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ACQUEOUS SOLUTIONS OF METALLIC CATIONS SUITABLE FOR THE
FORMATION OF A HIGH- T_c SUPERCONDUCTOR AND CONTAINING
ONE OR MORE NOBLE-METAL CATIONS, PRECURSORS OBTAINABLE
BY DECOMPOSITION OF SAID SOLUTIONS AND COMPOSITES
OBTAINABLE FROM SAID PRECURSORS

The present invention concerns homogeneous aqueous solutions which are obtained from cheap reagents and contain the metallic cations necessary for the formation of a high- T_c -Superconductor and one or more noble-metal cations such as Ag, Au or Pd for example.

The invention also concerns the process for the exsiccating of said solutions and for the decomposition of the organic part, the exsiccates and the precursors prepared in said way and the composites obtained from these.

Superconductors are defined as those systems consisting of metals, alloys or metal compositions usually having no resistivity at very low temperatures. The temperature at which the resistivity of a superconductor becomes zero or reaches at least a minimum value, is defined as critical superconductivity temperature (T_c). The T_c of known superconductors, consisting of special alloys or of intermetallic compounds, ranges from about 10 K to about 25 K; therefore their applications (superconductive wires for the manufacture of magnets; magnetic suspensions; special electronic apparatuses) are possible only using liquid helium as cooling liquid, with all the technological and economic problems connected with said

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use.

More recently, superconductors with higher T_c were obtained, so as to allow the substitution of liquid helium with remarkably less expensive and more easy-to-handle fluids such as liquid nitrogen (b.p. 77 K instead of 4 K of helium). These are systems consisting of complex oxides, for instance yttrium, barium, copper oxides or the like, shortly referred to with the abbreviation "L-M-Cu-O", wherein

10 L = yttrium, lanthanum and lanthanides
 M = barium, strontium, calcium.

Said Y-Ba-Cu-O system turned out to be particularly interesting from the practical point of view.

15 These superconductors, with T_c higher than 90°C, are prepared by finely grinding predetermined amounts of metal compounds, particularly oxides and/or carbonates, and heating the homogeneous mixture of the compounds to temperatures of 800-1000°C in air or
20 oxygen stream.

The so obtained "calcined" product is subjected again to a very fine grinding, then to pressing and forming; a further heating to the above temperature, always in the presence of oxygen, causes the sintering
25 of the superconductive compound.

As already stated, this process requires particularly careful grinding steps in order to impart a very high homogeneity to the superconductor: however the homogeneity is never perfect since it depends not
30 only on the granule size but also on the surface characteristics thereof. Moreover, the prolonged

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heating at high temperature involves an increase in the particle size, with the double effect of impairing the homogeneity, and making the sintering difficult.

In order to overcome said drawbacks and the technological complications connected therewith, several attempts have been carried out, mainly based on the initial use of solutions of soluble compounds of the desired metals, (nitrates, citrates, tartrates and the like) instead of powder mixtures. These solutions are then concentrated to a more or less marked level of anhydrification. The so obtained residue is then subjected to thermal decomposition in oxidizing atmosphere, so as to remove (besides the residual water) the organic carbon; the last process step consists of a calcination of the precursor which is transformed thereby in the actual superconductor.

It is evident that in the initial step the use of solutions provides homogeneity characteristics which cannot otherwise be achieved even by the most careful grinding of solid starting compounds. However, the concentration and decomposition steps involve drawbacks comprising uncontrolled oxidation phenomena (even actual combustions) or of other nature, impairing sometimes irreparably the necessary homogeneity of the desired precursor and limiting in some way the preparation scale because of the difficulty of controlling the phenomenon with amounts of a certain entity.

Proceedings of this kind are reported, for instance, in Powder Technology 7 (1973), 21-38; FR 1.604.707; IT 1.205. 041; J.Am.Ceram.Soc. 70 (12) C-

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375-C-377 (1987); Proc. European Workshop of High T_c Superconductors and Potential Applications, Genoa, Italy (1987), Paper 18; Physica 145B (1987) 222-226.

5 A serious problem in the precursors preparation consists in the difficulty of obtaining actual solutions, i.e. clear and homogeneous solutions containing simultaneously the different metal ions.

10 The use of nitrates as starting materials assures this homogeneity but leads in the decomposition step (or even in the concentration step) to the previously mentioned phenomena of uncontrolled combustion, especially when copper is present [Powder Technology, above cited]. The use of other salts usually involves the above problems of partial insolubility which may be
15 overcome by the contemporaneous use of hydroxypolyacids and glycols producing condensed polymers. The drawback of this process consists in the increase of the carbon content of the solution and in the consequent complication of the oxidative decomposition.

20 Moreover these superconductors as ceramic materials, are intrinsically brittle and thus difficult to work mechanically. The realization of composites noble metal(s) - superconducting oxide is intended to improve the workability of the cited superconductors
25 during the production and the mechanical resistance during the use, due to the pronounced malleability and ductility of the noble metals such as Ag, Au and Pd, which do not impair the superconducting phase even at the above mentioned calcination temperatures.

30 Ag has the advantage of a good permeability for oxygen, which is necessary for the conferring of

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superconducting properties to the final product of YBCO. Namely, it is easier to obtain the right oxygen stoichiometry also for dense and compact materials because of the elevated coefficient of diffusion of oxygen in Ag. The drawback of the low melting point of Ag (960.8°C in air and 939°C in oxygen at 1 atm) can be overcome by alloying Ag with Au or Pd. For every mixing ratio, Ag and Pd form a solid solution whose melting temperature increases with the Pd content.

10 Other purposes of the fabrication of composites are:

a) the protection of the superconductor from chemical agents, particularly those present in the atmosphere such as humidity and CO₂,

15 b) the establishment of a parallel path of high electrical conductivity for the case of local return of the superconductor in the normal state.

According to the traditional techniques, the noble metal is added to the superconductor by a mechanical mixing of powders. For example, powders of Y₂O₃, CuO, BaCO₃ and Ag₂O are mixed together and calcined to obtain composites Ag-YBCO

[C.F.Shen, Mat.Res.Bull., 24, 1231-1239 (1989)]. Otherwise powders of already reacted YBCO and powders of metallic Ag can be mixed [T.Nishio, Y.Itohi et al., J.Mater.Sci., 24, 3228-3234 (1989)]. These techniques generally have the disadvantage of a non optimal interspersion between metal and superconductor and of repeated grindings. From this point of view a wet method which makes use of a solution of the cations of Y, Ba, Cu and the noble metal is certainly preferable

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because it carries out an atomic-scale mixing of the mentioned cations. This elevated level of interspersion is then maintained in the following steps of the treatment up to the final product.

5 Where the primary object of the present invention is concerned, homogeneous aqueous solutions have now been found which contain not only the cations of the kind and in the ratios necessary for the formation of a high- T_c superconducting oxide, but also one or more
10 noble-metal cations such as Ag, Au or Pd. In the following the process for the preparation of these solutions and the process for their concentration and exsiccation, and the oxidative decomposition of the exsiccated product to "precursor" are illustrated.
15 According to the invention, the process includes the following steps:

a) (1) an aqueous solution of an Yttrium salt (solution A), (2) an aqueous solution of a Copper salt (solution B) and (3) an aqueous solution of Barium
20 peroxide or oxide (solution C), all three solutions containing a hydroxypolyacid and ammonia, are mixed;

b) by rapid evaporation the solution obtained in a) is concentrated up to a viscosity of more than 0.2 kg/m*s (200 cps) at 20°C;

25 c) possible addition of an alkaline solution containing Ag (solution D) or other metals which are soluble at the employed pH, and successive re-concentration up to a viscosity of more than 0.2 kg/m*s (200 cps) at 20°C;

30 d) exsiccation at a pressure of less than 0.1 bar up to a weight substantially constant at about 90°C;

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e) possible addition of solutions of Gold salts or of other metals which are soluble at acid pH values, eventually containing a hydroxypolyacid (solution E), followed by exsiccation according to point d) and
5 coarse grinding until the desired granulometry is reached.

In particular, starting from a solution of yttrium acetate (or, respectively, the acetate of a rare-earth metal) and from an aqueous solution of citric acid or
10 of another hydroxypolyacid (in the following we refer synthetically to citric acid; for the extension to other hydroxypolyacids it has to be considered that citric acid is tricarbossilic), a suspension is first prepared at a temperature of less than 60°C and
15 preferably less than 10°C and then added to an ammonia solution with the same temperature prescriptions. The so obtained clear solution (A) is then added to a second solution (C), prepared by dissolving copper acetate and citric acid in water and by adding aqueous
20 ammonium hydroxide with the above temperature prescriptions; a third solution (B) is obtained by dissolving of barium peroxide in an aqueous solution of citric acid and by adding this solution (at less than 60°C and preferably less than 10°C) to aqueous
25 ammonium hydroxide and finally added to the mixture of (A) and (C). The mixing order of A, B and C isn't critical.

The final pH of the solution has to be greater than 7 and conveniently equal to about 10.

30 Naturally the concentrations and the relative quantities of the various solutions are arranged to

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reach the desired ratios of the various metals in the final solution(A+B+C).

According to the present invention, the amount of citric acid used in relation to the metals which are present in the precursor is, as a rule, higher than that of already known techniques. Thus the molar ratio of citric acid to metal ion is 0.5-1.5 for solution A; 0.5-3.0 for solution B and 0.5-1.0 for solution C. Also the ammonium hydroxide is employed in rather high relative amounts, the molar ratio of NH_4OH to metal ion being 2-3 in solution A, 2-4 in solution B and 1-2 in solution C.

The so prepared final solution (A+B+C) is evaporated under vacuum, e.g. in a rotary evaporator heated by means of a bath having a temperature from 80 to 100°C; the pressure is about 15-30 mm Hg and heating is continued until the viscosity of the residue, measured at 20°C, exceeds 0.2 kg/m*s (200 cps). It is important to carry out the concentration step immediately after the preparation of the final solution and absolutely essential before the barium begins to precipitate, which may occur within 12-24 h.

It may be advantageous for the homogeneity of the precursor to add at this point a volatile acid, for example aqueous HCl, to the viscous residue, so as to lower the pH and to allow the formation of $[\text{H}_2\text{citrate}]^-$ instead of $[\text{citrate}]^{3-}$ -anions. (This step can also be carried out later on, as will be specified.)

The addition of the ammoniacal Ag-citrate solution (solution D) can also be conveniently made at this point. In comparison to the direct addition to the

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(A+B+C) solution, there is the advantage of handling more concentrated solutions.

At this point may also be added the solutions of other metals which are soluble in ammoniacal solutions (basic pH) as citrates.

Solution D can be prepared by dissolving AgNO_3 corresponding to the Ag desired in the final product (except a slight excess to compensate the losses in the following steps of precipitation and filtration).

By means of a strong base, e.g. tetramethylammonium hydroxide, in a slight excess in comparison to the stoichiometric amount, Ag_2O precipitates which is filtered and washed directly on the filter with deionized water up to neutrality of the filtrate.

An aqueous solution of citric acid is prepared, with a molar ratio of citric acid to Ag included in the interval 0.2-2.0 and preferably 0.3-1.0. In this solution the fresh precipitate of Ag_2O is dispersed. To the so obtained and ice-cooled suspension cold ammonium hydroxide is added drop by drop until the complete dissolution is obtained.

The so obtained solution (solution D) is added to the concentrated (A+B+C) product, obtaining a perfectly clear solution of a strong blue colour, which is again concentrated in a rotary evaporator.

Another critical step of the proceeding is then started, namely the thermal decomposition of the mentioned residue to give the precursor.

In a first step this residue is heated from room temperature to about 60°C within about 1 hour in a

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vacuum oven (< 0.1 bar) and then to 80-95°C, preferably 90°C, within a further hour and kept at this level for at least 18 hours, preferably 24 hours. The so obtained solid undergoes a coarse grinding (particle size lower than 420-1190 µm), placed again in the mentioned vacuum oven at 90°C and kept at this temperature for at least one day, preferably for four-six days.

Au and other metals which precipitate in alkaline solutions can be added at this point.

In fact it is possible to re-fluidize the exsiccate with a minimum amount of water. The pH of the so obtained product is acid because of the nearly total evaporation of ammonia during the exsiccation. An aqueous solution of auric chloride containing citric acid is added. The content of citric acid in the auric-chloride solution depends on the excess of citric acid in the exsiccate. Hence it can vary from zero to 1.5 moles of citric acid / g-atoms of Au. The so obtained solution is placed in a rotary evaporator and exsiccated in about 40 minutes.

The residue is then heated, at a rate of about 25°C/hour, up to 160-200°C, preferably 170°C, and this temperature is kept for about five-twenty hours. The treatment with the volatile acid may be carried out also during or after the drying step, after treatment of the solid with the minimum amount of water sufficient to obtain a stirrable viscous solution. In this case the drying under vacuum is, of course, repeated after the acidification.

The product of this first step of treatment, a grey-black powdery solid, is ground to a particle size

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of about 50-70 mesh and placed in a gas flow reactor consisting of a glass or quartz cylindrical body with a porous septum at the bottom on which the product is placed and through which gas can flow, said cylindrical
5 body being surrounded by a tubular oven whose temperature, as well as the product temperature, is controlled by means of one or more thermocouples.

The second step is also characterized by a very accurate programming of the heating rate ($^{\circ}\text{C}/\text{hour}$)
10 and the duration of persistence at the various temperature levels. This accuracy is of critical importance for the precursor's characteristics. Similarly critical are the kind of flowing gas, its flow rate relative to the charged amount of product,
15 and the flowing regime of the gas itself. The flow rate, constant over all the thermal treatment, is about $1/10 \text{ SY} - 1/2 \text{ SY ml/minute}$ (measured under normal conditions) where S is the internal section of the reactor, measured in cm^2 , and Y is the amount of solid
20 charged in the reactor, and it is adjusted anyway so as to minimize drag of the powdered precursor. The gas is initially nitrogen, at least for 12 hours at about 200°C .

The gas flow rate may be enhanced significantly by
25 using a downwards gas flow reactor so as to avoid powder drag and to reduce the duration of the decomposition.

After this initial conditioning period, the slow decomposition herein claimed is started, controlled
30 according to two criteria limiting the increase of both the predetermined temperature and of the oxygen percent

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in the flow gas. Said criteria are:

a) the temperature difference between the reactor's internal and the oven, difference (due to reaction heat) which has to be preferably less than 5-
5 10°C; and

b) the oxygen consumption of the precursor, which is preferably less than 1 % of the total flow of oxygen and nitrogen.

To meet these limitations, the temperature is
10 first increased from about 200°C to the settled maximum temperature (of about 360°C) constantly feeding about 1% of ozone-enriched oxygen, then the fed oxygen percent is increased keeping the temperature constant at about 360°C e.g.. Finally there follows at least 24
15 hours at e.g. 360°C in ozone-enriched pure oxygen flow.

At the end of this process the temperature may be further increased up to about 420°C to further decrease the carbon content.

As can be understood from what is above reported,
20 a particularly important feature of the process according to this invention consists in the long heating time, combined with the graduality of the temperature increase. For instance, the oven of the flow reactor is brought from room temperature to 180-
25 220°C, preferably 200°C, within only 2-4 hours; but this temperature is maintained for at least 5 hours, after which the programmed temperature is increased according to the previously mentioned criteria. At any
30 rate the complete operation of this second step takes several days, typically about 200-400 hours depending on the linear velocity of the gas and on the charged

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amount of product.

However, if the gas flow is descendent, the duration of the decomposition may be reduced significantly.

5 The various critical factors just mentioned (overall duration of treatment; increasing rate of the programmed temperature; maximum product temperature; increasing rate of oxygen content) may be reciprocally adjusted within certain limits, provided that the
10 maximum temperature of the precursor does not exceed 380-420°C; the overall duration of the treatment in the gas-flow reactor should not be shorter than 40-50 hours; the oxygen percent should be kept at very low values (i.e. less than 3% by volume) for at least three
15 quarters of the overall heating time.

 As has already been mentioned, the oxygen can contain (for all the duration of the treatment and for temperatures lower than 260-360°C) a certain amount of ozone. This amount suitably ranges from 0.5 to 5.0 %
20 (v/v) with respect to the oxygen.

 The precursors obtained at the end of this treatment have low cristallinity, are relatively homogeneous with a carbon content preferably lower than 4 % (b.w.), and can be transformed in composited
25 superconductors with the above specified advantages.

 It is possible in this way to obtain superconductors which are much more satisfactory from the cristallographic point of view and which have a considerable higher critical current intensity.

30 These superconductors can also be obtained as films by deposition of the solutions directly on

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substrates and following exsiccation, decomposition of the organic part and calcination at high temperatures. A specific advantage of the precursors containing Ag and other noble metals is the possibility of obtaining superconductors containing alloys with a higher fusion point than Ag (>930°C).

The manufacturing process according to the invention is illustrated by the following example, which is, nevertheless, not limiting.

10 **PREPARATION OF YBCO PRECURSOR WITH (a) 10% OF SILVER,
(b) 1.95% OF GOLD**

Reagent

	Yttrium Acetate, Y(CH ₃ COO) ₃ nH ₂ O	M.W.=335.7	99.9% Ventron
15	Copper Acetate, Cu(CH ₃ COO) ₂ H ₂ O	M.W.=199.65	99% CARLO ERBA
	Citric Acid, C ₆ H ₈ O ₇ H ₂ O	M.W.=210.14	99.8% CARLO ERBA
20	Barium Peroxide, BaO ₂	M.W.=169.34	95% Fluka
	Ammonium Hydroxide, NH ₄ OH	M.W.=35.04	30.04±2% CARLO ERBA
	Silver Nitrate, AgNO ₃	M.W.=169.88	MP
25	Tetramethylammonium Hydroxide, N(CH ₃) ₄ OH	M.W.=91.15	10% MERCK
	Auric Chloride, AuCl ₃	M.W.=303.33	K&K

Preparation of the solutions:

30 **(Y):** 34.12 g of yttrium acetate are poured into 200 ml of H₂O and the mixture is heated to 90°C

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obtaining a colourless and transparent solution (A). 23.52 g of citric acid are separately dissolved in 200 ml of H₂O. This solution is added to the previous, ice-cooled solution A, obtaining a milky emulsion (B). 39.6
5 ml of ammonium hydroxide are cooled in an ice-bath and emulsion B is added thereto. A colourless and transparent solution is obtained.

(Ba): 34.498 g of barium peroxide are added under strong stirring and at room temperature to a solution
10 obtained by dissolving 88.0 g of citric acid in 360 ml of H₂O (solution D). 80 ml of ammonium hydroxide are cooled in an ice-bath and the barium solution (D) is added thereto. A colourless solution is obtained, opalescent, because of a slight gas bubble development.

15 (Cu): 61.0 g of copper acetate are dissolved in 150 ml of H₂O at room temperature together with 46.7 g of citric acid. The solution is ice-cooled after dissolution and 72.6 ml of ammonium hydroxide are added to give a transparent solution of intense blue colour.

20 (Ag): 11.873 g of AgNO₃ are dissolved in 40 ml of H₂O. 70 ml of N(CH₃)₄OH (10%) are added. Ag₂O precipitates which must be washed on a filter until neutral pH of the filtered water. 5.4 g of citric acid are dissolved in 200 ml of H₂O. Thereto Ag₂O is added.
25 The resulting suspension is ice-cooled and 80 ml of previously cooled ammonium hydroxide are added.

(Au): 2.084 g of auric chloride are added to 30 ml of H₂O.

Preparation of the exsiccated YBCO-precursor.

30 In an ice-bath the yttrium-containing solution and then, with caution, the barium-containing solution are

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added to the solution containing copper. The waters used for washing of the beakers is added. The total volume is about 1600 ml.

5 The final solution is then placed into a rotary evaporator at a temperature between 80 and 100°C and exsiccated under vacuum in about 50 minutes, until a homogeneous product with viscosity higher than 0.2 kg/m*s (200cps) is obtained. During this operation the colour turns from dark blue to dark green.

10 (a) (silver composite): To the exsiccated residue the silver solution is added under stirring until a solution of dark blue colour is obtained. Again the solution is placed into the rotary evaporator for the final exsiccation.

15 The residue is heated from room temperature to 90°C within one hour under vacuum ($P=13.3\div 1.33$ Pa) and mantained at this level for one day. The so obtained solid is subjected to a coarse grinding (up to a grain size lower than 420-1190 μm).

20 (b) (gold composite): The residue is heated from room temperature to 90°C within one hour under vacuum ($P=13.3\div 1.33$ Pa) and mantained at this level for one day. The so obtained solid is subjected to a coarse grinding (up to a grain size lower than 420-1190 μm).

25 At this point, due to the reversibility of the exsiccation, the residue can be re-fluidized in about 120 ml of water, using a 500 ml glass balloon, heating to 50-60°C up to complete dissolution. After this the viscous solution is cooled to 40°C (better 25°C) in an

30 ice-bath. Finally a solution of 2.084 g of auric chloride in 30 ml of water is added. The so obtained

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solution is immediately placed in the rotary evaporator and exsiccated in about 40 minutes. The temperature must not exceed 40-60°C.

Thermal decomposition of the amorphous dried precursor.

5 The first step of the decomposition is carried out in a vacuum oven. After a treatment at 90°C for about 48h a coarse grinding is carried out. The product is then heated first to 90°C with a rate of 45°C/h and then to 170°C with a rate of 15°C/h; the heating
10 duration at 170°C is 7h.

 When this treatment is over, the product, in form of a grey-black pulverulent solid, is transferred in a glass- or quartz flow reactor provided with a porous septum. The temperature program and the composition of
15 the gaseous feed are reported in the following table.

TABLE (a)

Decomposition of Ag-composite

total gas flow: 5000 ml/min

ozonized oxygen

Time (h)	Temperature (°C)	%O ₂	Operations
0	20	0	start increase 90°C/h
2	200	0	constant 200°C
14	200	0	start increase 15°C/h
25			O ₂ adjusted to 1%
20	290	1	constant 290°C
140	290	1	O ₂ adjusted to 1.5%
152	290	1.5	O ₂ adjusted to 2%
200	290	2	O ₂ adjusted to 3%
30	250	3	O ₂ adjusted to 7.5%
256	290	7.5	O ₂ adjusted to 10%

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262	290	10	O ₂ adjusted to 20%
265	290	20	O ₂ adjusted to 50%
290	290	50	O ₂ adjusted to 100%
320	290	100	end of activation

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TABLE (b)

Decomposition of Au-composite
total gas flow: 800 ml/min
ozonized oxygen

	<u>Time (h)</u>	<u>Temperature (°C)</u>	<u>%O₂</u>	<u>Operations</u>
	0	20	0	start increase 90°C/h
	2	200	0	constant 200°C
	19	200	0	start increase 15°C/h O ₂ adjusted to 1%
15	24	280	1	constant 280°C
	43	280	1	start increase 60°C/h
	44	300	1	constant 300°C
	51	300	1	start increase 60°C/h
	51	305	1	constant 305°C
20	169	310	1	start increase 60°C/h
	169	310	1	constant 310°C
	186	310	1	start increase 30°C/h
	186	320	1	constant 320°C
	195	320	1	start increase 30°C/h
25	195	330	1	constant 330°C
	210	330	1	start increase 60°C/h
	211	360	1	constant 360°C
	213	360	1	O ₂ adjusted to 2%
	214	360	2	O ₂ adjusted to 4%
30	215	360	4	O ₂ adjusted to 8%
	216	360	8	O ₂ adjusted to 16%

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217	360	16	O ₂ adjusted to 32%
218	360	32	O ₂ adjusted to 64%
219	360	64	O ₂ adjusted to 100%
282	360	100	end of activation

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CLAIMS

1. Homogeneous aqueous solutions of the metal cations of the kind and in the proportions required for the formation of a high- T_c superconducting oxide and containing one or more metallic cations like Ag, Au or Pd, and exsiccated products obtained from therefrom.
2. Method for the preparation of the above mentioned solutions and exsiccates, characterized in that:
 - a) there are mixed: (1) an aqueous solution of an yttrium salt containing a hydroxypolyacid and ammonia (solution A); (2) an aqueous solution of a copper salt containing a hydroxypolyacid and ammonia (solution B) and (3) an aqueous solution of barium peroxide or oxide containing a hydroxypolyacid and ammonia
 - b) the solution obtained in a) is rapidly concentrated by evaporation up to a viscosity of more than 0.2 kg/m*s (200 cps) at 20°C;
 - c) optional addition of an alkaline solution containing Ag (solution D) or other metals which are soluble at the employed pH, and successive re-concentration up to a viscosity of more than 0.2 kg/m*s (200 cps) at 20°C;
 - d) exsiccation at a pressure of less than 0.1 bar up to a substantially constant weight at about 90°C;
 - e) optional addition of solutions of Gold salts or of other metals which are soluble at acid pH values, containing if necessary a hydroxypolyacid (solution E), followed by exsiccation according to point d) and coarse grinding until the desired granulometry is

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reached.

3. A process according to the previous claim, wherein the exsiccation step preceeding the final grinding is carried out at a temperature of about 170°C.

5 4. A process according to claims 2 or 3, wherein the ratio of moles of citric acid to g-atoms of metallic ion is 0.5-1.5 for solution A, 0.5-3.0 for solution B, 0.5-1.0 for solution C, 0.2-2.0 for solution D and 0-1.5 for solution E.

10 5. A process according to any one of claims 2-4, wherein the ratio of moles of ammonium hydroxide to g-atoms of metal ions is 2-3 in solution A, 2-4 in solution B, 1-2 in solution C and the amount necessary for complete dissolution in solution D.

15 6. A process according to any one of claims 2-5, wherein the mixing of the various solutions during the preparation of solutions A, B and C is carried out at a temperature not higher than 10°C.

20 7. A process according to any one of claims 2-6, wherein in step d) the solid after grinding (particle size less than 420-1190 μm) is heated under vacuum for 4-6 days.

8. Precursors of superconducting composites obtainable by exsiccation of the solutions of claim 1.

25 9. A process for the decomposition of the organic part of the above mentioned exsiccates, wherein the product of step e), ground to a particle size of less than 250-177 μm , is heated in a gas-flow reactor for at least 12 hours while a nitrogen flow passes through the product itself; then 0.5-3.0% (b.v.) of oxygen, 30 eventually enriched with ozone, are added to the

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nitrogen, and the temperature is slowly increased up to about 360°C, keeping the temperature difference between the reactor's internal and the oven lower than 10°C and the oxygen consumption lower than 1% of the total gas flow; when the oxygen content of the output stream returns to values close to those of the input stream the oxygen feed (containing eventually ozone) is gradually increased up to 100% of the total gas flow keeping the temperature constant at about 360°C; at the end there follows at least 24 hours at 360°C in that gas flow.

10 10. A process according to claim 9 wherein 1% (b.v.) of oxygen is added to the nitrogen at the beginning of the decomposition.

15 11. A process according to claim 9 wherein the oxygen introduced in the gas flow contains from 0.5 to 10% (b.v.) of ozone for at least a part of the treatment.

20 12. Films of various thicknesses obtained from the mentioned solutions by deposition on a suitable substrate and following decomposition of the organic part.

13. Superconducting composites and artifacts obtainable from the precursors of claim 7.

25 14. Superconducting composites and artifacts according to claim 13, wherein the metal alloy melts at $T > 930^\circ\text{C}$.

INTERNATIONAL SEARCH REPORT

PCT/EP 91/02404

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 Int.Cl. 5 H01L39/24; C04B35/00

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl. 5	H01L

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US,A,4 971 944 (WESTINGHOUSE) 20 November 1990 see column 3, line 40 - column 4, line 6; claims 1-4	1
A	--- JOURNAL OF THE CERAMIC SOCIETY OF JAPAN vol. 98, no. 7, July 1990, TOKYO, JP pages 96 - 102; UMEDA T. ET AL: 'Thermal Decomposition of Metal Acetate Gel as a Precursor of YBa ₂ Cu ₃ O _{7-y} Superconductor' see page 96, paragraph 5 see page 99, paragraph 4 -paragraph 6 see page 101, paragraph 6 -paragraph 7 --- -/--	2,4-5

° Special categories of cited documents :¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

21 FEBRUARY 1992

Date of Mailing of this International Search Report

27.02.92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

HAMMEL E.J.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		Relevant to Claim No.
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	
A	NIPPON SERAMIKKUSU KYOKAI GAKUJUTSU RONBUNSHI vol. 96, no. 6, June 1988, TOKYO, JP pages 710 - 713; NASU, H. ET AL: 'High Tc superconducting Ba ₂ YCu ₃ O _x films prepared by pyrolysis of organic or inorganic acid salts' see page 710, paragraph 2 ---	2,12-13
A	EP,A,0 308 338 (RHONE-POULENC CHIMIE) 22 March 1989 see claims 1-18 ---	2

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. EP 9102404
SA 54061**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 21/02/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4971944	20-11-90	JP-A- 2247385	03-10-90

EP-A-0308338	22-03-89	FR-A- 2620866	24-03-89
		AU-A- 2223388	23-03-89
		JP-A- 1122924	16-05-89
