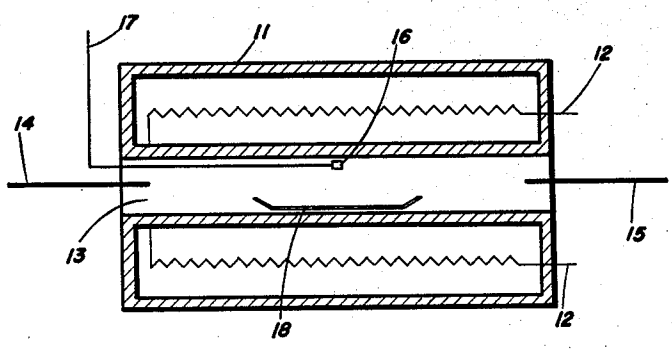
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PROCESS FOR PRODUCING TERNARY THIO COMPOUNDS

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PROCESS FOR PRODUCING TERNARY THIO COMPOUNDS

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This invention relates to ternary sulfides of alkali metals and alkaline earth metals with titanium and zirconium. It is particularly concerned with a novel process for producing such compounds and with certain novel thiozirconates and thiotitanates.

It has previously been known that thiotitanates of alkaline earth metals can be prepared by heating together a mixture of an alkaline earth metal sulfide and titanium sulfide. The reaction involved presumably is represented by:

$$BaS+TiS_2 \rightarrow BaTiS_3$$

However, since the separate preparation of titanium disulfide is necessary in this method, an easier way of producing these compounds has been considered desirable. It has also been desired to produce other double sulfides of titanium as well as those of zirconium.

An object of the present invention is, therefore, to provide a practical and convenient process for the preparation of alkali metal and alkaline earth metal thiozirconates and thiotitanates.

Another object of the present invention is to provide a process for the preparation of alkali metal and alkaline earth metal thiozirconates and thiotitanates which utilizes only easily obtained reacting materials.

A further object of the invention is to provide novel ternary sulfides of alkali metals and alkaline earth metals with titanium and zirconium.

Other objects and advantages of the present invention will be apparent from the following description of the nature and practice of the invention taken in conjunction with the accompanying drawing which illustrates diagrammatically apparatus by which the novel process may be carried on.

The preparation of thiozirconates and thiotitanates (which terms are meant to designate ternary compounds, in which sulfur has replaced the oxygen of metallic zirconates or titanates, with typical formulas such as $BaZrS_3$ and $BaTiS_3$) according to the present invention involves the heating of alkali metal or alkaline earth metal zirconates or titanates, as the case may be, in an atmosphere of carbon disulfide and in the absence of air. This is preferably done in apparatus like that schematically illustrated in the accompanying drawing. In this, the numeral 11 indicates an electrically heated furnace of the "Lindberg" type provided with electrical leads 12 and a heating chamber 13 from which air may be excluded. An inlet line 14 is provided to supply dry argon and carbon disulfide vapor to the chamber 13 and an exhaust line 15 is provided to lead waste gases to suitable apparatus where the sulfur-containing gases may be removed. A pyrometer 16 with leads 17 is provided in the chamber 13 for determining the temperature therein.

In the following two examples there is described, respectively, the preparation of barium thiozirconate and barium thiotitanate according to the present novel process.

EXAMPLE 1

A quantity of barium zirconate ($BaZrO_3$) is placed in a zircon boat 18 in the heating chamber 13 of the furnace 11. The chamber 13 then is evacuated by connection of a vacuum pump (not shown) to the exhaust line line 15 therefrom. After evacuation the chamber is filled with argon through the line 14. The temperature in the chamber is then raised to 1050° C. and argon carrying the CS_2 vapor is passed through the chamber for 4 hours. The product in the boat is found to be a bluish-black, granular material of approximately 4.8 specific gravity, analyzing Ba 42.3%, Zr 28.1%, S 28.6%. The analytical results are within normal experimental error of the theoretical composition: Ba 42.16%; Zr 28.31%, S 29.53% for barium thiozirconate ($BaZrS_3$). It is also found that the X-ray diffraction pattern of the product is distinct and unlike that of barium zirconate, barium sulfide, or zirconium sulfide. It does, however, correspond to the X-ray diffraction pattern of barium thiozirconate produced by heating together barium sulfide and zirconium disulfide.

EXAMPLE 2

Using procedures similar to that employed in Example 1, barium titanate ($BaTiO_3$) is heated for 4 hours at 1000° C. in an argon and carbon disulfide atmosphere to obtain a black, crystalline product which analyzed Ba 47.8%, Ti 17.2%, S 33.5%. This corresponds to the theoretical composition for barium thiotitanate ($BaTiS_3$) which is Ba 48.80%, Ti 17.02%, S 34.18%. The product has the same X-ray diffraction pattern as that found for barium thiotitanate prepared by the known method previously mentioned.

The preparation, according to the present invention, of lithium thiozirconate and lithium thiotitanate, is described in the following two examples. These examples typify the production of alkali metal thio compounds with titanium and zirconium.

EXAMPLE 3

Lithium thiozirconate is made by procedure like that described in Example 1, using as a starting material lithium zirconate (Li_2ZrO_3) and heating it in argon and carbon disulfide vapor for 16 hours at 1050° C. The novel product is a granular crystalline material, deep violet in color. It has an X-ray diffraction pattern with strong peaks at 6.11 A., 2.62 A., and 1.85 A. that appears to be unique and is distinct from the patterns of lithium zirconate, lithium sulfide and zirconium sulfide. Analysis of the product shows Li 6.09%, Zr 45.4%, S 45.31%. This is very close to the theoretical composition of Li 6.86%, Zr 45.59%, S 47.55%.

EXAMPLE 4

Using the same procedure described in Example 1, lithium titanate (Li_2TiO_3) is heated for 20 hours at 900° C. in an atmosphere of carbon disulfide vapor and argon to obtain lithium thiotitanate. This is a granular, crystalline, brownish-black material. It is also found to have a distinctive X-ray diffraction pattern characterized by peaks which are not found in the patterns of the individual sulfides or the original lithium titanate.

Other novel alkali metal and alkaline earth metal thio-

zirconates and thiotitanates are produced by employing the same procedure as that described above in Example 1. The following examples give details concerning the production of these products.

EXAMPLE 5

Potassium thiozirconate (K_2ZrS_3) is prepared from potassium zirconate (K_2ZrO_3) by reaction with CS_2 in argon at 1000° C. for 24 hours. It is a well crystallized, granular material with a purple or violet color and a hitherto undescribed X-ray diffraction pattern which, however, resembles that of lithium thiozirconate.

EXAMPLE 6

Potassium thiotitanate (K_2TiS_3) is prepared from potassium titanate (K_2TiO_3) by reaction with CS_2 at 900° C. for 24 hours. The granular, crystalline product is brownish-black in color. Like the other thiotitanates and thiozirconates this product has a distinctive and apparently unique X-ray diffraction pattern. The X-ray pattern is very similar, however, to that of lithium thiotitanate.

EXAMPLE 7

Sodium thiozirconate (Na_2ZrS_3) is produced by the reaction of sodium zirconate (Na_2ZrO_3) with CS_2 in argon at 1000° C. for 17 hours. The granular crystalline product is black and has an apparently unique X-ray diffraction pattern which, however, is quite similar to that of lithium thiozirconate.

EXAMPLE 8

By reacting sodium titanate (Na_2TiO_3) with CS_2 in argon at 1000° C. for 24 hours sodium thiotitanate (Na_2TiS_3) is produced. This is a black, crystalline material which has a distinct X-ray diffraction pattern which is not characteristic of sodium titanate, sodium sulfide or titanium sulfide but closely resembles the X-ray patterns of potassium and lithium thiotitanates.

EXAMPLE 9

Calcium thiozirconate ($CaZrS_3$) is obtained by reacting, at 1000° C. for 24 hours, calcium zirconate ($CaZrO_3$) with CS_2 in an argon atmosphere. The granular, crystalline product is black and has a distinct and previously unknown diffraction pattern. Analysis showed it to have the composition: Ca 17.7%, Zr 39.5%, S 42.0%. This corresponds closely to the theoretical composition: Ca 17.54%, Zr 40.37%, S 42.09%.

EXAMPLE 10

Strontium thiozirconate ($SrZrS_3$) is produced by the reaction of strontium zirconate ($SrZrO_3$) with CS_2 in argon at 1000° C. for 20 hours. The X-ray diffraction pattern of the black crystalline product shows it to be novel and isomorphous with calcium thiozirconate.

It has also been possible to produce, by the present novel method, calcium thiotitanate ($CaTiS_3$) and strontium thiotitanate ($SrTiS_3$), both of which have been previously prepared by another procedure. Temperatures of 900° C.–1100° C. are employed with heating times of from 6 to 24 hours.

In Examples 1 and 2 the production of barium thiozirconate and barium thiotitanate is described. It has been found that by varying the temperature of reaction in the described method novel colored products of varying composition can be obtained. This is illustrated in the following examples.

EXAMPLE 11

Using apparatus like that shown in the drawing and the general procedure described in Example 1 barium zirzconate is heated in an atmosphere of argon and carbon disulfide for 4 hours at a temperataure of 800° C. There is obtained a dark maroon, crystalline powder containing 15.3% sulfur. X-ray examination indicates that

the product consists of approximately 45% $BaZrO_3$, 40% $BaZrS_3$ and 15% of an unidentified third phase.

By varying the temperature of reaction, powders having a wide range of color and sulfur content and varying degrees of crystallinity are obtainable, as set forth in the following table. In each case the heating time was 4 hours and the composition was estimated from X-ray data.

Table A

Reaction Temperature, Degrees C.	Product		
	Percent S	Color	Estimated Composition
400		Yellowish	$BaZrO_3$.
500		Yellow-orange	$BaZrO_3$.
600		Deep orange	$BaZrO_3$.
700	4.18	Orange-red	$BaZrO_3$ 88%, $BaZrS_3$ 12%.
750	9.65	Rust	$BaZrO_3$ 65%, $BaZrS_3$ 25%, X 10%.
900	21.2	Violet	$BaZrO_3$ 20%, $BaZrS_3$ 65%, X 15%.
1,000	27.1	Grey-black	$BaZrS_3$.
1,100	28.6	Blue-black	$BaZrS_3$.

NOTE.—"X" in composition column refers to a phase which has not been identified.

A similar series of colored products is obtained by heating barium zirconate in a carbon disulfide and argon atmosphere at constant temperature for varying periods of time. In the following table examples of products resulting from such variation are described.

Table B

Reaction Temperature, Degrees C.	Reaction Time, Hours	Product	
		Color	Percent S
750	4	Rust	9.65.
750	6	Deep red	
750	12	Maroon	
750	18	Violet	20 (approx.).

Products having different colors can also be obtained by varying the reaction conditions during the heating of barium titanate in an argon-carbon disulfide atmosphere. At temperatures of 700° C.–1000° C. a heating time of 4 hours results in the production of a black, crystalline barium thiotitanate. However, if a temperature of 400° C. is employed the product is pale violet in color and the composition as determined by X-ray is still $BaTiO_3$. At a temperature of 500° C. the color of the granular product is a deeper violet and the composition is found to be 95% $BaTiO_3$-5% $BaTiS_3$. Carrying out the reaction for 4 hours at 600° C. results in a violet-black crystalline composition which is shown by X-ray diffraction to be 70% $BaTiO_3$-30% $BaTiS_3$.

It is to be noted that the colored products obtained by heating barium titanate and barium zirconate in carbon disulfide vapor are produced only by the method described. Attempts made to produce them by heating mixtures of barium sulfide with titanium disulfide and with zirconium disulfide have been unsuccessful.

In carrying out the process of the present invention to produce thiotitanates and thiozirconates of the alkali and alkaline earth metals one may start, as in the preceding examples, with a titanate or zirconate of the desired metal. If desired, however, one may use as a starting material a compound, such as barium titanium oxalate, which decomposes to form barium titanate on heating to 1000° C. It is also possible to use other oxygen-containing compounds such as mixtures of oxides or hydrous oxides or compounds such as carbonates, etc. which at the temperatures involved in the process decompose to oxides or react like oxides to form zirconates or titanates. The term "oxide" as employed in the claims

includes such compounds. The following examples illustrate such variations.

EXAMPLE 12

Using apparatus like that illustrated in the drawing and the procedure described in Example 1 finely divided barium titanium oxalate is heated for 4 hours at a temperature of 1000° C. in an atmosphere of argon and CS_2 vapor. A black, crystalline, granular product is obtained that by X-ray diffraction appears to be identical with the barium thiotitanate product of Example 2.

EXAMPLE 13

If an intimate mixture of finely divided lithium carbonate and ZrO_2 in equi-molar amounts is heated for 20 hours at 1050° C. in an atmosphere of argon and carbon disulfide vapor there is produced a black, crystalline product. This is found by X-ray diffraction to be the same as the lithium thiozirconate of Example 3.

As shown by the following example, the materials employed may be, if desired, more or less impure commercially available products.

EXAMPLE 14

On heating a finely divided mixture of lithium carbonate and rutile, the latter being a titanium ore comprising principally TiO_2, in equimolar amounts in CS_2 vapor and argon for 20 hours at 900° C. there is obtained a black, crystalline powder. This is determined by X-ray diffraction to be the same as the lithium thiotitanate obtained in Example 4.

The novel thiozirconates and thiotitanates of the present invention may be utilized as pigments in coating compositions as illustrated in the following example.

EXAMPLE 15

A brushing lacquer is produced by compounding the following:

	Parts by weight
Cellulose acetate-butyrate ester	18
Acetone	20
Butyl acetate	25
Ethyl lactate	10
Ethyl alcohol	22
Tricresyl phosphate	5

The cellulose ester is dissolved in the acetone and butyl acetate and the viscous mixture is thinned by adding the ethyl lactate, alcohol, and tricresyl phosphate plasticizer. There is then dispersed in the vehicle 30 parts by weight of very finely ground lithium thiozirconate. This results in a lacquer which when brushed on metal tile and dried gives a very pleasing violet-colored coating.

Coatings of other colors can be obtained by substituting for the lithium thiozirconate in the lacquer above described other ternary sulfides of the group disclosed herein or the variously colored products resulting from the heating of barium titanate and barium zirconate with CS_2 under different conditions. A variety of attractive appearing coatings can thus be produced. Other vehicle compositions may, of course, be employed and, if desired, mixtures of the colored pigments with each other and/or with other suitable pigments may be used. Since the pigments of the present invention contain sulfur, it will, of course, be recognized that lead pigments, for example, are not suitable ones for such mixtures.

It will be understood that in carrying out the process of the present invention other suitable apparatus may be used. Further, other inert gases may be used instead of argon with equally good results.

I claim:

1. A process for producing ternary sulfides which comprises heating at a temperature of from about 400° C. to about 1100° C. and for a period of at least about 4 hours in the presence of carbon disulfide vapor and in the absence of air, a charge comprising an oxide of a metal selected from the group consisting of zirconium and titanium and an oxide of a metal selected from the group consisting of alkali metals and alkaline earth metals.

2. A process as set forth in claim 1 in which said charge comprises an oxygen-containing compound of a metal selected from the group consisting of zirconium and titanium and a metal selected from the group consisting of alkali metals and alkaline earth metals said compound at the temperatures involved in the process decomposing to form a compound of the group consisting of zirconates and titanates of alkali and alkaline earth metals.

3. A process for producing ternary sulfides of alkali metals and alkaline earth metals with zirconium and titanium which comprises heating at a temperature of from about 400° C. to about 1100° C. and for a period of at least about 4 hours in the presence of carbon disulfide vapor and in the absence of air a compound selected from the group consisting of zirconates and titanates of alkali metals and alkaline earth metals.

4. A process as set forth in claim 3 in which said alkali metals and alkaline earth metals are selected from the group consisting of Na, K, Li, Ba, Sr, and Ca.

5. Colored compositions resulting from the heating to partially but not completely replace the oxygen thereof with sulfur of a compound of the group consisting of $BaTiO_3$ and $BaZrO_3$ in an atmosphere of carbon disulfide vapor and in the absence of air at temperatures of from 400° C. to 1100° C., said compositions being variable in composition but containing sulfur and being composed in at least major part of at least one compound selected from the group consisting of $BaTiO_3$ and $BaTiS_3$ in the case of those compositions derived from $BaTiO_3$ and being composed at least in major part of at least one compound selected from the group consisting of $BaZrO_3$ and $BaZrS_3$ in the case of those compositions derived from $BaZrO_3$ and the color of said compositions and the sulfur content thereof being variable with the time and temperature of heating.

6. A colored composition as set forth in claim 5 in which $BaTiO_3$ is heated.

7. A colored composition as set forth in claim 5 in which $BaZrO_3$ is heated.

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