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PROCESS FOR MAKING ELECTRICAL CONDUCTORS CONSISTING OF CHROMIUM OXIDE AND TITANIUM OXIDE

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1 Claim. (Cl. 23—51)

This invention relates to new and useful compositions comprising chromium titanates and methods of making the same.

In electrical circuits involving the use of high frequency currents, materials which have the combination of electrical properties of low or median resistance, high power factor and fairly high dielectric constant, plus a large negative temperature coefficient (that is, as the temperature increases the dielectric constant and power factor values rapidly increase) would be of considerable value in such circuits, particularly if available in a chemical form stable over a wide range of temperature, pressure and chemical conditions, and if available in a variety of controlled particle sizes. Such materials would be useful as volume controls for radio circuits where such volume control is determined by uniform variation of a standard resistance, as safety valves in high tension high frequency circuits for limiting voltages, as safety valves in circuits involving changes in frequency where a limit is desired on the extent of frequency change, and as temperature limiting devices in high frequency and/or high tension circuits. Furthermore, should such materials be of a highly refractory nature the utility of the material is still further expanded by the possibility of preparing a resistance heater for development of temperature between 2000° and 3000° F. by passing a high voltage high frequency current through a suitably prepared and supported body.

In accordance with this invention, an entirely new group of compounds has been discovered. These compounds are suitable for the uses listed above, are highly refractory, and develop a large amount of heat when a high voltage high frequency current is passed through them. These compounds are those which vary in composition from 2 moles of Cr_2O_3 per mole of TiO_2 to 1 mole of Cr_2O_3 per 27 moles of TiO_2, and are identified as chromium titanates. A number of definite compounds may exist in this series, some of which may have the following formulae: Cr_4TiO_8, Cr_2TiO_5, $Cr_2Ti_8O_{19}$, $Cr_2Ti_{16}O_{35}$, $Cr_2Ti_{27}O_{57}$. On the other hand, certain of the members of this series may exist as mixtures of chromium titanates of different formulae, or mixtures of certain chromium titanates with TiO_2 or Cr_2O_3. In fact mixtures outside the molecular limits specified above have useful electrical properties.

In general, however, a composition varying from 6% to 79% Cr_2O_3 and 94% to 21% TiO_2 is preferred. Each member of this series possesses the required electrical properties, and finds utility in high frequency circuits for the purposes mentioned above. All have relatively low resistance, high power factor, high dielectric constant, high temperature coefficients, and tend to act as enormous reservoirs of high frequency power as the temperature rises, in view of the fact that as the temperature increases the power factor and dielectric constant also increase. Since the amount of energy dissipated (in the form of heat) in the above described bodies is proportional to the product of the dielectric constant and power factor, the application of such materials as safety valves in high frequency circuits and as high frequency resistance heaters (in view of their refractoriness) is obvious.

These compounds may be made in a variety of ways. For example, solutions of the oxides in sulphuric acid may be mixed, evaporated to dryness and suitably calcined, or a mixture of hydrates may be prepared by precipitation from a solution of the oxides by the addition of alkalies, followed by calcination of the mixed hydrates. However, it is preferred to make these compounds by suitably calcining (in ordinary calcination atmospheres, such as air, which are sufficiently oxidizing in nature to insure that chromium is kept in the trivalent state and titanium in the quadrivalent state) an intimate mixture of the finely divided oxides themselves, such as at a temperature in excess of 2000° F. We have found that a fairly rapid and complete reaction is obtained at 2400° F. through the complete series, but we have also found that an enhancement of the desirable electrical properties is obtained if the calcination is carried out at 2600°–2700° F. for a period about twice the time required to obtain complete reaction. A steel grey hard but friable sinter is obtained.

In preparing these compounds directly from the oxides, appropriate quantities of the oxides are mixed together, water is then added, and the mixture is ground in a ball mill for a few hours to insure completely intimate mixture. The slip thus formed is dried and then fired. The reacted product is then ground to coarse sizes by crushing in rolls. If a finely divided product is desired, the material is milled with water in a ball mill to the desired size, dried and then disintegrated. If a solid body is desired, the milled material may be pressed into the required shape and refired at an elevated temperature.

Examples of specific methods of practicing the invention are as follows:

Example 1

To prepare Cr_2TiO_5: 152 grams of green chromium oxide is mixed with 80 grams of pigment grade TiO_2. 160 cc. of water is added and the batch is ground in a ball mill for 2 hours. The

slip is discharged and thoroughly dried and then calcined for 8 hours at 2600° F., cooled, and then ground to −325 mesh. Yield is 230 grams or approximately theoretical.

Example 2

To prepare $Cr_2Ti_8O_{19}$: 152 grams of green chromium oxide is mixed with 640 grams of pigment grade TiO_2. 550 cc. of water is added and the batch is ground in a ball mill for 2 hours. The slip is discharged, thoroughly dried and calcined for 8 hours at 2600° F., cooled and then ground to −325 mesh. Yield is 790 grams or approximately theoretical.

Example 3

To prepare $Cr_2Ti_{27}O_{57}$: 152 grams of green chromium oxide is mixed with 2160 grams of pigment grade titanium oxide. 1500 cc. of water is added and the batch is ground in a ball mill for 2 hours. The slip is discharged, thoroughly dried and calcined for 8 hours at 2600° to 2700° F., cooled and then ground to −325 mesh. Yield is 2300 grams or approximately theoretical. The power factor and dielectric constant of this material at various temperatures are represented in the following table (measured at 1 megacycle):

Table

Temperature, °C.	Power factor	Dielectric constant
18	6.82	74.7
30	8.31	75.3
40	9.01	75.4
50	10.19	75.8
60	12.23	76.4
70	14.07	77.3
80	17.57	78.8
90	21.68	81.0
100	27.47	84.8
110	32.68	88.9
120	38.27	94.8
130	44.72	102.0
140	51.69	110.8
150	60.00	123.6

Examples 4–10

		Cr_2O_3	TiO_2
4	1 mole Cr_2O_3 + 1 mole TiO_2 = 152 g. :	80 g.	
5	2 moles Cr_2O_3 + 3 moles TiO_2 = 304 g. :	240 g.	
6	1 mole Cr_2O_3 + 2 moles TiO_2 = 152 g. :	160 g.	
7	1 mole Cr_2O_3 + 4 moles TiO_2 = 152 g. :	320 g.	
8	1 mole Cr_2O_3 + 8 moles TiO_2 = 152 g. :	640 g.	
9	1 mole Cr_2O_3 + 12 moles TiO_2 = 152 g. :	960 g.	
10	1 mole Cr_2O_3 + 20 moles TiO_2 = 152 g. :	1600 g.	

Chromium oxide of ceramic grade and titanium oxide of pigment grade were wet mixed in a ball mill in the above proportions, dried, and then calcined as indicated in zircon crucibles. The calcined residues were milled through 325 mesh, dried, and then pressed into squat cylinders approximately 1 inch in diameter and ½ inch in thickness. These cylinders were then refired to 2650° for 3 hours, reaching that temperature in 3 hours, to form a hard, dense mass.

The materials made according to Examples 4–10 were prepared for testing by applying a lead foil of 0.003 inch thickness to the flat surfaces and attached by means of a thin film of petrolatum. The resistance characteristics of these sintered bodies were then determined by means of a General Radio type 650A impedance bridge. Resistance was measured first under a direct current of 10 volts and then under an alternating current of 1000 cycles. The change of resistance with temperature of the material of Example 10 was determined under direct current from room temperature to 150° C. The results of these tests are indicated in the following tables:

Tables

Example No.	D. C. resistivity at 10 volts	A. C. resistivity at 1,000 cycles
	Meg./cm.	*Meg./cm.*
4	2.72	1.18
5	2.02	0.95
6	2.80	1.44
7	1.59	0.82
8	0.91	0.47
9	1.56	0.61
10	2.02	0.91

TEMPERATURE D. C. RESISTIVITY OF EXAMPLE 10

Temperature:	Resistivity, Meg./cm.
25° C.	2.02
70° C.	1.69
85° C.	1.57
95° C.	1.45
115° C.	0.95
130° C.	0.76
150° C.	0.66

Preliminary measurements also indicate that at higher voltages, higher exciting frequencies, or higher temperatures or any combination of these conditions, much lower resistivities are obtained.

Example 11

900 grams of pigment grade TiO_2, previously heated to a temperature of 1350° C. and maintained there for several hours, and 100 grams of chromium titanate according to Example 1, are thoroughly mixed by ball milling with water, dried and disintegrated. To this mixture 10% by weight of 5% gelatin solution is added and thoroughly incorporated and the batch passed through a 20 mesh screen. 125 grams of the batch is placed in the cavity of a steel mold 4 inches in diameter and the specimen formed under a pressure of 1200 pounds per square inch. The body is then fired according to the following schedule: it is brought to the peak temperature (2600° F.) at the rate of 40° F. per hour. It is held twelve hours at the peak temperature, the temperature then decreased at the rate of 50° F. per hour to 1200° F., then at the rate of 100° F. per hour from 1200° F. to 800° F., and the furnace then shut down. The resistivity of this material was less than 3 megohms per centimeter, while the power factor was 8.8% and the dielectric constant 73.0.

In addition to the uses mentioned above, some of the chromium titanates of the present invention possess properties which indicate possibilities in connection with the rectification of alternating electric currents. Furthermore, they may be utilized, in combination with titanium oxide, to enhance the photosensitive properties of the latter.

As many variations are possible within the scope of this invention, it is not intended to be limited except as defined by the appended claim.

We claim:

The method which comprises calcining a mixture consisting essentially of 6 to 79% chromic oxide (Cr_2O_3) and 94 to 21% titanium dioxide at a temperature in excess of 2000° F. for a period of time sufficient to insure change of color of the mixture to a black color and under conditions sufficiently oxidizing to insure that the chromium is kept in the trivalent state and the titanium in the quadrivalent state.

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