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**METHOD OF MAKING PIEZOELECTRIC LAYERS  
BY FLAME SPRAYING**

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The present invention relates to a method of making piezoelectric layers and more especially relates to a flame spraying process whereby such layers or coatings may be readily and conveniently made.

Accordingly a primary object of our invention is to provide a flame spraying method of making thin piezoelectric layers, films or coatings.

A more specific object of our invention is to provide a flame spraying method of making piezoelectric barium titanate multicrystalline coatings.

Another object of our invention is to provide an improved flame spraying method of forming piezoelectric thin films wherein the material being so sprayed is impinged upon a heated substrate and the cooling rate of the coating so controlled as to prevent or deter conversion of the sprayed material from a piezoelectric to a non-piezoelectric crystal structure.

These and other objects, features and advantages of our invention will become apparent to those skilled in this art from the following detailed disclosure thereof.

As is well known to those skilled in this art, it has been most difficult to prepare thin piezoelectric coatings of perovskite type structures by known techniques. In distinction to such problems we have discovered that by the flame spraying of particulate materials as herein taught, that such films may be readily fabricated.

By the term "flame spraying" as used in the present specification and claims is meant the passage of particulate materials through a continuous flame generating device such as an oxyacetylene torch, oxyhydrogen torch or a plasma flame unit and the deposition of said materials as an adherent, coherent coating upon the substrate being so treated. Such flame generating members are well known. Generally speaking the present process represents an improvement over the flame spraying techniques disclosed in U.S. Patent 2,904,449.

Our invention is based upon our discovery that by flame spraying for example barium titanate ( $BaTiO_3$ ) onto a heated substrate that we can maintain the piezoelectric properties of the material. Mere flame spraying of such materials upon a chilled substrate destroys the piezoelectric properties of the sprayed layer. On the other hand by flame spraying onto a heated substrate we are able to maintain such desirable piezoelectric properties. This feature is a controlled cooling rate phenomenon whereby one controls crystallographic transformation.

Before proceeding further in a discussion of our process reference should first be had to an example thereof:

**EXAMPLE 1**

Particulate barium titanate of a particle size ranging from -44 to +5 microns was passed through a oxyhydrogen flame onto an Inconel substrate. The gun to substrate distance was maintained at from 2 to 3 inches and we used a gas ratio of 55 cubic feet per hour oxygen to 100 cubic feet per hour hydrogen. The Inconel was in disc form,  $\frac{3}{4}$  inch thick and was maintained at a temperature of from 1100° F. to 1300° F. while the barium titanate was being deposited thereon. We determined that the thin, dense layer of barium titanate was piezoelectric.

It is known that barium titanate at room temperature exists in the tetragonal crystal form. At temperatures of approximately 126° C. the tetragonal form converts to the cubic and at temperatures of approximately 1400° C. the latter in turn converts to the hexagonal crystalline structure. It is the tetragonal form which is piezoelectric. If one merely flame sprays barium titanate onto a chilled substrate in their passage through the flame the barium titanate particles are converted to the hexagonal crystalline form, a non-piezoelectric embodiment. Conversion of the hexagonal to the cubic is most sluggish and for practical purposes can be said to be almost non-existent. On the other hand the intermediate temperature cubic structure readily reverts to the piezoelectric tetragonal. Accordingly an essential feature of our invention is the flame spraying of crystal structure material which can easily be converted under controlled conditions to avoid the formation of the high temperature crystal structure. We have found that by the avoidance of the quenching of the barium titanate, for example, in the high temperature hexagonal form and that is by flame spraying onto a heated substrate, that we can maintain the piezoelectric qualities of the material being sprayed. After the flame spraying onto the heated substrate the material may be air-cooled and while in layer form it reverts to the piezoelectric tetragonal structure.

In addition to using a heated substrate in the carrying out of our process we have also found that it is important to control the particle feed rate into the flame. If the feed rate is too low the particles become very hot thus increasing the probability of obtaining reduced  $BaTiO_3$ , a material which is non-piezoelectric. If on the other hand the feed rate is too high the temperature of the particles in the flame would be too low and a dense coating would not be obtained. Both reduced barium titanate and reduced but porous  $BaTiO_3$  layer do not have the desirable piezoelectric properties we wish to provide. Preferably we use a deposition rate of approximately 23 grams per minute in order to make the desired new coatings of this invention. At 40 grams per minute the deposited barium titanate was found to be porous and did not adhere well to the substrate and at approximately 14 grams per minute reduced barium titanate was formed. A range of from 20 to 35 grams per minute can be employed to make the present piezoelectric coatings.

Even more specifically, our process is applicable for the deposition of titanates, niobates, vanadates and zirconates characterized by a perovskite crystallographic structure and to the solid solutions of such materials. Examples of such materials are barium titanate, potassium titanate, sodium tantalate, potassium niobate, lead titanate, lithium tantalate, lithium niobate, cadmium niobate and lead zirconate titanates. These materials are flame sprayed onto a heated substrate maintained at such a temperature to prevent rapid chilling of the impinging particles with the resulting formation of a non-piezoelectric crystal structure. Obviously the substrate material employed must be capable of withstanding the particular heating involved.

It will be understood that various modifications and variations may be effected without departing from the spirit or scope of the novel concepts of our invention.

We claim as our invention:

1. The method of making a layer of piezoelectric material upon a substrate which comprises the steps of: flame spraying an oxygen containing material of perovskite structure onto a heated substrate while maintaining said substrate at a temperature whereby said material is not chilled in a non-piezoelectric crystal phase and permitting the resulting layer to cool.

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2. The method of making a multicrystalline piezoelectric layer upon a substrate which comprises the steps of: flame spraying particles of a material selected from the group consisting of titanates, tantalates, niobates and zirconates which material is characterized by a relatively low temperature piezoelectric structure and a relatively high temperature non-piezoelectric structure onto a heated substrate while maintaining said substrate during spraying at such an elevated temperature whereby said particles upon impingement and deposition are not chilled in the high temperature, non-piezoelectric structure, and then permitting said layer to cool.

3. The method as defined in claim 2 wherein said material being flame sprayed is barium titanate.

4. The method as defined in claim 2 wherein said material being flame sprayed is a lead titanate zirconate.

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## References Cited

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