface layer upon exposure to an oxygen environment (e.g. air). Therefore, the oxygen content in the tantalum metal powder under this circumstance is proportional to the surface area.

In an alternate embodiment, the oxygen content was also controlled by varying the amount of hydrofluoric (HF) acid used in the leaching process. HF dissolves tantalum surface oxide thereby reducing the surface area of tantalum and the associated oxygen content. In yet a further embodiment, oxygen content was adjusted by varying the time and temperature during drying in air after acid and water leaching.

The nitrated and oxygenated tantalum material having a BET of less than .6 m²/g and preferably between .25 and .55 m²/g was then pressed into a pellet, sintered, and evaluated for electrical leakage characteristics in accordance with the procedures identified below. These procedures are generally known and recited in US Patent Nos. 4,441,927 and 4,722,756, currently assigned to the present assignee Cabot Corporation.

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With excessively high oxygen content in the powder (e.g. over 3500 ppm), the oxygen tends to form crystalline tantalum oxide after pressing, sintering, and cooling. The tantalum oxide crystal formed before anodization acts like an impurity which serves as a site for crystal formation of tantalum oxide during sintering. Therefore, there is an optimal oxygen concentration in the powder. The optimal level is generally in the range of between 700 and 3000 ppm depending in part on the available surface area and the sintering and formation conditions.

The behavior and effects of nitrogen in the sintering and anodization processes of tantalum metal are similar to those of oxygen, except for the fact that solubility of nitrogen is about twice as high as that of oxygen in tantalum at a given temperature. Therefore, higher nitrogen content in the powder can result in lower electrical leakage in the capacitor. Furthermore, at normal capacitor application temperatures (ambient to 100°C), nitrogen as tantalum nitride, having a high density and low mobility in the tantalum matrix, tends to limit movement of oxygen with respect to the dielectric layer. This can prevent the formation of a sub-oxide which would have a higher electrical leakage than the amorphous tantalum pentoxide layer.

Tantalum oxide is more resistant to sintering than tantalum metal within the normal temperature range. A higher oxygen content in tantalum powder preserves surface area during sintering and results in higher capacitance. The addition of nitrogen to tantalum powder has similar effects, in that surface area is preserved during sintering and specific charge is increased.

Notwithstanding the advantages of doping with nitrogen or oxygen separately, the inventor has discovered that the reaction of a limited range of oxygen and nitrogen with the tantalum base material results in a synergistic effect which



in the manner discussed above for 200 and 400 volt anodization levels.

The following Examples are provided to further clarify the invention and demonstrate the improvements over previous processes for making capacitor grade powder. Those skilled in the art will recognize that the Examples are for illustrative purposes and not for limiting the scope of the invention.

EXAMPLE 1

Over 500 lbs of a base nodular powder was heat treated under vacuum at 1500°C, and crushed down to -40 mesh (hereafter referred to as HTA in the subsequent Examples). 60 lbs of the HTA powder was then blended with 0.9 lbs of magnesium. The blend was placed in a retort, and sealed from the atmosphere. The sealed retort was evacuated with vacuum pump, heated up to 900°C for a period of 3 hours, and cooled to ambient temperature. The powder taken out of the retort was leached with nitric acid and rinsed with water to remove the residual magnesium and magnesium oxide before being air dried at 100°C for 6 hours. The powder was further dried at 180°C for 8 hours.

A sample of this powder was measured for its surface area via a BET method, and oxygen and nitrogen by the procedure discussed below. The results are listed in Table 1.

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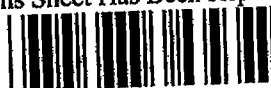
Oxygen and Nitrogen Analysis

The oxygen and nitrogen analysis was made using the Leco TC-30 O₂ and N₂ analyzer which is an inert gas fusion technique.

5 BET Surface Area

The total surface area of the tantalum was measured using a Numinco Orr surface area pore volume analyzer (manufactured by Numec Corporation). The BET (Braunauer-Emmet-Teller) surface areas obtained in this manner include the external surface area as well as the internal surface area contributed by the presence of the pores.

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The powder was leached, dried and tested in accordance with the procedure of Example 1.

EXAMPLE 3

5 The base powder of Example 1 was heat treated at 1500°C, and deoxidized.

EXAMPLE 4

10 The base powder of Example 1 was heat treated, deoxidized, and reacted with nitrogen in accordance with the procedure of Example 2. The procedure for acid leaching, water rinsing, and drying employed in Example 3 were utilized.

EXAMPLE 5

15 120 lbs of base nodular powder was heat treated at 1500°C and crushed to an average particle size of -40 mesh. The powder was then mixed with 1.8 lb of magnesium and sealed in a retort. The retort was then evacuated with a mechanical pump and heated to the reaction temperature as described in Example 1. After reaction, 1500 ppm by weight of nitrogen gas was introduced into the powder retort when the powder was cooled to a temperature of 500°C. The powder and the retort were
20 then cooled to ambient temperature. The cooled powder was acid leached, rinsed with water, and dried using the same procedure as that used in Example 1.

EXAMPLE 6

25 300 grams of the heat treated powder from the batch described in Example 1 were mixed with 3.2 grams of magnesium nitride and 2.2 grams of magnesium. The blended powder was held in a tantalum metal tray which is placed in a retort, and deoxidized. The deoxidized powder was then leached and dried in accordance with the procedure described in Example 1.

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About 5 lbs of dried tantalum base material was introduced into a retort and heated to 500°C. About 13 grams of nitrogen gas was introduced into the retort during the cooling process.

5 The results of Examples 8 through 10 are found below in Table 2.

TABLE 2

	EX 8	EX 9	EX 10
10			
Oxygen, ppm	2440	1922	1900
Nitrogen, ppm	85	2572	4365
BET, m ² /g	0.53	0.44	0.44
15			
CAPACITANCE			
100V anodization			
1425C sinter	23090	24100	23950
1475C sinter	21285	22255	22265
1525C sinter	17651	19381	19510
20			
150V anodization			
1425C sinter	B.D.	17930	17510
1475C sinter	16160	17835	17790
1525C sinter	14195	15745	15985
CURRENT LEAKAGE			
25			
100V anodization			
1425C sinter	1.28	0.53	0.90
1475C sinter	0.50	0.33	0.33
1525C sinter	0.29	0.22	0.22
150V anodization			
30			
1425C sinter	B.D.	6.08	5.85
1475C sinter	7.07	2.84	2.16
1525C sinter	3.61	1.28	0.77

35 Note: "B.D." is defined as the failure point or point of break down of the anode dielectric before the anodization voltage of 150V was reached. The capacitance and leakage can not be measured under this condition.

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EXAMPLE 14

The twice heat treated powder, described in Example 11, was deoxidized and nitrided using the procedure discussed in Example 12, except that the dried powder was dried a second
5 time at 185°C for 6 hours.

TABLE 3

	EX 11	EX 12	EX 13	EX 14
10				
Oxygen, ppm	979	976	1151	1333
Nitrogen, ppm	109	1852	140	1906
BET, m ² /g	0.27	0.29	0.27	0.29
15				
CAPACITANCE (μ F-V/g)				
400V anodization 1700C sinter	5207	5533	5186	5622
CURRENT LEAKAGE (nA/ μ F-V)				
20				
400V anodization 1700C sinter	0.98	0.34	25.09	0.34

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I Claim:

1.. A process for making low leakage capacitors from a base material containing at least one metal powder selected from Group V-B, comprising:

5 reacting a quantity of nitrogen with said base material sufficient to form at least 500 to 7000 ppm by weight of nitrogen in said material,

 reacting a quantity of oxygen with said base material sufficient to form at least 700 to 3000 ppm by weight of
10 oxygen in said material,

 forming pellets from said base material and sintering said pellets at temperatures between 1400°C to 1800°C,

 subjecting said sintered pellets to anodization voltages of 100 volts or greater,

15 forming capacitors from said anodized pellets, and detecting a specific charge of up to about 25,000 uFV/g and improved electrical leakage characteristics.

2. A process in accordance with claim 1 wherein said base material contains at least tantalum metal powder.
20

3. A process in accordance with claim 2 wherein said base material comprises nodular, chip, fiber, and flake powders.

4. A process in accordance with claim 3 wherein said base material is agglomerated at a temperature between about 1200°C
25 to 1600°C.

5. A process in accordance with claim 4 wherein said base material is agglomerated at a temperature between about 1400°C to 1500°C.

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6. A process in accordance with claim 4 wherein said agglomerated material is reduced in size to a powder having a particle size of -40 mesh.
7. A process in accordance with claim 3 wherein said
5 quantity of nitrogen is reacted as nitrogen gas.
8. A process in accordance with claim 3 wherein said quantity of nitrogen is reacted as ammonia gas.
9. A process in accordance with claim 3 wherein said quantity of nitrogen is reacted as magnesium nitride.
- 10 10. A process in accordance with claim 3 wherein said quantity of nitrogen and oxygen are added in the same step.
11. A process in accordance with claim 3 wherein said quantity of oxygen in said base material is limited by a controlling means.
- 15 12. A process in accordance with claim 11 wherein said controlling means comprises the addition of quantities of hydrofluoric acid to said base material.
13. A process in accordance with claim 11 wherein said
controlling means comprises a getter material having a higher
20 affinity for oxygen than tantalum.
14. A process in accordance with claim 13 wherein said getter material is magnesium.
15. A process in accordance with claim 1 wherein said
electrical leakage is reduced by greater than 28% with respect
25 to capacitors formed from said base material.
16. A process in accordance with claim 1 wherein said quantity of nitrogen reacted is between 1400 and 4400 ppm by

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16 reacting a quantity of nitrogen with said agglomerated material sufficient to form between 1400 to 4400 ppm by weight of nitrogen in said material,

5 reacting a quantity of oxygen with said agglomerated material sufficient to form between at least 700 to 3000 ppm by weight of oxygen in said material,

11 reacting a quantity of a reducing metal with oxygen present in said reacted material and forming a quantity of metal oxide,

18 controlling said quantity of metal oxide to a level of between about 950 ppm to 2900 ppm by weight of oxygen in said material,

19 forming pellets from said reacted material and sintering said pellets at temperatures between about 1400°C to 1800°C, subjecting said sintered pellets to anodization voltages of between 150 and 400 volts, and

20 forming capacitors from said anodized pellets having a specific charge of between about 5,100 to about 18,000 uFV/g and electrical leakage which is reduced by greater than 36% with respect to capacitors prepared from said base material.

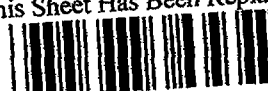
23. A process in accordance with claim 22 wherein said quantity of nitrogen is reacted as nitrogen gas.

24. A process in accordance with claim 22 wherein said quantity of nitrogen is reacted as magnesium nitride.

25. A powder in accordance with claim 22 wherein said quantity of nitrogen is reacted as ammonia gas.

26. A process in accordance with claim 22 wherein said reducing metal is magnesium.

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forming electrodes from said anodized pellets having a specific charge of between about 9,800 to about 15,300 uFV/g and electrical leakage which is reduced by between about 75% to 84% with respect to capacitors prepared from said base material.

30. A tantalum powder for the manufacture of solid capacitors having high specific charge and low electrical leakage characteristics comprising:

- a BET of less than about .6 m²/g,
- an average agglomerated particle size of -40 mesh,
- a quantity of nitrogen in the range of about 500ppm to 7000 ppm by weight nitrogen, and
- a quantity of oxygen in the range of about 700ppm to 3000ppm by weight of oxygen.

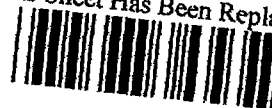
31. A powder in accordance with claim 30 where said powder has a BET value of between about .25 and about .55 m²/g.

32. A process in accordance with claim 30 wherein said quantity of nitrogen reacted is between 1400 and 4400 ppm by weight of nitrogen and said quantity of oxygen is between 950 and 2900 ppm by weight of oxygen.

33. A capacitor produced from the powder of claim 32 wherein said electrical leakage is reduced by greater than 36% at anodization voltages of 150 to 400 volts and said specific charge ranges from 5,100 to 18,000 uFV/g.

34. A capacitor having low electrical leakage characteristics comprising:

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38. A capacitor in accordance with claim 34 which exhibits a specific charge of between 5,500 and 13,200 $\mu\text{FV/g}$ for sintering temperatures of 1400°C to 1700°C.

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