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A CHEMICAL PRECIPITATION METHOD FOR THE PRODUCTION OF A HOMOGENEOUS, HIGH PURITY POWDER APPLICABLE TO THE LEAD ZIRCONATE TITANATE SOLID-SOLUTION SERIES

by

V. M. McNAMARA & W. A. GOW

EXTRACTION METALLURGY DIVISION

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V. M. McNamara[*] and W. A. Gow[**]

SUMMARY OF RESULTS

A chemical precipitation method has been developed for application to the production of dry powders of mixed lead, zirconium and titanium hydroxides. The method involves neutralization of an acidic nitrate solution of the metals, followed by the filtration, washing and drying of the precipitate. The purity and homogeneity of the precipitate has indicated its chemical suitability for use as a feed powder for the calcining, milling, fabrication and sintering steps which are necessary in the formation of the piezoelectric ceramic, lead zirconate-lead titanate. Investigation of the electrical properties of the sintered material, fabricated in the form of wafers, will establish the degree of merit of this approach to the production of a high purity source powder for this specialized ceramic industry.

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INTRODUCTION

Stoichiometric mixtures of the oxides of lead, zirconium and titanium will yield, upon sintering, a solid-solution series, $PbZrO_3$-$PbTiO_3$. Within this series there exists a range of compositions that, when fabricated and fired (at 1150 to 1250°C) as ceramic bodies, will exhibit the piezoelectric properties required in transducer applications. The ceramic feed material must be better than 99.95 per cent pure, homogeneous, and of uniformly small particle size (the order of 0.5 to 1μ). Any compromise in these requirements interferes with the sintered ceramic density and with such electrical properties as the dielectric constant, planar coupling coefficient and hysteresis loop characteristics. The most promising composition range appears to be from 55/45 to 50/50 molar ratio $PbZrO_3$/$PbTiO_3$. The impurity which is considered to be the most difficult to eliminate from these products is silica.

Research carried out within the Mines Branch prior to the present work was concerned with the mixing and comminution of fine powders of PbO, ZrO_2 and TiO_2, all reagent grade chemicals. These mixtures were subsequently calcined ($\approx$800°C), pressed in the form of pellets or wafers and sintered to ceramic bodies. It is possible to obtain lead zirconate-lead titanate electronic ceramic commercially, this material similarly prepared from oxide mixtures. However, existing methods of preparation have not produced a material that exhibits to a sufficient degree the electrical characteristics required of ceramic bodies intended for use in the fabrication of transducers.

Mr. I.F. Wright is coordinator of the Mines Branch effort directed toward the Defense Research Board Project No. D-108-55-25-02. The aim of this project is the development of a chemical process for quantity production of electronic ceramic powders purer and more uniform than those available commercially, and of closely controlled composition. It is hoped that the electrical properties of ceramic bodies produced from such powders would be superior. This report covers the development of a promising chemical method to produce such superior powders which involves the co-precipitation of lead, titanium and zirconium from a nitrate solution of the desired stoichiometry. The evaluation of the ceramic bodies made from these powders is not part of this report.

In the present work chemically pure reagents were used as source chemicals. Inconsistency in the source materials may be undesirable and it may become necessary in the future to obtain more uniform raw materials of extreme purity. However, the emphasis in this work has been on obtaining reasonable purity, homogeneity and controlled composition for the product. Some workers spectrographically analyse raw materials, apply weight corrections and assume that weight ratios are satisfactory

evidence of product stoichiometry. In this project wet methods of chemical analysis were utilized to a considerable extent to control the composition of the precipitation feed and to determine the stoichiometry of the final product.

The Mineral Sciences Division and the Mineral Processing Division are responsible for evaluating the sintering of electrical properties of the dried mixed-hydroxide precipitate powders produced in this work. Dr. A.H. Webster of the Mineral Sciences Division has reported(1) on the sintering characteristics of a portion of the first group of chemically precipitated powders.

The present report covers the preliminary laboratory investigations and constitutes the basis for a planned pilot plant study. The Analytical Section is continuing work directed to the development of analytical procedures for adequate control of the operation.

EXPERIMENTAL PROCEDURE

Source Chemicals

The chemical preparations initially involved the use of relatively pure metal oxides of Pb^{2+}, Zr^{4+} and Ti^{4+}. They were reagent grade PbO, ZrO_2 and TiO_2. Subsequently, salts of the metals were used. The salts are specified in Table 1. They were "purified" compounds that were relatively inexpensive. Also tabulated are the semi-quantitative spectrographic analyses of all the source chemicals.

Figure 1 outlines the procedures employed to bring the source chemicals into solution, blend them into a high purity composite nitrate feed solution, precipitate the metals and finally filter, wash, dry and mortar the precipitate to a powder. It is shown that PbO, $PbCO_3$, $TiCl_4$ and $ZrOCl_2 \cdot 8H_2O$ were readily taken into solution. The TiO_2 and ZrO_2 required a combined fusion with $K_2S_2O_7$ to become acid soluble. The $Ti(SO_4)_2 \cdot 9H_2O$ could only be dissolved, very slowly, in hot concentrated H_2SO_4 (50 per cent w/w). However, it was discovered after some experimenting that if the titanium sulphate nonahydrate, which is very lumpy, is crushed fine and heated at 150°C for 2-3 hr, it becomes readily soluble in dilute (10 per cent) sulphuric acid.

Preparation of the Feed Solution

The oxides, or salts, of Zr and Ti were taken into appropriate solution, clarified, and precipitated as the hydroxide by the addition of aqueous ammonia to pH 7. The precipitates were washed free of all traces of soluble salts by successive decantations and dilutions with ammonia water

TABLE i

Semi-Quantitative Spectrographic Analyses[*]

Impurities in Starting Materials for Hydroxide Precipitation Process

Chemical	Source	Elements, %											
		Si	Mg	Ca	Al	Fe	Bi	Cu	Nb	Ni	Mn	Na	Ag
PbO	Fisher certified reagent	Tr	Tr	ND	ND	0.02	0.02	0.002	ND	--	--	--	0.0008
ZrO_2	Fisher laboratory chem. purified	0.4	0.03	0.4	0.1	Tr	ND	ND	ND	--	--	--	ND
TiO_2	Baker's analyzed CP reagent	0.3	0.03	ND	0.3	Tr	ND	ND	0.08	--	--	--	ND
$PbCO_3$	Fisher certified reagent	Tr	0.02	0.02	Tr	0.01	0.03	Tr	--	ND	Tr	Tr	--
$ZrOCl_2 \cdot 8H_2O$	National Lead Co. TAM (bulk) high purity grade	0.05	0.007	ND	0.005	0.02	ND	Tr	--	0.009	ND	ND	--
$Ti(SO_4)_2 \cdot 9H_2O$	Fisher laboratory chem. purified	0.05	0.02	0.02	0.004	0.02	ND	Tr	--	0.007	Tr	ND	--
$TiCl_4$ (liq)	Fisher laboratory chem. purified	--------not analyzed--------											

Tr = Trace
ND = Not detected

[*]by spectrographic laboratory, Mineral Sciences Division

PbO
or
PbCO₃

(1) PbO   2) PbCO₃

5g. of 15%   3g. of 15%
$^w/_w$ HNO₃ $^w/_w$ HNO₃
per gram Pb   per gram Pb

CLARIFY

TiO₂
+
ZrO₂

K₂S₂O₇
8g. per gram   fusion in
combined   platinum
oxides

K₂ZrO₃
K₂TiO₃

5Dg. of 10% $^w/_w$
HNO₃/ g(Ti,Zr)O₂

CLARIFY

Zr (NO₃)₄
Ti (NO₃)₄

NH₄OH (12 ml/g (Ti,Zr) O₂)

FILTER   WASH

ZrO₂·X H₂O
TiO₂·X H₂O

HNO₃
22g 20% $^w/_w$
per g(Ti,Zr)O₂
CLARIFY

Ti (SO₄)₂ · 9 H₂O

(I) Crush and   2) H₂SO₄
dry at 150°C   (50% $^w/_w$)
for 2-3 hours   3.3 g/g salt
Dissolve in 3g   HEAT
of 10% $^w/_w$
H₂SO₄/g salt

Ti(SO₄)₂
Sol'n

NH₄OH
(5.2 mL/g. Ti(SO₄)₂·9H₂O)

FILTER
WASH SO₄²⁻ free

≈ [20 g/l Zr
10 g/l Ti]
SOLUTION OF
Zr (NO₃)₄
Ti (NO₃)₄

TiCl₄ (Liq)

Slowly add to 2% $^w/_w$ HCl
(5 mL. 2% HCl/ml. TiCl₄)

Stir and Cool

TiCl₄ Sol'n
DILUTE 25 FOLD

NH₄OH   (2.8 ml/ml TiCl₄)
FILTER   WASH Cl⁻ free

TiO₂·x H₂O

15% $^w/_w$ HNO₃ — cold (15°C)
(42 g/g TiO₂)   Dilute to
≈ 1½ g/l Ti

SOLUTION OF
Ti (NO₃)₄
Zr (NO₃)₄

ZrOCl₂ · 8 H₂O

Water   3.4 g/g salt

ZrOCl₂ Sol'n

NH₄OH (0.6 ml/g salt)
FILTER   WASH Cl⁻ free

ZrO₂·x H₂O

HNO₃ (30% $^w/_w$) 6.5 g/g ZrO₂
Dilute 3 fold

≈ 40 g/l Zr

CLARIFY

CLARIFY

Pb(NO₃)₂
Sol'n

> 200 g/l Pb

Ti sol'n should be stored as Pb–Zr–Ti
composite nitrate sol'n to prevent hydrolysis of
the titanium. Ti(NO₃)₄ sol'n. required for
stoichiometric adjustment should be < ½ g/l Ti

Stoichiometric   Composite
Precipitation   Feed Sol'n

[Approx. sol'n content
Pb : 10 – 25   g/l
Zr : 2 – 6,   g/l
Ti : 1 – 2½   g/l
NO₃ : 40 – 50   g/l
pH ≈ 0.2 – 0.6]

Sol'n of Pb (NO₃)₂ +
Zr(NO₃)₄ + Ti (NO₃)₄

(NH₄)₂CO₃ to pH6
NH₄OH to pH 7
45° – 60°C

NH₃: N₂   50° – 60°C
at pH 8   Consumed 0.55g NH₃ gas
per g. pure, dry mixed
oxides of Pb, Zr, Ti.

H₂C₂O₄
60°C

BASIC Pb CARBONATE
ZrO₂ · x H₂O
TiO₂ · x H₂O

BASIC Pb NITRATES+
Pb HYDROXIDE·
ZrO₂ · x H₂O
TiO₂ · x H₂O

Investigate Possibility
of obtaining Pb oxalate+
Titanyl and Zirconyl
Oxalate Complexes

FILTER   WASH

SLURRY (free of soluble nitrate)

FILTER   THOROUGH WASH

DRY 110°C
CRUMBLES READILY

DRY 110°C
OR
Vac.(29" Water) Ambient

GRIND CAKE
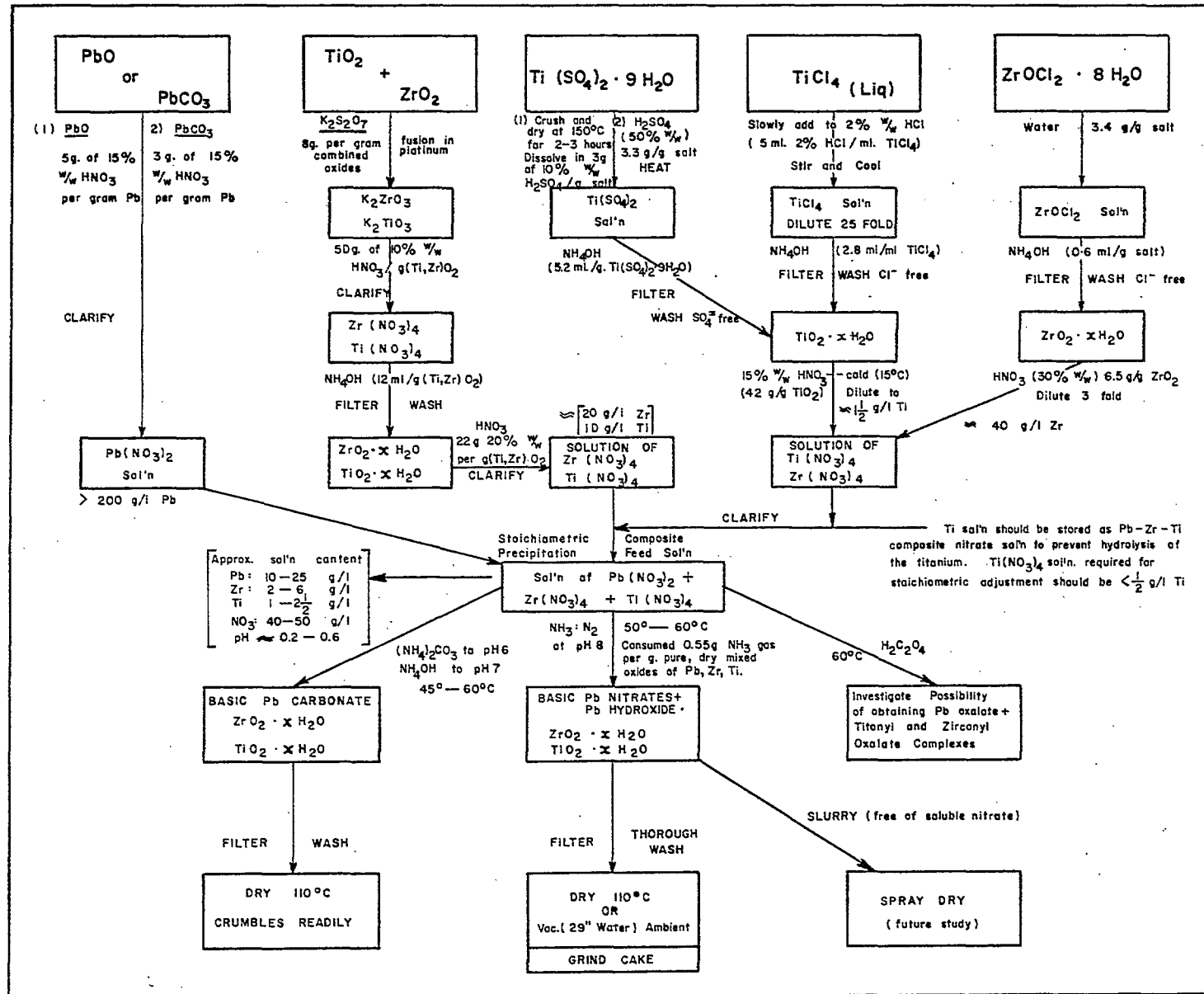
SPRAY DRY
(future study)

FIGURE I

GENERAL METHODS: PRODUCTION OF DRY POWDER FEED FOR FABRICATION
OF THE PIEZOELECTRIC CERAMIC PbZrO₃ — PbTiO₃

(pH 8), followed by filtration on a Buchner filter and final washing of the cake with ammonia water. Separan (0.05 per cent w/w aq. soln) was titrated into each slurry in just sufficient amount to give rapid settling for decantation. A precipitation slurry must contain less than 10 per cent soluble salts if settling is to be efficient. For wash slurries some salt (about 0.3 g/l NH_4NO_3) was required in the ammonia water, along with Separan, to ensure satisfactory settling. Thorough washing of all hydroxide precipitates was required to free them from the soluble contaminants (e.g. SO_4, Cl, K). Testing of wash solution for SO_4 and Cl ions was carried out to indicate when washing of the precipitates was complete. The precipitates were then redissolved in HNO_3, diluted, clarified and combined with filtered $Pb(NO_3)_2$ solution, which was obtained from the dissolution of PbO or $PbCO_3$ in nitric acid solution.

The treatment just described allowed the removal of a certain amount of impurity (particularly silica) from the nitrate solutions by filtration. It is also possible that traces of silica and other undesirable elements may have been discarded in the barren sulphate and chloride solutions. The procedure employed to obtain nitrate solutions of Pb, Zr and Ti are not, however, intended as purification steps. The objective was to obtain metal nitrate solutions, free of SO_4 and Cl, for compositing as precipitation feed solution. The block diagram (Figure 1) indicates the least difficult route to these nitrate solutions and any purification achieved is incidental.

It was not necessary to maintain specific metal concentrations in solution. Minimum quantities of nitric acid were used to dissolve the PbO or $PbCO_3$, as well as the zirconium and titanium hydroxide precipitates. The volumes of stock solutions of the lead and zirconium nitrates were relatively small for facility in handling and storing. This caused no problems at any concentrations below saturation. When titanyl nitrate solution was prepared, the concentration of the Ti was adjusted to less than 1.5 g/l and further, major portions ($\approx$ 80 per cent) of the stoichiometric requirement of lead and zirconium nitrate solutions were added. These precautions were necessary to prevent hydrolysis of the titanium in dilute nitric acid solutions (pH $\approx$ 0.1 to 0.5). A quantity of titanyl nitrate solution was stored to allow for final Ti adjustment of the analysed composite feed solution. This titanium solution was adjusted to less than 0.5 g/l Ti to extend the interval of usefulness prior to titanium hydrolysis.

The final composite feed solution preparation required precise blending of the metal nitrate solutions. Therefore accurate analyses of all solutions are considered necessary in this method. The composite solution was diluted to the maximum volume that could be accommodated in the batch reaction vessel in which the mixed hydroxides were to be precipitated. Such dilution would limit the occlusion of impurites that might tend to co-precipitate with the hydroxides and would also enhance opportunities for displacing soluble nitrate and combined nitrate from the precipitate, as will be discussed later. A typical composite precipitation feed solution, based

on 500 g of mixed dry oxides of Pb, Zr and Ti, was 14 litres analyzing 22.7 g/l Pb, 5.42 g/l Zr, 2.42 g/l Ti and 50.5 g/l total NO_3. This particular solution can be calculated as 54.1 moles per cent $PbZrO_3$ and 45.9 moles per cent $PbTiO_3$.

Precipitation Methods

Three precipitation methods were considered as possible routes to the production of finely-divided, homogeneously mixed compositions of Pb, Zr and Ti which would be suitable for fabrication and firing as ceramic material. It was considered advantageous to completely precipitate the metals from solution, thus discarding "barren" solution containing no appreciable metal values. The methods were:

(a) Rapid neutralization of the composite nitrate feed solution with ammonia. The metals were precipitated as gelatinous mixed hydroxides and were considered to be intimately blended in the slurry. This method is the simplest and most promising and is the main consideration of this report.

(b) First, adjustment of the composite nitrate solution pH to a value just below the point at which a precipitate first appears. Secondly, precipitation of basic lead carbonate by addition of ammonium carbonate, followed by rapid neutralization with ammonia to pH 7 to complete the precipitation of Zr and Ti as hydroxides. Advantages of this more complicated procedure are:

(i) The carbonate-containing precipitate filtered and washed readily, whereas the gelatinous precipitates of method (a) were tedious to handle.

(ii) The precipitate dries to an excellent, crumbly texture. The gelatinous precipitates of method (a) normally dry as hard, brittle cakes.

(c) Precipitation of mixed oxalate-hydroxides mixtures by the addition of ammonium oxalate as precipitant. This method has not, thus far, accomplished complete precipitation of the metals from solution. Stoichoimetric dry powders were not obtained so this approach was abandoned.

Precipitation Variables

There are a number of variables involved in the production of homogeneous mixed precipitates. To completely study the range of variables would be too time-consuming. Therefore assumptions were made based upon

previous experience with precipitates of various metals. The variables are:

1. Concentrations of components in the precipitation feed solution. The hydroxide precipitation method involved complete precipitation of the metals so this variable is of minor importance. The metal concentrations were kept low for reasons discussed elsewhere in the report. Free nitric acid was maintained at a near-minimum value required for a clear solution.

2. Concentration of the precipitant. Hydroxide precipitation was best accomplished by using ammonia gas since it is easy to control the flow and there is a minimum loss of NH_3. The dilution of the ammonia by N_2 gas was known to give better filtering characteristics to the precipitate, that is, filtration was more rapid since the precipitate was less gelatinous. The gas dilution range that has been most effective in this type of precipitation was from 2:1 NH_3/N_2 to 1:2 NH_3/N_2.

3. Precipitation pH. This value should be greater than 7 but less than 8.2 for precipitation by ammonia. If carbonates are present then the maximum pH value should be 7 so as to limit the solubility of Zr and Ti in carbonate solution.

4. Temperature. It is known that a temperature between 50°C and 60°C is most favourable for ammonia precipitation methods in which excessive ammonia atmosphere is not desirable.

5. Excess of precipitant over theoretical requirements. This variable is applicable to more complicated procedures, such as the oxalate precipitation method, where more than pH control is required.

6. Rates of addition of reactants. To ensure homogeneity in the mixed hydroxide precipitate it was decided to combine ammonia and feed solution in such a manner that neutralization of the feed solution (pH 8) would occur instantaneously. Flow rates were adjusted to allow a batch run to be completed in one working day.

7. Total reaction time. This involves contact time in the precipitation vessel and digestion time in contact with barren solution or other media.

8. Method of contacting feed solution and precipitant in precipitation vessel
    (a) each dropwise, as liquids
    (b) feed solution sprayed, ammonia dropwise
    (c) feed solution sprayed, ammonia as gas.
    The method (c) is most promising.

9. Molar ratios of major components, $PbO.ZrO_2$ and $PbO.TiO_2$. Of particular interest is the range 50/50 $PbO.ZrO_2$/$PbO.TiO_2$ (molar ratio) to 60/40 molar ratio. A brief investigation of the region 60/40 to 70/30 molar ratio will be carried out.

10. Doping of the major constituents with minor constituents to enhance or modify the piezoelectric properties. Minor constituents would be of the order of 1 per cent or less and could include Fe, Cr, Sr, Ta, Ce, Ni, or Nb. Co-precipitation techniques may be required.

11. Precipitate washing techniques.

    1. Filtration -- wash filter cake.
    2. Decantation washing -- filter.
    3. Decantation washing -- spray dry.

12. Precipitate drying.

    1. Filter cake dried at 110°C.
    2. " " " " ambient temp under vacuum (30" water).
    3. " " " " 30-50°C " " "
    4. Spray drying of precipitate slurry.

Batch Method for Mixed Hydroxide Precipitation

The most promising method for precipitation of the mixed hydroxides of Pb, Zr and Ti involved spraying of the nitrate feed solution onto the surface of a thoroughly agitated bulk solution which was maintained at pH 8 by the injection of ammonia gas. The temperature of the bulk solution was held at some desired value, usually 55-60°C, by the use of external steam coils. Figure 2 shows the equipment employed for tests which involved the production of 400-500 grams (dry basis) of precipitate. It consists of a polyethylene precipitation tank, impeller, pH electrodes, gas sparging tube, thermometer, heating coils, steel outer tank and feed solution spray nozzle. The spray nozzle consisted of 3 drawn glass tips; the center one for the metered flow of feed; the two outer nozzles for compressed air jets which atomized the feed stream and directed the spray onto the surface of the bulk solution. The spray head unit was adjustable so that it could be positioned 3 or 4" above the solution. The spray pattern striking the surface is circular, about 3" in diameter. In this manner very fine droplets of acid feed solution (pH ≈ 0.5) were instantly neutralized on striking the surface of the agitated bulk liquid (pH 8). Each precipitated particle would therefore consist of the desired proportions of the three metal hydroxides. Locallized pH variations at the surface of the bulk liquid were negligible. The nitrate solution feed rate was 60 ml/min, requiring approximately 1000 cc NH_3 gas per minute to stabilize the bulk solution at pH 8. Nitrogen gas was blended into the ammonia gas stream in a 1:1 volume ratio for the following reasons:
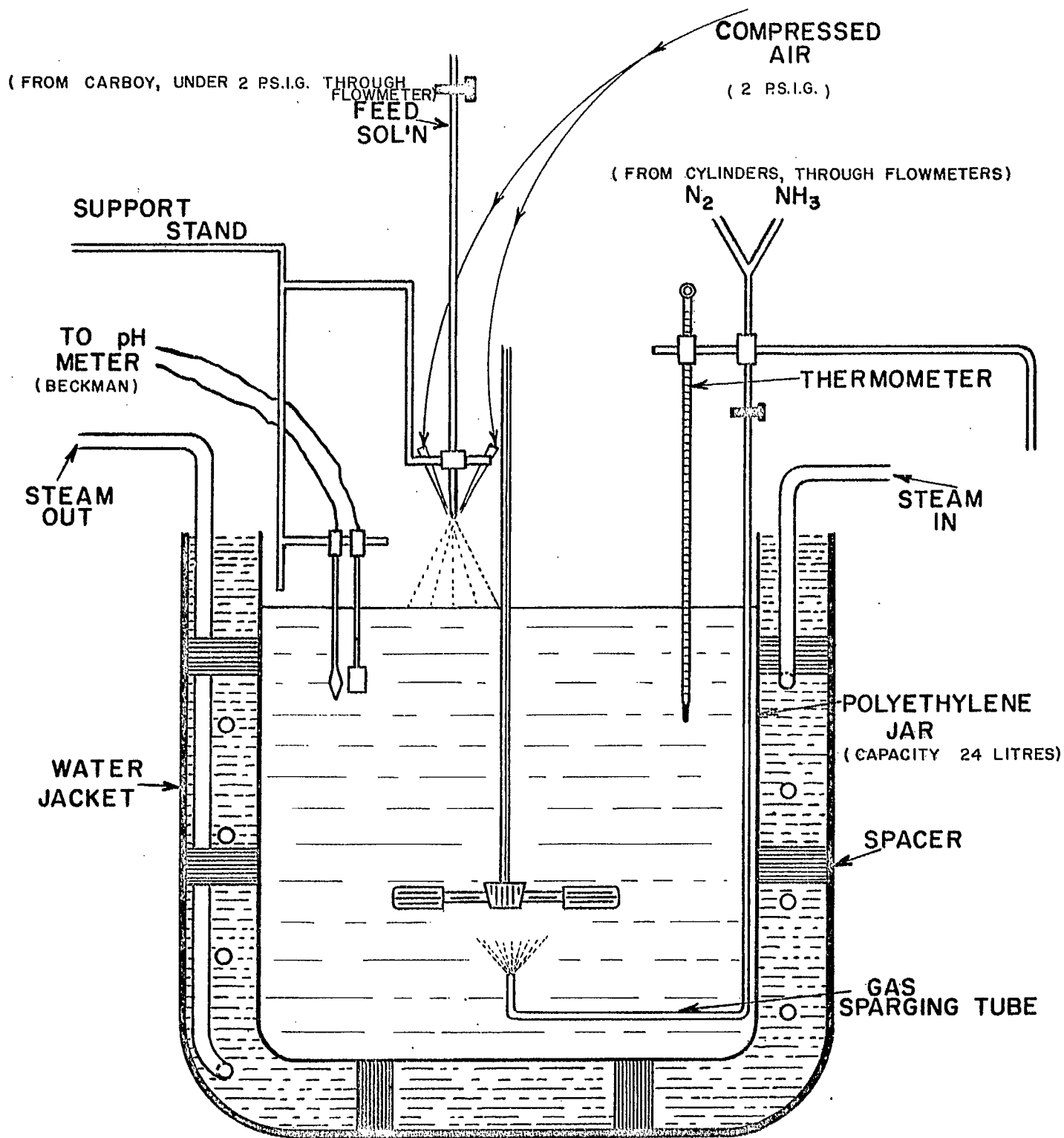
FIGURE 2   BATCH PRECIPITATION EQUIPMENT

) (a) Improved mixing of the bulk solution and the precipitate.
(b) Improved NH_3 gas distribution throughout the bulk liquid.
(c) Improved precipitate filtering characteristics by causing
   the hydroxide precipitate to be less gelatinous.

At start-up of a precipitation run 10 litres of ammonia water
(pH 8) were added to the polyethylene tank (capacity of 24 litres) to cover the
impeller sufficiently to prevent splashing, and the electrodes were lowered
into the water. About 60g ammonium nitrate were added to stabilize operation
of the pH electrodes. The temperature was raised to 55-60°C (water jacket)
and the pH raised to 8 by a slight ammonia addition. The feed solution supply
tank (polyethylene) was under 2 1/2 psig air pressure, which allowed the
flowmeter setting to hold steady throughout the 6 hr run. The gas mixture
of N_2+NH_3 was injected through a sparging tube directly under the impeller.
Adjustments, when necessary, in the setting of the ammonia gas flowmeter
reading enabled good pH control.

For most of the reported tests it was convenient to allow the
precipitate to stand overnight in contact with barren solution since there was
not sufficient time to filter off the precipitate. However this procedure is
being revised. In test number 62 one decantation of the supernatant solution
was accomplished before the end of the day. Water was added to dilute the
remaining nitrate solution. In this way the precipitate did not remain in
contact with a nitrate-rich (50 g/l) barren solution.

Discussion of the Batch Method

(a) Spraying of the feed solution. To ensure instant neutralization and
   thus mixed-precipitation of the three hydroxides, the spray method
   of feed solution delivery was chosen. The minute droplets of the
   acidic solution would not cause undesired local pH fluctuations in
   the bulk slurry which could cause momentary partial redissolution
   of particles of precipitate.

(b) Agitation. Thorough mechanical stirring is required in order to
   maintain a uniformly controlled bulk pH. Fresh slurry from the
   liquid surface must be quickly pulled into the bulk liquid, and the
   ammonia gas rapidly distributed throughout. Nitrogen gas diluent
   complements impeller action in the dispersal of the ammonia. The
   gas mixture was injected at a point underneath the impeller so that
   gas bubbles were dispersed outward.

(c) Temperature. An elevated temperature encourages rapid reaction
   rates and aids in densification of the precipitated particles. Subse-
   quent filtration and washing procedures are benefitted. They are
   difficult under the most favourable conditions when handling larger
   quantities of ammonia-produced hydroxide precipitates. A temp-
   erature of 50-60°C in the reaction vessel was most suitable. A

temperature in excess of 60°C caused excessive ammonia loss from the bulk solution surface. The temperature was controlled by a steam-heated water jacket surrounding the polyethylene vessel.

(d) pH. Close control of the bulk solution at pH 8 appeared to be optimum. A barren filtrate was achieved. Conditions distinctly on the basic side of neutral might favour a decrease in the formation of basic lead nitrate. A pH greater than 8 is unjustified in hot solutions because of considerably increased ammonia consumption.

(c) Material of Construction. In this process, plastic must be used to prevent contamination of the product by silica. The vessel and impeller were polyethylene. The thermometer and pH electrodes were standard laboratory equipment. The gas sparging tube was of glass in this work but should also be polyethylene.

Electric motors and support metal must be shielded. Moisture and ammonia vapour must not be allowed to accumulate on metal equipment and drip into the slurry.

Drying of Hydroxide Precipitates

Most oven-dried hydroxide precipitates are hard and brittle. Vigorous grinding is required which creates the problem of contamination by silica. Precipitates were slowly dried in partial vacuum. An attempt was made to displace precipitate-held moisture with methanol (followed by ether) prior to drying. This last method will give a fine crumbling dry powder if the displacement of the water is complete. The particular precipitate produced in this work contains an exceedingly large quantity of water even when thoroughly pressed-out on a Buchner filter. Excessive methanol is required to displace this moisture thoroughly. Furthermore the filter cake does not readily repulp in methanol. Standard drying techniques for such precipitates are not efficient or economical.

RESULTS OF TEST WORK

Table 2 is a summary of the test conditions for the eleven tests which produced mixed-hydroxide precipitates suitable for subsequent thermal studies.

Table 3 indicates the quantities of solution involved in the precipitation method and the extent of metal losses in the discarded solutions.

TABLE 2

TEST CONDITIONS

Precipitation of the Mixed Hydroxides of Pb, Zr and Ti from Nitrate Solution with Ammonia

| Run No. | Source Material | Feed Solution pH | Precipitant | Temp (°C) | Run Time (hr) | Procedure Variations | | | | * Ppt washing method (till ppt is free of soluble nitrate) |
						Feed Solution	Precipitant Addition	Reaction Vessel	pH Control	
37	ZrO_2 TiO_2 PbO	0.35	Conc NH_4OH	Ambient	2.	dropwise	dropwise	Contained 50 ml water at pH 8, impeller; pH electrodes	8	Ammonia water pH 9
38	"	0.20	NH_3+N_2 (2:1)	60	6.5	"	fine stream of gas	Contained 1 litre hot water at pH 8, gas injected at bottom; impeller; electrodes	"	pH 9
39	"	0.25	NH_3+N_2 (1:1)	45	4.5	"	fine stream of gas	Contained 1.5 litre hot water at pH 8. Equipped as above	"	pH 10
40	"	0	$(NH_4)_2CO_3$ Conc NH_4OH	45	(rapid)	bulk	added as rapidly as possible	$(NH_4)_2CO_3$ to pH 1.6--adjust--no ppt " " " " 6.0--rapid NH_4OH " " 7.0-- "	7.0	pH 9
45	"	0.20	NH_3+N_2 (1:1)	45	5	atomized with air	fine stream of gas (under impeller)	Contained 2 litres hot water at pH 8, feed atomized onto surface of thoroughly agitated bulk liquid. Equipped as test 38	7.5	Ammonia water pH 9 0.5 litre ethyl alcohol 0.25 litre ether
46	"	0	"	45	6.5	"	"	Started with 1.8 litre ammonia water. Otherwise as in test 45	"	Ammonia water pH 9 0.4 litre ethyl alcohol 0.4 litre ether
47		1.0	"	45	7	"	"	Started with 1.2 litre ammonia water. Otherwise as in test 45	"	"
55	$ZrOCl_2 \cdot 8H_2O$ $Ti(SO_4)_2 \cdot 9H_2O$ $PbCO_3$	--	NH_3+N_2 (1:2)	60	7	"	"	See Figure 1. initial volume ammonia water = 8 litres	7.0	Ammonia water pH 7
57	Same as 55 except Ti from liquid $Ti(Cl)_4$	--	"	55	6	"	"	As test 55; initial volume=10 litres	7.5	Ammonia water pH 7.5
60	Same as 55	--	"	55	6	"	"	"	8.0	Ammonia water pH 8
62	Same as 55	--	NH_3+N_2 (1:1)	55	6	"	"	"	8.0	Decantation Water+0.5% (w/w) NH_4OH

* Ppt filtered and washed directly following precipitation--tests 37, 39 and 40.
All other tests--ppt remained in contact with NH_4NO_3 solution for > 15 hr.

TABLE 3

RESULTS

Precipitation of the Mixed Hydroxides of Pb, Zr and Ti from Nitrate Solution with Ammonia

Run No.	Solution Volumes (l)			Losses in Waste Solutions (g/l)*						Drying of Precipitate			Dry Mixed Powder (-100 m Tyler)	
				Barren			Water Wash			Temp	Conditions	Observations		
	Feed	Barren	WaterWash	Pb	ZrO$_2$	Ti	Pb	ZrO$_2$	Ti	°C		Dry Cake	Total	to M.S.D.**
37	1.03	1.18	2.0	< 0.001	< 0.02	< 0.002	--	--	--	110	Atm	hard-brittle	20	12
38	2.46	2.46	1.5	0.010	< 0.01	< 0.001	0.010	< 0.01	< 0.001	"	"	"	103	85
39	1.5	3.0	3.0	0.001	< 0.01	< 0.002	< 0.001	< 0.01	< 0.002	"	"	"	62	47
40	0.6	1.2	0.8	< 0.001	0.11	< 0.002	< 0.001	0.04	< 0.002	"	"	soft-crumbles	66	47
45	1.4	3.1	2.0	0.003	< 0.02	< 0.002	0.034	< 0.02	< 0.002	Ambient	Vac	"	78	33
45 a										235	"	slightly yellow		31
b										150	"	powder from test 45		7
c										100	"			7
d										50	"			7
46	2.2	2.3	3.5	0.006	< 0.02	< 0.002	0.006	< 0.02	< 0.002	Ambient	"	soft-crumbles	106	91
46 a										150	"	powder from test 46		7
b										100	"			7
c										50	"			7
47	2.8	3.7	2.5	< 0.001	< 0.02	< 0.002	< 0.002	< 0.02	< 0.002	Ambient	"	soft-crumbles	108	93
55	12	20	14	0.050	< 0.02	< 0.001	0.21	< 0.02	< 0.002	"	"	hard-brittle	429	416
57	12	16	17	0.009	< 0.02	< 0.001	0.11	< 0.02	< 0.001	"	"	"	534	522
60	14	16	21	0.001	< 0.02	< 0.002	0.029	< 0.02	< 0.002	"	"	"	507	495
62	14	30	Decant 1	0.006	< 0.02	< 0.001				35	"	"	560	519
		30	Decant 2	0.003	< 0.02	< 0.001		(See Table 5)						
		65	Final Decant + Wash	< 0.001	< 0.02	< 0.001								

*Solution analyses: Control Analysis Section, Extraction Metallurgy Division.
**M.S.D.: Mineral Sciences Division (for Dr. A.H. Webster).

These losses are obviously negligible from the economic standpoint. They have not been proven unimportant in stoichoimetric considerations. Related to the solution volumes are the quantities of dry powder obtained. Observations on the texture of the precipitates are recorded.

For tests 37-40 and 45-47 the metal oxides were used as source material. These tests were each based on 100g or less of dry precipitate. A considerable amount of time was required to fuse the combined ZrO_2 and TiO_2 with $K_2S_2O_7$ using platinum crucibles with covers. This method was the only way in which these oxides could be converted to a nitric acid soluble form. Subsequently, for tests 55, 57, 60 and 62, more readily soluble metal salts were employed as source chemicals. The salts used were zirconium oxychloride and titanium sulphate (tests 55, 60 and 62) or titanium tetrachloride (test 57). A new supply of lead salt was required; certified reagent grade lead carbonate was purchased. This group of four tests were scaled up for the production of 400-500 grams of dry precipitate, sufficient for a subsequent electrical study of the fabricated, sintered ceramic.

In test 37 concentrated NH_4OH and also the nitrate feed solution were added, dropwise, from burettes into a beaker of water at room temperature. In tests 38 and 39 the nitrate feed solution was added dropwise into hot water, the pH of which was controlled at 8 by ammonia-nitrogen gas mixture. In test 40 ammonium carbonate salt was added to the bulk feed solution until the pH increased to 6, thus precipitating the Zr, Ti and some Pb. The precipitation was completed by ammonia addition to pH 7. If carbonate addition was carried beyond pH 6 in an attempt to complete the lead precipitation, then the concentration of carbonate required was excessive and resulted in solubilization of zirconium and titanium at pH 7.

These tests indicated that the hydroxide precipitation method was promising but that the procedure used would not provide conditions ensuring instantaneously complete reaction and thus the ultimate in homogeneously mixed precipitates. The method was revised to provide for atomization of the nitrate feed solution onto the surface of a thoroughly agitated bulk solution. In each batch test this bulk solution is initially ammonia water (pH 8). Test 45-47 and 55, 57, 60 and 62 involved the spray technique for feeding the Pb-Zr-Ti composite nitrate solution into the precipitation vessel. Reaction temperature for these tests ranged from 45 to 60°C, the higher temperature producing the best precipitate characteristics while maintaining a reasonably limited ammonia loss from the hot bulk solution (see "Discussion of Batch Method" page 10).

Tables 2 and 3 also show the importance of pH control. In similar tests, 55, 57 and 60, the loss of lead to the barren solution decreased as the precipitation pH increased from 7 to 7.5 to 8.0 respectively. Similarly, when the precipitate wash water pH was increased there was considerably less lead discarded in the wash solutions. Zirconium and titanium losses appear to be unaffected by the fore-mentioned pH variations.

Chemical analysis of the thoroughly washed precipitates (Table 4) showed a considerable amount of combined nitrate, particularly when the precipitate remained in the nitrate-rich barren solution for an extended period of time (> 15 hr; see Tables 2 and 4). It became apparent that the only possibility of decreasing the nitrate content of the precipitate to a value significantly less than 5 per cent was to decrease the salt concentration in the supernatant liquid. The precipitate from tests 37, 39 and 40 was filtered and washed soon after completion of precipitation. The precipitate from test 38 stood overnight as slurry. However, all four precipitates were dried at 110°C. Analyses for NO_3 gave the following results: 0.12 per cent for precipitates 37 and 40, 0.53 for number 39 and 1.02 per cent for number 38. This comparison shows that the chemically-bound nitrate can be decreased by prompt separation of precipitate from the nitrate solution, followed by immediate washing out of soluble nitrate. The nitrate can also be decreased by heating the precipitate to 110°C where some basic lead nitrate may decompose. In tests 45-47, 55, 57 and 60 the precipitates remained in contact with the nitrate solution for many hours before filtering. They were also dried under vacuum without heating. In tests based on 500 grams of dry precipitate, there was insufficient time to filter the slurry the same day. Therefore a partial decantation method was set up for test 62 (Table 5). The precipitate was allowed to settle, the solution was drawn off, the slurry was diluted with 0.5 per cent w/w NH_4OH and allowed to agitate gently overnight. Due to this treatment a precipitate was obtained that, when dried, analyzed 2.48 per cent NO_3. A small quantity of the slurry had been withdrawn at the completion of precipitation, filtered immediately and washed thoroughly. This was readily done because of the few grams of material involved. The analysis of the dry precipitate showed 0.74 per cent NO_3.

Conditions under which the precipitates were dried are shown in Table 3. In tests 37-39, in which the filter cake was dried at 110°C, and in tests 55, 57, 60 and 62 where drying occurred at ambient temperature under vacuum (26-29" water), the precipitate dried hard and brittle. Such precipitates required considerable mortaring in order to pass through a 100 mesh Tyler screen. However, when the relatively large quantity of water in the wet filter cake was completely displaced by methanol, the methanol displaced by ether, and the cake then dried under vacuum, it was found that the precipitate crumbled readily (tests 45, 46 and 47). The precipitate obtained from test 40, which contained slightly more than 52 per cent basic lead carbonate, dried to a soft powder at 110°C, readily passing through a 100 mesh Tyler screen.

Table 4 records the analytically determined composition of the mixed hydroxide powders and indicates their proximity to the desired stoichiometry. Deviations from the desired relationships can be significantly reduced, possibly to less than 0.4 mole per cent in regard to lead, with the Zr/Ti ratios being essentially exact. Attainment of this degree of control would necessitate extensive analyses and re-adjustments of the solutions which are composited into a precipitation feed solution. The discrepancies indicated

TABLE 4

RESULTS OF ANALYSIS

Mixed Precipitates of Pb, Zr and Ti Hydroxides

Run No.	Moles % Zr:Ti Nominal	Analysis	*Percentage Composition Pb	ZrO_2	Ti	*Major Contaminants (%) NO_3	CO_2	Molar Ratio $PbO:NO_3$	$PbO:CO_3$	Moles % Pb Deviation from Stoichiometry
37	52:48	52.2:47.8	61.3	18.9	6.70	0.12		152		+ 0.8
38	"	52.6:47.4	60.3	18.5	6.48	1.02		17		+ 2.1
39	50:50	51.0:49.0	59.5	17.7	6.62	0.53		34		+ 1.8
40	"	50.3:49.7	57.6	16.5	6.34	0.12	8.58	143	1.43	+ 4.5
45	"	50.8:49.2	56.6	17.2	6.46	5.04		3.4		- 0.5
46	52:48	52.5:47.5	57.0	17.5	6.16	5.25		3.3		+ 1.9
47	54:46	54.4:45.6	56.3	17.8	5.80	4.76		3.5		+ 2.4
55	58:42	57.6:42.4	55.5	18.4	5.27	6.75		2.5		+ 3.3
57	54:46	55.6:44.4	55.5	18.5	5.75	6.00		2.8		- 0.1
60	"	53.8:46.2	55.1	18.0	6.01	5.30		3.1		- 2.1
62	"	53.4:46.6	56.9	18.1	6.13	2.48		6.9		0

*By Control Analysis Section, Extraction Metallurgy Division

TABLE 5

Optimum Operating Conditions and Results (Test No. 62)

BASIS: 500 g pure, dry oxides of Pb^{2+}, Zr^{4+} and Ti^{4+}
to yield the ratio $PbZrO_3$:$PbTiO_3$=54:46 (Moles %)

	Quantity	Analytical Results				Moles % Zr:Ti	Pb Deviation from Stoich.	Per Cent Volatile	
		Pb	ZrO$_2$	Ti	NO$_3$			from Analyses	from Ppt Wts
Feed Soln (sprayed)	14 l	22.7g/l	7.32g/l	2.42g/l	50.5g/l	54.1:45.9	- 0.003%		
Precipitation Vessel	10 l of pH 8 ammonia water, at 55°C and thoroughly agitated. Controlled pH at 8 for 6 hr run with N$_2$+NH$_3$ (1:1) at rate ≈ 2 l/min								
Final Ppt Slurry	24 l	(a) 1 litre filtered immediately and washed with ammonia water (Ppt 1) (Obtained Barren 1 and Wash 1). (b) 23 litres (1) diluted to 50 l with 0.5% NH$_4$OH. Agitated slowly overnight. (2) settled and decanted (Decant 1). (3) repulped (0.5% NH$_4$OH), settled and decanted (Decant 2). (4) repulped (0.5% NH$_4$OH), filtered and washed with 20 l 0.5% NH$_4$OH, i.e., till wash was free of NO$_3$--(Decant, Wash 3)(Ppt 2).							
Barren 1	1 l	0.006g/l	< 0.02 g/l	< 0.001 g/l					
Wash 1	3 "	< 0.001 "	"	"					
Decant 1	30 "	0.006 "	"	"					
Decant 2	30 "	0.003 "	"	"					
Decant, Wash 3	65 "	< 0.001 "	"	"					
Precipitate 1	24 g				0.74%				
Precipitate 2 (Vac Dried) 35°C	536 "	56.9%	18.1%	6.13%	2.48%	53.4:46.6	- 0.001%	10.4	10.7

in Table 4 were primarily due to insufficient analytical data on metal concentrations in solution. In the development of the method it was necessary only to carefully weigh out calculated quantities of the source chemicals, with analyses requested only for barren solutions and for precipitates. Analysis of feed solutions was done for test 62 (Table 5) and the results show that stoichiometry can be very closely controlled in this precipitation method. Since test number 62 represented the best test conditions established thus far, and since it presents a cross-checking of metal ratios, a complete tabling of all the results of this run is available in Table 5. The precipitate appears to be the most satisfactory of those produced to date. This observation is based solely on chemical considerations.

Table 6 gives the semiquantitative spectrographic analyses of the precipitates obtained from two groups of source chemicals (refer to Table 1). The precipitates obtained using high purity oxides as source material (test 38-40, 47) are approximately 99.9 per cent pure. The precipitates derived from the metal salt sources (tests 55, 57, 60, 62) appear to have a greater purity ($\approx$99.95 per cent) but still contain an average 0.03 per cent silica.

The possibilities that exist for the presence of basic lead nitrates in neutralized nitrate solutions have been discussed in the literature (2) (3)(4). It appears that a rather complex equilibrium is established in the slurry and that no single formula for basic lead nitrate can be expected. The percentage of basic lead nitrate in the dry cake would depend on conditions within the precipitation slurry, the method of precipitate washing, and the temperature at which the precipitate is dried.

Table 7 shows the results of calculations, based on analyses of precipitates, which are an attempt to arrive at the possible composition of the various dry powders. It was unlikely that all the basic lead nitrates would decompose below 110°C, the literature indicating some thermal stability for these compounds. The results of tests 38 and 47, involving about equal weights of precipitate which had been standing in nitrate-rich solution for greater than 15 hours, show 12.7 per cent basic lead nitrate after drying at 110°C (test 38) and 59.1 per cent basic lead nitrate after drying at ambient temperature (test 47).

The ZrO_2 and TiO_2 hydrates which exist in the precipitate probably have a water content that varies continuously with temperature. There appears to be approximately one half molecule of water of hydration for each oxide. Mellor (5) records a slightly greater amount of water associated with ZrO_2 than with TiO_2 under similar conditions. Tests 39 and 60 (Table 7) show total percentage compositions deviating farthest from 100 per cent. If the water of hydration is increased fractionally from the formula amounts given in Table 7, then total composition percentages are acceptably close to one hundred (Table 8). Relatively small variations in drying conditions (temperature or time) could cause this formula variation.

TABLE 6

Semi-Quantitative Spectrographic Analyses [*]

Impurities in precipitated hydroxide mixtures (dried and powdered)

Test No.	Source Chemicals (see Table 1)	Elements, Per Cent							
		Si	Mg	Ca	Al	Fe	Bi	Cu	Mn
38	PbO; ZrO$_2$; TiO$_2$	0.03	0.04	ND	0.02	Tr	Tr	0.004	ND
39	"	0.03	0.001	Tr	0.03	Tr	Tr	0.003	Tr
40	"	0.03	0.01	0.02	0.03	Tr	Tr	0.002	Tr
47	"	0.04	0.03	Tr	0.07	0.03	Tr	Tr	Tr
55	ZrOCl$_2$.8H$_2$O Ti(SO$_4$)$_2$.9H$_2$O PbCO$_3$	0.03	Tr	ND	0.03	0.1	ND	0.004	Tr
57	Same as 55 except Ti from liq Ti(Cl)$_4$	0.03	Tr	Tr	Tr	Tr	ND	0.003	ND
60	Same as 55	0.05	Tr	ND	0.01	Tr	0.02	0.003	Tr
62	"	0.03	Tr	ND	0.009	Tr	0.02	0.005	Tr

[*] By Spectrographic Laboratory, Mineral Sciences Division.
Tr=Trace
ND=not detected

TABLE 7

Calculated Per Cent Composition of Dry, Mixed-Hydroxide Precipitates Submitted as a Feed Material for Calcining and Sintering Tests

Based on Analytical Results

Test No.	37	38	39	40	45	46	47	55	57	60	62
Drying Temp	←————110°C————→				←————————Ambient-Vacuum Dry————————→						35°C
TiO$_2$	11.2	10.8	11.0	10.6							
ZrO$_2$	18.9	18.5	17.7	16.5							
TiO$_2$.1/2 H$_2$O					12.0	11.4	10.8	9.8	10.7	11.2	11.4
ZrO$_2$.1/2 H$_2$O					18.5	18.8	19.1	19.8	19.9	19.3	19.5
3Pb(OH)$_2$.Pb(NO$_3$)$_2$								30.9	11.9		
5Pb(OH)$_2$.Pb(NO$_3$)$_2$	1.5	12.7	6.6	1.5	62.5	65.1	59.1	38.6	57.0	65.8	30.8
Pb(OH)$_2$	70.0	57.3	63.2	18.6	7.0	5.1	10.0	none	none	2.3	37.3
5PbCO$_3$.2Pb(OH)$_2$				52.1							
TOTAL	101.6	99.3	98.5	99.3	100.0	100.4	99.0	99.1	99.5	98.6	99.0

TABLE 8

Dry Precipitate Composition-Adjusted

	Test No. 39	Test No. 60
$TiO_2 \cdot 1/4\, H_2O$	11.6	
$TiO_2 \cdot 3/4\, H_2O$		11.8
$ZrO_2 \cdot 1/2\, H_2O$	19.0	
$ZrO_2 \cdot H_2O$		20.3
	30.6	32.1
Basic lead nitrates (Table 7)	69.8	68.1
Total	100.4	100.2

DISCUSSION

This preliminary report has dealt with the development of a chemical precipitation method for the preparation of homogeneously blended powders which are required as source material in the fabrication of electronic ceramic wafers. The particular ceramic under study was a portion of the lead zirconate-lead titanate solid solution series. The specific chemical composition within this series that will yield a source material capable of imparting optimum electrical properties to the fabricated ceramic is the next requirement. A controlled series of compositions are in preparation. The range to be scanned is from 70/30 moles per cent $PbZrO_3/PbTiO_3$ to 50/50 moles per cent $PbZrO_3/PbTiO_3$.

More reliable dry precipitate stoichiometry should result from the application of extensive analytical control of feed solution concentrations. Adequate control will necessitate several readjustments of the metal concentrations of each solution. This amount of analytical effort was not justified in the present work since standardization of a satisfactory precipitation procedure was of first importance.

The chemical results of this report indicate the existence of a reversible equilibrium between lead hydroxide and basic lead nitrates within the slurried precipitate. Such an equilibrium might be written as

$$Pb(OH)_2 \cdot Pb(NO_3)_2 \rightleftharpoons 3Pb(OH)_2 \cdot Pb(NO_3)_2 \rightleftharpoons 5Pb(OH)_2 \cdot Pb(NO_3)_2 \rightleftharpoons Pb(OH)_2$$
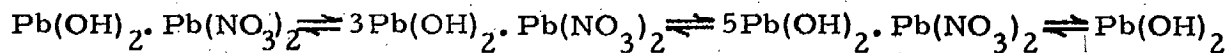
The zirconium and titanium form complex hydrated oxides, as $(Zr, Ti)\,O_2 \cdot xH_2O$ and do not become involved with the nitrate ion.

The variables which affect the above equilibrium are:

(a) The nitrate concentration in the bulk solution. The higher this concentration, the farther the equilibrium moves to the left. Since this equilibrium is reversible while the wet precipitate is slurried in aqueous solution, it would appear to be possible to force it to the right by slurry dilution.

(b) The pH of the slurry. The higher the pH of the bulk liquid, the more favourable are conditions for the displacement of nitrate from the precipitate. Pauley and Testerman (4) showed, as has been indicated by the present work, that a pH environment greater than 7 encourages a higher hydroxide to nitrate ratio in the precipitate. The pH limit is about 8 for the neutralization process.

(c) The extent of contact time of the precipitate with the barren ammonium nitrate solution. This report indicated that, when filtration and washing of the precipitate followed immediately upon completion of the precipitation, the lead hydroxide to basic lead nitrate ratio was considerably increased. It is therefore important to remove the precipitate from contact with the ammonium nitrate in the barren solution as quickly as possible. Alternatively, the nitrate-rich supernatant solution may be diluted and then decanted directly following the precipitation of the Pb, Zr and Ti as mixed hydroxides.

(d) The temperature at which precipitation is carried out. The effect of this variable has not been determined. It is set at approximately 60°C by other considerations.

Although it has not been demonstrated that the chemically-bound nitrate in the precipitates has caused specific difficulties in obtaining suitably sintered ceramics, the presence of acidic gases upon partial decomposition of the precipitates may cause corrosion difficulties in the calcination step.

The feed material for ceramic fabrication must have a uniform particle size in the range 0.5 to 1 micron. This size range is required in order to achieve high sintered densities in the fabricated components. Precipitation techniques do not appear to yield such fine particles, principally because of agglomeration or flocculation of particles in the precipitate slurry and the densification which takes place when the filter cake is dried. Therefore it is probable that the use of the "jet-mill" equipment will be required to produce such a fine particle size without the risk of contamination as would occur when employing conventional grinding methods. Furthermore, spray drying of the aqueous mixed precipitate slurry, thoroughly washed by decantation, will be given a close study in future work. The spray drying method should give spherical particles of quite uniform size, thereby enhancing jet-

mill operation. Spray drying will also enable partial calcination to take place within a very small particle (perhaps 15-40μ dia) and thus premature grain growth would be limited. Furthermore, a spray dried material will eliminate all possibility of precipitate segregation which could occur during conventional pan filter operation. Finally, the risk of contamination of the product is lessened and losses due to dusting can be reduced to a minimum.

The advantages of the chemical precipitation method as a source of feed powders for electronic ceramic fabrication would appear to be, principally:

(a) Maximum possible control over the stoichiometry and repro-
ducible homogeneity of the powder

(b) The opportunity to control the purity of the material, if re-
quired, by additional purification procedures

(c) The method should allow uniform blending of very small quan-
tities ($\ll 1$ per cent) of desirable doping agents for modification
of the electrical properties of the final ceramic component.
The doping agents are metals (very pure salts or oxides will be
required) which possibly will require application of co-precipita-
tion techniques for satisfactory blending.

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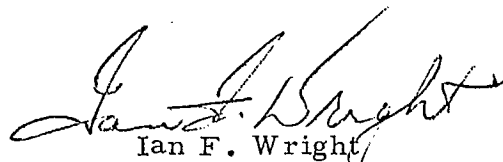
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Operational

	Function
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J.C.Ingles EMD	Control analyses
Dr.A.H. Webster MSD	Sintering and structural studies
V.A.McCourt N	Lapidary and electroding
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T.B. Weston MPD	Electronic Test methods and component evaluation
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