

265a and 265b to select one output from delay sections 267a -267e to be coupled to a combiner 268 and coupled to summing circuit 270, shown in Figure 14A, through a combiner output 269. The delay section output selected by tap selection networks 265a and 265b determines length of delay through delay 251. Delay through delay 251 can thus be selected by control 261 in 62.5 nanosecond increments. If smaller increments are desired, shorter delay sections with fewer inverters and/or shorter propagation time through each inverter can be designed.

Figure 15 is a simplified block diagram of an FM detector embodying the present invention (For a general discussion of the use of delay lines in FM detectors, see Synchronous Delay-Line Detector Provides Wideband Performance, by Joseph F. Lutz, Microwaves & RF, November, 1982). A limited FM signal V_{fm} , for instance an amplitude limited FM signal with a carrier wave frequency of 10.7 MHz, is coupled to a delay 282, typically cascaded inverters as described above. Delay 282 is typically selected to perform a $(n+1)90^\circ$ phase shift at the carrier wave frequency (10.7 MHz). An output 283 from delay 282 and the limited FM signal V_{fm} are coupled through a Boolean Exclusive Or (XOR) gate 284 to a low pass filter 286. XOR gate 284 could be replaced by other logic gates, for instance, an "AND" gate, or an "OR" gate or by various types of "FLIP- FLOPS", which have an output signal with a duty cycle which varies according to the relative phase between two input signals. A digital signal V_{ds} at an output 285 of XOR gate 284 is essentially a pulse width modulated signal. Low pass filter 286 removes the carrier wave from pulse width modulated signal V_{ds} and produces a demodulated analog signal V_{a15} . A low pass filter 287 with a cutoff frequency below the FM signal range may also be added to provide enhanced stability. Low pass filter 287 can be electrically coupled to delay 282 providing feedback to assure delay 282 continues to perform a $(n+1)90^\circ$ phase shift at the carrier wave frequency.

In order to perform a 90° phase shift or an odd multiple of a 90° phase shift (e.g. 90° , 450° , or 810°), delay 282 must time delay limited FM signal V_{fm} for the 90° phase shift or for one of its odd multiples. As the graph of Figure 15A demonstrates, increasing the time delay to a higher multiple of a 90° phase shift increases the sensitivity of the FM detector. This effect is analogous to the increase in sensitivity with increasing Q (where Q is the figure of merit of a resonance circuit and is the ratio of reactance over resistance) for a conventional FM detector constructed from tuned circuits. The graph of Figure 15A shows the calculation of sensitivity verses delay, where the carrier wave frequency is 10 MHz. Sensitivity in radians/hertz x

10^{-6} is on the vertical axis, while length of delay in nanoseconds is on the horizontal axis.

Figure 16 is a block diagram of a circuit which calibrates a delay element to a fixed duration. Such calibration of delay elements is important for many applications, for instance, in the design of delay 251 shown in Figure 14B.

In Figure 16, a delay line 512, typically comprising cascaded inverters as discussed above, has a control voltage input 513. A voltage V_{c16} on input 513 is used to vary the duration of signal delay through delay line 512. A counter 504 is coupled to an input 512a of delay line 512. A counter 511 is coupled to an output 512b of delay line 512. Counters 504 and 511 are selected to provide signals which have a period greater than the maximum possible delay through delay line 512.

Outputs from counters 504 and 511 are coupled to a timing element 507. Timing element 507 is typically a comparator or a flip-flop. Timing element 507 serves to align the output from counter 504 and the output from counter 511 by comparing the outputs and coupling a signal through a filter 510 to produce signal V_{c16} on input 513 of delay line 512. Signal V_{c16} acts as feedback to delay line 513 calibrating the duration of propagation delay through delay line 512. A reset input 502 is coupled to counter 504 through a reset input 505, to counter 511 through a reset input 508, and to delay 512 through a Boolean logic "AND" gate 503.

In Figure 17 an embodiment of the circuit in Figure 16 is shown which can be used to calibrate delays 267a - 267e of Figure 14B. A 1 microsecond delay line 544 corresponds to delay line 512 of Figure 16. Delay line 544 is coupled to a tap selection network 531 through a series of tap lines 533. Select lines 530 select which tap of series of tap lines 533 is coupled to delay output 532. When different tap lines are selected propagation delay from a system input 547 and to output 532 vary accordingly.

Divide-by-64 counters 560 and 545 respectively correspond to counters 504 and 511. A Delay (D) flip-flop 562 corresponds to timing element 507. A low pass filter 563 corresponds to filter 510. Reset inputs 548, 561, 562 and 565 correspond to reset inputs 502, 505, 509 and 508 respectively. A Boolean logic "AND" gate 549 corresponds to gate 503.

A pulse modulated 32 megahertz (MHz) signal V_{m17} is coupled to input 547 and through AND gate 549 to counter 560 and through delay line 544 to counter 545. Divide-by-64 counter 560 couples a .5 MHz signal V_{c17} to a clock input CL of D flip-flop 562. Divide-by-64 counter 545 through "NOT" gate 564 couples a .5 MHz signal V_{d17} to a D input of D flip-flop 562. When delay line 544 is calibrated at 1 microsecond, V_{d17} and V_{c17} will be in phase.

Description**FIELD OF INVENTION**

- 5 The invention is directed to thick film electronic materials having improved burnout properties, particularly when they are fired in low oxygen-containing atmospheres.

BACKGROUND OF INVENTION

- 10 In the processing of thick film electronic materials--conductors, resistors and dielectrics--, it is frequently difficult to effect removal of the organic medium during firing without leaving carbonaceous residues and stains on the fired material layers. This is especially true when the electronic material is dispersed in an organic medium which contains cellulosic components such as ethyl cellulose, hydroxyethyl cellulose and ethylhydroxyethyl cellulose.

- 15 Cellulosic materials are often preferred components for organic media because they impart to thick film dispersions made therefrom excellent dispersion stability and printing rheology. Such thick film layers typically have good printability, can be printed rapidly, and yield smooth printed layers.

- Heretofore, it has been necessary to substitute all or part of the cellulosic materials with acrylic polymers, which ordinarily have better burnout characteristics. However, such acrylic polymers do not have as good rheological properties as the cellulosic binders.

Therefore, it would be very desirable to have a means by which one could retain the use of cellulosic binder materials in thick film electronic compositions while simultaneously obtaining the good burnout characteristics usually associated only with acrylic polymers.

SUMMARY OF THE INVENTION

In one aspect, the invention is directed to thick film electronic compositions comprising finely divided particles of electrically functional material and a lead oxide-compatible glass, either or both having coated on the surfaces thereof from 0.1 to 10.0% by weight lead nitrate, dispersed in an organic medium.

- 30 In a second aspect, the invention is directed to electrically functional layers formed by applying at least one layer of the above-described thick film composition and firing the layer(s) at a temperature sufficient to effect volatilization of the organic medium and sintering of the lead oxide-compatible glass.

PRIOR ART

- 35 U.S. 1,763,268 Slepian

Molded resistor plates containing lamp black and a residue of oxidizing agents such as KNO_3 or BaNO_3 for the purpose of oxidizing the lamp black, thus increasing the resistivity of the resistors made therefrom.

- 40 U.S. 2,033,103 Beyersdorfer

In the manufacture of lead-containing glasses, the lead component is added as $\text{Pb}(\text{NO}_3)_2$ which upon oxidizing fusion is converted to PbO , which dissolves in the glass.

- 45 U.S. 2,617,773 Nagy

Calcium tungstate phosphors are formulated with lead nitrate which decomposes to the oxide upon firing the phosphors.

- 50 U.S. 3,343,984 Saums et al.

A glass-forming oxide LiNO_3 is incorporated in an enamel which is baked on wire insulation to improve the organic medium burnout characteristics of the enamel.

- 55 U.S. 3,348,918 Kruse

Method for removing carbon from carbon-diamond mixtures by contacting the mixture with PbO and

oxygen at 250-500 C.

U.S. 3,370,966 Schwartz et al.

- 5 An oxidizing agent such as PbO_2 is added to $\text{PbO/ZnO/B}_2\text{O}_3$ glass to facilitate burnout of adulterants from the glass.

U.S. 3,973,975, 4,038,091, 4,099,977 and 4,120,678, Francel et al.

- 10 The reduction of PbO during firing of sealing glass paste is avoided by incorporating, inter alia, Pb_3O_4 particles into the paste.

U.S. 4,058,387 Nofziger

- 15 In a PbO -containing sealing glass composition particles of $\text{Pb}(\text{NO}_3)_2$ are added to prevent reduction of the PbO to Pb during firing.

U.S. 4,098,611 Francel et al.

- 20 Reduction of PbO during firing of sealing glass pastes is avoided by incorporating LiNO_3 and/or AgNO_3 particles into the paste.

U.S. 4,476,039 Hormadaly

- 25 Staining in ruthenium oxide-based resistors is reduced by addition of particles of a metal compound which thermally decomposes to release O_2 therefrom. Among the suitable metal compounds mentioned are nonalkaline nitrates among which $\text{Pb}(\text{NO}_3)_2$ is mentioned.

DETAILED DESCRIPTION OF THE INVENTION

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Electrically Functional Material

- The use of $\text{Pb}(\text{NO}_3)_2$ coatings on electrically functional materials to facilitate burnout of organic media from thick film compositions is applicable to materials having any type of electrical functionality, i.e.,
35 conductors, resistors, and dielectrics as well as the inorganic binders which may be used in conjunction with them. The amount of $\text{Pb}(\text{NO}_3)_2$ which may be used relative to the total solids is from 0.1 to 10% wt. with from 0.2 to 5% wt. being preferred. Below 0.1% wt. the beneficial effect is not sufficiently evident and above 10% wt. the amount of PbO formed may have an adverse affect on the rheology of the inorganic binder.

- 40 So long as the $\text{Pb}(\text{NO}_3)_2$ is within the above described range, it does not matter if it is coated on the primary electrically functional material particles or on the inorganic binder particles or on both of them. The particle size distribution of the solids, both the electrically functional material and the inorganic binder, is not critical with respect to the operability of the invention. It may therefore be freely adjusted to conform with the rheological, printing and other concerns of the user.

- 45 The electrically functional material may be a resistance oxide on the particle surfaces of which lead nitrate is coated.

In another embodiment of the present invention the lead nitrate is coated on the particle surfaces of both the resistance material and the inorganic binder. Specifically the electrically functional material is a dielectric ceramic oxide on the particle surfaces of which lead nitrate is coated.

- 50 As a consequence, in another embodiment of the present invention the lead nitrate is coated on the particle surfaces of both the dielectric ceramic oxide and the inorganic binder.

The electrically functional material can also be a conductive metal on the particle surfaces of which lead nitrate is coated. The lead nitrate can also be coated on the particle surfaces of both, the conductive metal and the inorganic binder.

- 55 Though lead nitrate and other metal nitrates have been used for various purposes and in various ways in the prior art, the use of lead nitrate in accordance with the invention is both different from the prior art and more effective because it is utilized in the form of a coating on particles in thick film pastes. An important function of the lead nitrate in this form is to facilitate the burnout of residual organic medium.

Because it is so intimately associated with the particles onto which it is coated, the burnout is achieved more homogeneously than when used simply as a powder additive and the lead nitrate functions effectively at lower concentration levels than if it were added in the form of a particulate additament.

Lead nitrate is superior to other nitrates in thick film compositions for several reasons. One advantage is that it decomposes at a relatively low temperature. Consequently burnout is achieved before glass flow takes place in thick film compositions which contain an inorganic binder. Such low temperature burnout is particularly useful in nitrogen firing where residual carbon can reduce glasses at higher firing temperatures.

Another advantage of the use of lead nitrate is the fact that its decomposition product, PbO, can in many instances act to enhance glass flow by dissolving in the glass during firing. Furthermore, the PbO can itself function as an agent for bonding metal films to the substrates both in air and nitrogen firing.

A still further advantage of lead nitrate is that it does not form hydrates which have been observed to cause viscosity instability by adsorption of water. This can be seen by adding a drop of water to a paste and noting that a subsequent viscosity increase occurs. Pastes with lead nitrate-coated powder are by contrast stable.

The present invention also pertains to a thick film encapsulant composition comprising finely divided particles of PbO-compatible glass coated with 0.1 to 10 % by weight lead nitrate dispersed in an organic medium.

The invention further pertains to a resistor comprising a patterned thick film of the composition in which the electrically functional material is a resistance oxide on the particle surfaces of which lead nitrate is coated or in which the lead nitrate is coated on the particle surfaces of both the resistance material and the inorganic binder which composition has been printed upon a substrate and fired to effect complete volatilization of the organic medium therefrom.

Another object of the present invention is a dielectric layer comprising a thick film of the composition in which the electrically functional material is a dielectric ceramic oxide on the particle surfaces of which lead nitrate is coated or in which the lead nitrate is coated on the particle surfaces of both the dielectric ceramic oxide and the inorganic binder which composition has been printed upon a substrate and fired to effect complete volatilization of the organic medium therefrom and densification of the dielectric ceramic oxide.

Still another object of the present invention is a conductive layer comprising a thick film of the composition in which the electrically functional material is a conductive metal on the particle surfaces of which lead nitrate is coated or in which the lead nitrate is coated on the particle surfaces of both the conductive metal and the inorganic binder which composition has been printed upon a substrate and fired to effect complete volatilization of the organic medium therefrom and sintering of the conductive metal.

Finally the present invention pertains to an encapsulant coating comprising a thick film layer of the composition of the thick film encapsulant composition comprising finely divided particles of PbO-compatible glass coated with 0.1 to 10 % by weight lead nitrate dispersed in an organic medium which composition has been printed upon an electrically functional substrate and fired to effect complete volatilization of the organic medium therefrom and liquid phase sintering of the glass.

Inorganic binder

The inorganic binder may be any glass of suitable sintering temperature in which PbO is substantially soluble. Thus, the glass may be either a vitrifying or devitrifying glass. In the case of the devitrifying glass it is necessary merely that PbO be soluble in the noncrystalline matrix glass.

Formulation

It is necessary that the composition of the invention contain at least 0.1% wt. lead nitrate, basis solids, but no more than about 10% wt. Furthermore, for use in nitrogen-fired systems, it is preferred to use at least 2.5% wt. lead nitrate. Because the organic medium constitutes only about 25 to 30% wt. of the total composition, the required amount of lead nitrate burnout agent is 0.3 to about 30%, basis organic medium.

The lead nitrate is dispersed in the composition by applying it as a coating on either or both of the solids components. That is, the lead nitrate can be coated on either the electrically functional material or it can be coated on the glass or it can be coated on both materials.

The coating process can be carried out by either of the following described processes with equivalent effectiveness:

Process A:

- (1) Form slurry of the functional solids and frit in water;
- (2) Deagglomerate the suspended solids as may be necessary by additional mixing;
- (3) Add lead nitrate to the slurry and continue agitation of the slurry to dissolve completely the lead nitrate; and
- (4) Evaporate the slurry containing the dissolved lead nitrate to dryness.

Process B:

- (1) Dissolve the lead nitrate in water;
- (2) Form a slurry of the functional solids and frit in the water containing dissolved lead nitrate;
- (3) Evaporate the slurry containing the dissolved lead nitrate to dryness.

The evaporation is not difficult and can be carried out at any temperature below the decomposition temperature of the lead nitrate, i.e. below about 473° C. Vacuum evaporation can, of course, be employed in this step, but is not necessary.

Thick film compositions are then formed from the solids by conventional methods, for example by mixing the solids with organic medium and then roll milling the admixture to obtain uniform dispersion of the solids.

Test Procedures

A. Adhesion

The adhesion was measured using an "Instron" pull tester in a 90° peel configuration at a pull rate of 1.27 cm (0.5 inches) per minute. Twenty gauge pre-tinned wires were attached to 80 mil x 80 mil (2 x 2 mm.) pads by dipping for 10 seconds in 62 Sn/36 Pb/2 Ag solder at 220 C or in 63 Sn/37 Pb solder at 230 C using Alpha 611 flux. Aging studies were carried out in a Blue M Stabil-Therm® oven controlled at 150° C. After aging, test parts were allowed to equilibrate several hours in air before the wires were pulled.

B. Capacitance

Capacitance may be defined as the proportionality constant between electric charge and applied voltage ($C = Q/V$).

For a parallel plate condenser, capacitance may be calculated from the formula

$$C = \frac{KA}{4\pi d}$$

wherein

- K is the dielectric constant,
- A is the plate area in cm²
- d is the dielectric thickness in cm.

Capacitance by this formula is given in electrostatic units. One farad = 9×10^{11} electrostatic units.

Capacitance was measured using a General Radio Automatic RLC Bridge Model 1683 at 120 Hz or 1 KHz frequency and 1 V.A.C. Capacitance was generally measured between the anode lead and the soldered cathode coating. In some cases leads were soldered to the cathode coating and were used for measurements.

C. Dissipation Factor

Dissipation factor is the tangent of the angle (σ) by which the current lags from the 90° vector to the voltage. Here it is expressed as percent dissipation factor ($100 \times \text{tangent } \sigma$).

Capacitance and dissipation factors are measured using Hewlett-Packard's HP 4274A multi-frequency LCR meter, while insulation resistance is measured using super megohm meter Model RM170 (Biddle Instruments, AVO Ltd., U.K.). Each number is the average of at least 10 measurements. Insulation resistance measurements are made after charging the capacitor with the respective working voltage for 1 minute. Measurements are made in both directions and, on the average, no differences of order of

magnitude in IR are found. In general, specifications for C and IR are established as minimum values and, for DF, as maximum permissible values for a given use.

D. Resistance Measurement and Calculations

The test substrates are mounted on terminal posts within a controlled temperature chamber and electrically connected to a digital ohm-meter. The temperature in the chamber is adjusted to 25° C and allowed to equilibrate, after which the resistance of each substrate is measured and recorded.

The temperature of the chamber is then raised to 125° C and allowed to equilibrate, after which the resistance of the substrate is again measured and recorded.

The temperature of the chamber is then cooled to -55° C and allowed to equilibrate and the cold resistance measured and recorded.

The hot and cold temperature coefficients of resistance (TCR) are calculated as follows:

$$\text{Hot TCR} = \frac{R_{125^{\circ}\text{C}} - R_{25^{\circ}\text{C}}}{R_{25^{\circ}\text{C}}} \times (10,000) \text{ ppm/C}$$

$$\text{Cold TCR} = \frac{R_{-55^{\circ}\text{C}} - R_{25^{\circ}\text{C}}}{R_{25^{\circ}\text{C}}} \times (-12,500) \text{ ppm/C}$$

The values of $R_{25^{\circ}\text{C}}$ and Hot and Cold TCR (HTCR and CTGR respectively) are averaged and $R_{25^{\circ}\text{C}}$ values are normalized to 25 μm dry printed thickness and resistivity is reported as ohms per square at 25 μm dry print thickness. Normalization of the multiple test values is calculated with the following relationship:

$$\text{Normalized Resistance} = \frac{\text{Avg. measured resistance} \times \text{Avg. dry print thickness, } \mu\text{m}}{25 \mu\text{m}}$$

E. Solder Acceptance Test

The solder acceptance test pattern contains different size solder pads ranging from 10 x 20 mil (250 x 500 μm) to 80 x 80 mil (2 x 2 mm) in size. The thick film conductor composition is printed and fired onto a 2.54 x 2.54 cm (1 x 1 inch) alumina substrate. Three firings to 850° C in air are used for precious metal conductor compositions to simulate end use conditions. Copper conductors are fired to 900° C in nitrogen. In both cases the conductor is held 10 minutes at peak temperature and the total firing cycle is about 60 minutes.

The fired test pattern is dipped in an RMA flux such as Alpha 611⁽¹⁾ and drained of excess flux. Then the part is preheated for 2-3 seconds by dipping the bottom edge of the substrate into the molten solder. The choice of flux, solder composition and solder pot temperature is selected to simulate end use conditions. After preheating, the entire part is immersed into the solder for 5 seconds. The rate of dipping and withdrawal is about 0.5 to 1.0 cm/sec. After withdrawal the soldered test pattern is allowed to cool. Flux residue is removed by washing the part in a suitable solvent such as trichloroethane or isopropanol.

Solder acceptance is evaluated by counting the number of pads completely wetted by solder. Any pad not completely wetted is considered nonwetted. The number of completely solder wetted pads is divided by the total number of pads to calculate solder acceptance on a percentage basis.

EXAMPLES

Example 1

Use of $\text{Pb}(\text{NO}_3)_2$ in Low Temperature N_2 -Fireable Encapsulant.

(1) Alpha Metals, Jersey City, NJ

Lead nitrate was coated on low softening (365° C) zinc lead borosilicate glass. The coating was done by dissolving 2.4 g $\text{Pb}(\text{NO}_3)_2$ in H_2O ; stirring in 50 g of the glass powder, and evaporating the coated powder to dryness at 120° C for 24 hours. The powder was made into a thick film paste by mixing on a muller with organic medium, and SiO_2 filler. The filler is intended to restrict excessive glass flow on firing.

5 The following mixture was made: 4.35 g of the above coated powder; 0.65 g SiO_2 powder, 0.25 g green pigment and 1.5 g organic medium. The medium contained 3.1% ethylcellulose, 95.84% Texanol⁽¹⁾ solvent and 1.06% tridecylphosphate.

The paste was tested as an encapsulant over previously fired Cu circuitry and two thick film resistors on alumina substrates. The paste was screen printed on the substrates, dried at 120° C for 10 minutes and
10 fired in a N_2 atmosphere belt furnace with an approximate 10-minute peak temperature of 535° C.

The resulting film was smooth and free of black bubbly areas thus indicating good vehicle burnout. Resistance shift and Cu stain were observed to be minimal.

Examples 2 and 3

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Lower Softening Encapsulant

A quantity of low melting encapsulant was prepared by the procedure of Example 1. A solution was prepared in which 121.86 g of $\text{Pb}(\text{NO}_3)_2$ was dissolved in 2538 g H_2O . The following low softening glasses
20 were added: Glass A from Example 1 and Glass B (wt. % PbO 82.7, B_2O_3 11.2, PbF_2 5, SiO_2 1.1) 846.72 g. The mixture was evaporated to dryness to coat the glasses. The powder was roll milled: Glass A and Glass B with $\text{Pb}(\text{NO}_3)_2$ coating 63.5% SiO_2 9.49%, Green Pigment 2.92% and the cellulosic vehicle described in Example 1 24.4%.

The paste was printed over Cu circuitry with resistors as described above and fired at 550° C in a N_2
25 belt furnace. The smoothness of the fired film indicated that the organic medium was burned out quite completely.

To determine the optimum $\text{Pb}(\text{NO}_3)_2$ level for complete burnout with minimal stain, a paste was prepared similar to that above, but with no $\text{Pb}(\text{NO}_3)_2$. It was blended with a portion of the paste with $\text{Pb}(\text{NO}_3)_2$ to reduce the amount of $\text{Pb}(\text{NO}_3)_2$ from 4.8 to 4.3% wt. It was printed and fired as described. The
30 resulting film showed evidence of incomplete vehicle burnout. Thus for this glass combination, the optimum amount of $\text{Pb}(\text{NO}_3)_2$ is between 4.3 and 4.8% wt.

Smooth, completely burned-out films were achieved down to 450° C in the N_2 belt furnace. Such lower firing temperatures are preferred to minimize resistor shift.

35 Example 4

Use of $\text{Pb}(\text{NO}_3)_2$ to Burn Out Vehicle in Higher Softening Point N_2 -Fireable Encapsulants

A glass having a softening point of 660 C (SiO_2 56.5, PbO 17.2, Al_2O_3 9.1, CaO 8.6, B_2O_3 4.5, Na_2O 2.4 and K_2O 1.7) was coated with $\text{Pb}(\text{NO}_3)_2$ by dissolving 0.54 g $\text{Pb}(\text{NO}_3)_2$ in water, adding 11.27 g glass
40 and evaporating to dryness. A paste was prepared using the same cellulosic vehicle described above (5 g $\text{Pb}(\text{NO}_3)_2$ -coated glass and 1.7 g of the above-described cellulosic vehicle). It was tested as an encapsulant for Cu-electroded capacitor previously prepared on alumina substrates. The paste was screen printed, dried and fired at 900° C/10 min peak in an N_2 atmosphere furnace. The resulting film was smooth and
45 completely burned out as indicated by the clarity or transparency of the fired film.

Example 5

Use of $\text{Pb}(\text{NO}_3)_2$ to Burn Out Vehicle in a High K Dielectric Capacitor

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Fifty grams of TiO_2 powder were mixed in water with 1.2 g $\text{Pb}(\text{NO}_3)_2$ then evaporated to dryness to coat the TiO_2 . The following mixture was prepared and roll milled: 48 g TiO_2 coated powder, 2.53 g glass binder, 13.0 g of the cellulosic vehicle (previously described). The paste was used to prepare capacitors on copper electrodes. Films were fired at 900° C in an N_2 belt furnace. The resulting dielectric films were
55 white indicating good burnout. The capacitors showed high K $\approx$ 200 with low dissipation factor 0.2%.

(1) 2,2,4-trimethylpentanediol-1,3-monoisobutyrate
Company, Rochester, NY.

manufactured by Eastman Kodak

Examples 6-8Use of $\text{Pb}(\text{NO}_3)_2$ in a Copper Conductor Composition

5 2% $\text{Pb}(\text{NO}_3)_2$ was coated on copper powder according to the following compositions and procedure:

Compositions

10

Lead Nitrate Solution (A)		
	%	grams (g)
$\text{Pb}(\text{NO}_3)_2$	10.00	100.0
Citric Acid	.05	0.5
D. I. Water	89.95	899.50
	100.00	1000.00

15

25

Copper Slurry (B)		
	%	grams (g)
Lead Nitrate Solution (A)	16.7	1000.0
Cu Powder	83.3	5000.0
	100.0	6000.0

30 Procedure

1. Prepare 1000 g Lead Nitrate Solution (A) by dissolving 10% $\text{Pb}(\text{NO}_3)_2$ and .05% Citric acid in D.I. water.

2. Transfer Solution (A) to high-shear mixer and gradually add 5000 g Cu powder.

35 3. Stir mixture slowly for 15 minutes to wet out powder. Then increase to high speed to break down agglomerates. Continue high-shear mixing for 15 minutes until copper paste has a smooth, uniform, "whipped cream" consistency.

4. Transfer copper slurry (B) into tray and freeze dry to produce a fine, deagglomerated copper powder coated uniformly with $\text{Pb}(\text{NO}_3)_2$.

40 The above lead nitrate-coated Cu powder was tested in the following paste composition and compared to standard Du Pont 9924Q (frit-bonded) and Du Pont 6022 oxide-bonded copper conductors. All Cu compositions were fired to 900° C for 10 minutes in a one hour cycle.

45

Composition of Cu conductor C	
	%
2% $\text{Pb}(\text{NO}_3)_2$ -Coated Cu powder	85.0
Organic Medium	15.0
	100.0

50

Properties of Cu Conductors			
	9924Q	6022	C
Sheet Resistivity mΩ/sq/10 μm	3.2	3.0	2.7
Solder Acceptance %	90	85	90
Adhesion, Peel Newtons	24	25	24
% Retained Carbon* %	0.042	0.020	.016

*Carbon analysis of Cu film after firing to burnout temperature of 600° C.

Examples 9 and 10

Use of Pb(NO₃)₂ in a Ag/Pt Conductor Composition

A mixture of 100 Ag:1 Pt powders was coated with 1.5% Pb(NO₃)₂ by a slurry process similar to that described above. This coated powder was then used in the following conductor composition D which exhibited excellent properties when fired in air to 850° C for 10 minutes in a one hour cycle.

Composition of Ag/Pt Conductor D	
	%
Pb(NO ₃) ₂ Coated Ag/Pt	79.8
Frit F	2.0
Cu Bi Rutenate	1.0
Organic Medium	17.2
	100.0

Properties of Cu Conductors		
	D	E
Sheet Resistivity mΩ/sq/10 μm	3.6	4.2
Solder Acceptance %	100	95
Initial Adhesion Newtons	27	18
Aged Adhesion, Peel		
100 hours at 150° C Newtons	26	13
2000 hours at 150° C Newtons	18	--

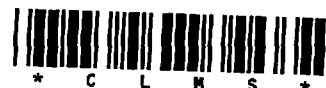
The superior properties of the Ag/Pt conductor (D) made from Pb(NO₃)₂ coated powder is evident by comparison with E. Sample E was a similar (not identical) composition made from an admixture of Ag and Pt powders. Adhesion was poor even though E contained 2% PbO in lieu of Pb(NO₃)₂ as a bonding agent.

Composition of E (No Pb(NO ₃) ₂ Coating):	
	%
Ag Powder	77.20
Pt Powder	0.77
PbO	2.00
Frit F	2.00
Cu Bi Ruthenate	1.00
Organic Medium	17.03
	100.00

Composition of Frit F (milled mixture):	
	%
Borosilicate glass	50.0
MnO ₂	21.5
ZnO	14.5
CuO	14.0

Claims

1. A thick film electronic composition comprising finely divided particles of an electrically functional material and a PbO-compatible inorganic binder dispersed in an organic medium, the improvement which comprises incorporating into the dispersion 0.1 to 10% wt., basis solids, of lead nitrate as a coating on the surface of at least one of the solids components.
2. The composition of claim 1 in which the electrically functional material is a resistance oxide on the particle surfaces of which lead nitrate is coated.
3. The composition of claim 2 in which the lead nitrate is coated on the particle surfaces of both the resistance material and the inorganic binder.
4. The composition of claim 1 in which the electrically functional material is a dielectric ceramic oxide on the particle surfaces of which lead nitrate is coated.
5. The composition of claim 4 in which the lead nitrate is coated on the particle surfaces of both the dielectric ceramic oxide and the inorganic binder.
6. The composition of claim 1 in which the electrically functional material is a conductive metal on the particle surfaces of which lead nitrate is coated.
7. The composition of claim 1 in which the lead nitrate is coated on the particle surfaces of both the conductive metal and the inorganic binder.
8. A thick film encapsulant composition comprising finely divided particles of PbO-compatible glass coated with 0.1 to 10% by weight lead nitrate dispersed in an organic medium.
9. A resistor comprising a patterned thick film of the composition of claim 2 or claim 3 which has been printed upon a substrate and fired to effect complete volatilization of the organic medium therefrom.
10. A dielectric layer comprising a thick film of the composition of claim 4 or claim 5 which has been printed upon a substrate and fired to effect complete volatilization of the organic medium therefrom and densification of the dielectric ceramic oxide.



Composition of E (No Pb(NO ₃) ₂ Coating):	
	%
Ag Powder	77.20
Pt Powder	0.77
PbO	2.00
Frit F	2.00
Cu Bi Ruthenate	1.00
Organic Medium	17.03
	100.00

Composition of Frit F (milled mixture):	
	%
Borosilicate glass	50.0
MnO ₂	21.5
ZnO	14.5
CuO	14.0

Claims

1. A thick film electronic composition comprising finely divided particles of an electrically functional material and a PbO-compatible inorganic binder dispersed in an organic medium, the improvement which comprises incorporating into the dispersion 0.1 to 10% wt., basis solids, of lead nitrate as a coating on the surface of at least one of the solids components.
2. The composition of claim 1 in which the electrically functional material is a resistance oxide on the particle surfaces of which lead nitrate is coated.
3. The composition of claim 2 in which the lead nitrate is coated on the particle surfaces of both the resistance material and the inorganic binder.
4. The composition of claim 1 in which the electrically functional material is a dielectric ceramic oxide on the particle surfaces of which lead nitrate is coated.
5. The composition of claim 4 in which the lead nitrate is coated on the particle surfaces of both the dielectric ceramic oxide and the inorganic binder.
6. The composition of claim 1 in which the electrically functional material is a conductive metal on the particle surfaces of which lead nitrate is coated.
7. The composition of claim 1 in which the lead nitrate is coated on the particle surfaces of both the conductive metal and the inorganic binder.
8. A thick film encapsulant composition comprising finely divided particles of PbO-compatible glass coated with 0.1 to 10% by weight lead nitrate dispersed in an organic medium.
9. A resistor comprising a patterned thick film of the composition of claim 2 or claim 3 which has been printed upon a substrate and fired to effect complete volatilization of the organic medium therefrom.
10. A dielectric layer comprising a thick film of the composition of claim 4 or claim 5 which has been printed upon a substrate and fired to effect complete volatilization of the organic medium therefrom and densification of the dielectric ceramic oxide.



11. A conductive layer comprising a thick film of the composition of claim 6 or claim 7 which has been printed upon a substrate and fired to effect complete volatilization of the organic medium therefrom and sintering of the conductive metal.

5 12. An encapsulant coating comprising a thick film layer of the composition of claim 8 which has been printed upon an electrically functional substrate and fired to effect complete volatilization of the organic medium therefrom and liquid phase sintering of the glass.

Patentansprüche

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1. Dickfilm-Elektronik-Zusammensetzung, umfassend fein zerteilte Teilchen eines elektrisch funktionellen Materials und eines mit PbO verträglichen anorganischen, in einem organischen Medium dispergierten Bindemittels, wobei die Verbesserung das Einarbeiten von 0,1 bis 10 Gew.-%, auf Feststoff-Basis, Bleinitrat in die Dispersion als Beschichtungsmittel auf der Oberfläche wenigstens einer der Feststoff-

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2. Zusammensetzung nach Anspruch 1, worin das elektrisch funktionelle Material ein Widerstands-Oxid ist, auf dessen Teilchen-Oberflächen das Bleinitrat als Schicht aufgetragen ist.

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3. Zusammensetzung nach Anspruch 2, worin das Bleinitrat auf die Teilchen-Oberflächen sowohl des Widerstandsmaterials als auch des anorganischen Bindemittels als Schicht aufgetragen ist.

4. Zusammensetzung nach Anspruch 1, worin das elektrisch funktionelle Material ein dielektrisches keramisches Oxid ist, auf dessen Teilchen-Oberflächen das Bleinitrat als Schicht aufgetragen ist.

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5. Zusammensetzung nach Anspruch 4, worin das Bleinitrat auf die Teilchen-Oberflächen sowohl des dielektrischen keramischen Oxids als auch des anorganischen Bindemittels als Schicht aufgetragen ist.

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6. Zusammensetzung nach Anspruch 1, worin das elektrisch funktionelle Material ein leitfähiges Metall ist, auf dessen Teilchen-Oberflächen das Bleinitrat als Schicht aufgetragen ist.

7. Zusammensetzung nach Anspruch 6, worin das Bleinitrat auf die Teilchen-Oberflächen sowohl des leitfähigen Metalls als auch des anorganischen Bindemittels als Schicht aufgetragen ist.

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8. Dickfilm-Verkapselungs-Zusammensetzung, umfassend fein zerteilte Teilchen eines mit PbO verträglichen Glases, das mit 0,1 bis 10 Gew.-% Bleinitrat, dispergiert in einem organischen Medium, beschichtet ist.

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9. Widerstand, umfassend einen strukturierten Dickfilm der Zusammensetzung des Anspruchs 2 oder des Anspruchs 3, die auf ein Substrat gedruckt und gebrannt wurde, um eine vollständige Verflüchtigung des organischen Mediums aus dieser zu bewirken.

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10. Dielektrische Schicht, umfassend einen Dickfilm der Zusammensetzung des Anspruchs 4 oder des Anspruchs 5, der auf ein Substrat gedruckt und gebrannt wurde, um eine vollständige Verflüchtigung des organischen Mediums aus diesem und eine Verdichtung des dielektrischen keramischen Oxids zu bewirken.

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11. Leitfähige Schicht, umfassend einen Dickfilm der Zusammensetzung des Anspruchs 6 oder des Anspruchs 7, der auf ein Substrat gedruckt und gebrannt wurde, um eine vollständige Verflüchtigung des organischen Mediums aus diesem und ein Sintern des leitfähigen Metalls zu bewirken.

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12. Verkapselungs-Beschichtung, umfassend eine Dickfilm-Schicht der Zusammensetzung nach Anspruch 8, die auf elektrisch funktionelles Substrat gedruckt und gebrannt wurde, um eine vollständige Verflüchtigung des organischen Mediums aus dieser und ein Flüssigphasen-Sintern des Glases zu bewirken.

Revendications



1. Une composition électronique pour couches épaisses comportant des particules finement divisées d'un matériau électriquement actif et d'un liant minéral compatible PbO dispersé dans un milieu organique, l'amélioration qui comprend l'incorporation de 0,1 à 10% en poids, sur la base des solides, de nitrate de plomb comme revêtement sur la surface d'au moins un des composants solides.
- 5 2. La composition de la revendication 1 dans laquelle le matériau électriquement actif est un oxyde pour résistances dont les surfaces des particules sont revêtues de nitrate de plomb.
3. La composition de la revendication 2 dans laquelle le nitrate de plomb recouvre les surfaces des
10 particules du matériau pour résistances et du liant minéral.
4. La composition de la revendication 1 dans laquelle le matériau électriquement actif est un oxyde céramique diélectrique dont les surfaces des particules sont revêtues de nitrate de plomb.
- 15 5. La composition de la revendication 4 dans laquelle le nitrate de plomb recouvre les surfaces des particules de l'oxyde céramique diélectrique et du liant minéral.
6. La composition de la revendication 1 dans laquelle le matériau électriquement actif est un métal conducteur dont les surfaces des particules sont revêtues de nitrate de plomb.
7. La composition de la revendication 1 dans laquelle le nitrate de plomb recouvre les surfaces des particules de l'oxyde céramique diélectrique et du liant minéral.
8. Une composition d'encapsulant pour couches épaisses comprenant des particules finement divisées de
25 verre compatible PbO revêtues de 0,1 à 10% en poids de nitrate de plomb dispersé dans un milieu organique.
9. Une résistance comprenant une couche épaisse à motif de la composition de la revendication 2 ou de la revendication 3, laquelle a été imprimée sur un substrat et cuite pour effectuer une volatilisation
30 complète du milieu organique.
10. Une couche diélectrique comprenant une couche épaisse de la composition de la revendication 4 ou de la revendication 5 qui a été imprimée sur un substrat, et cuite pour effectuer une volatilisation complète du milieu organique et une densification de l'oxyde céramique diélectrique.
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11. Une couche conductrice comprenant une couche épaisse de la composition de la revendication 6 ou de la revendication 7 qui a été imprimée sur un substrat et cuite pour effectuer une volatilisation complète du milieu organique et le frittage du métal conducteur.
- 40 12. Un revêtement encapsulant comprenant une couche de la composition pour couches épaisses de la revendication 8 qui a été imprimée sur un substrat électriquement actif et cuite pour effectuer une volatilisation complète du milieu organique et un frittage du verre en phase liquide.

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