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

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1 Claim. (Cl. 23—51)

This invention relates to new and useful compositions comprising vanadium 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.

In accordance with this invention, an entirely new group of compounds has been discovered, which are suitable for the uses listed above. These compounds are those which vary in composition from 2 moles of V_2O_5 per mole of TiO_2 to 1 mole of V_2O_5 per 31 moles of TiO_2 , and are identified as vanadium titanates. A number of definite compounds may exist in this series, some of which may have the following formulae: V_4TiO_{12} , V_2TiO_7 , $V_2Ti_8O_{21}$, $V_2Ti_{16}O_{37}$, $V_2Ti_{31}O_{67}$. On the other hand, certain of the members of this series may exist as mixtures of vanadium titanates of different formulae, or mixtures of certain vanadium titanates with TiO_2 or V_2O_5 . In fact mixtures outside the molecular limits specified above have useful electrical properties.

In general, however, a composition varying from 6% to 82% V_2O_5 and 94% to 18% 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 ammonia or organic amines, 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 vanadium is kept in the pentavalent state and titanium in the quadrivalent state) an intimate mixture of the finely divided oxides themselves, such as at a temperature in excess of $2000^\circ F$. For those compositions of TiO_2 and V_2O_5 containing 35 or more percent of V_2O_5 a rapid and complete reaction is obtained at 1700° to $1800^\circ F$; for those compositions containing 25% to 35% V_2O_5 a rapid and complete reaction is obtained at 1800° to $1900^\circ F$; while for those compositions containing less than 25% V_2O_5 a temperature of at least $2000^\circ F$ is preferred for complete combination. Although at the temperatures mentioned a complete reaction is obtained in a short period (30 to 45 minutes) an enhancement of the desirable electrical properties is obtained if the calcination is continued at the specified temperature for at least two hours after the period that previous reactions have shown chemical combination to be complete. The extra roasting period causes a decided increase in size of individual crystals. In each case, a highly crystalline glistening dark brown residue is obtained, in which the microscopical identity of either of the original constituents is lost. It is therefore presumed that a definite chemical combination, or a mixture of combinations, is formed in each case, and that they should be designated as vanadium titanates.

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 V_2TiO_7 , 214 grams of hydrated vanadium pentoxide (equivalent to 181.9 grams of V_2O_5) is mixed with 80 grams of pigment grade titanium dioxide. 200 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 3 hours at 1725° F. After cooling, it is ground in a ball mill with water to -325 mesh, dried, and then disintegrated. The yield is 260 grams or approximately theoretical.

EXAMPLE 2

To prepare $V_2Ti_{16}O_{37}$, 214 grams of hydrated vanadium pentoxide (equivalent to 181.90 grams of V_2O_5) is mixed with 1280 grams of pigment grade TiO_2 . 800 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 4 hours at 2000° F., cooled and then ground to -325 mesh. The yield is 1450 grams or approximately theoretical.

EXAMPLE 3

To prepare $V_2Ti_{16}O_{17}$, 214 grams of hydrated vanadium pentoxide (equivalent to 181.90 grams of V_2O_5) is mixed with 480 grams of pigment grade TiO_2 . 450 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 3½ hours at 1850° F., cooled, and then ground to -325 mesh. The yield is 658 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
	Per cent	
22.....	16.3	101.1
40.....	17.3	102.0
60.....	18.5	102.7
75.....	23.6	107.5
100.....	28.1	112.0
110.....	32.0	116.5
125.....	36.6	121.9
135.....	41.0	127.3
150.....	47.6	136.7

In addition to the uses mentioned above, some of the vanadium 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 6.8 to 82% vanadium pentoxide and 93.2 to 18% titanium dioxide at a temperature in excess of about 1700° 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 vanadium is kept in the pentavalent state and the titanium in the quadrivalent state.

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