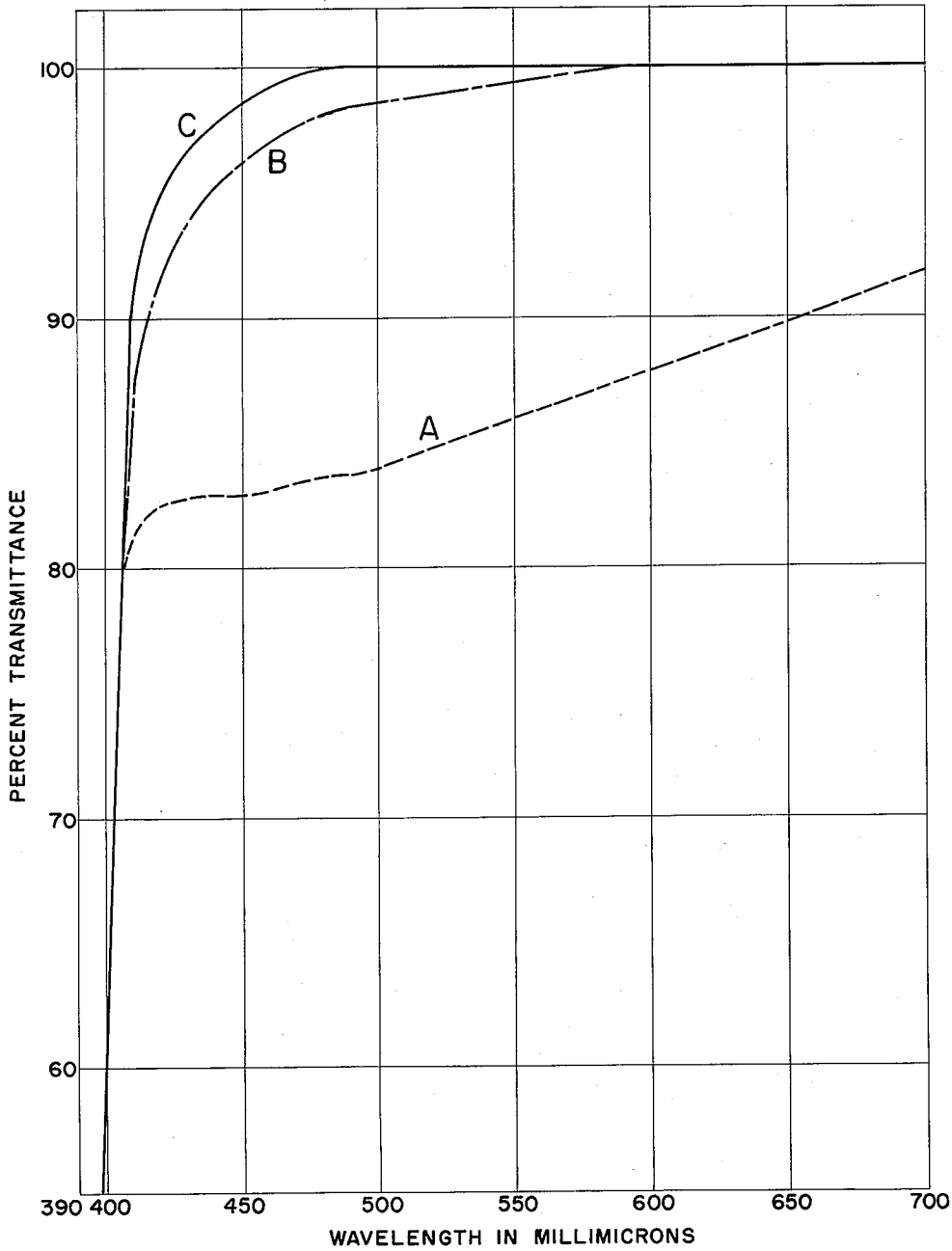


May 23, 1961

M. D. BEALS ET AL
METAL TITANATE PREPARATION

2,985,518

Filed Oct. 1, 1958



INVENTORS
MALCOLM D. BEALS
LEON MERKER
BY *Robert L. Holiday*
AGENT

1

2,985,518

METAL TITANATE PREPARATION

Malcolm D. Beals, Fanwood, N.J., and Leon Merker, Bronx, N.Y., assignors to National Lead Company, New York, N.Y., a corporation of New Jersey

Filed Oct. 1, 1958, Ser. No. 764,722

7 Claims. (Cl. 23—295)

This invention relates in general to a method for the preparation of single crystal boules. More specifically, it relates to a method for improving the color of strontium titanate single crystal boules.

Strontium titanate powdered material when melted and fused in an oxy-hydrogen flame forms a single crystal boule. A process for producing such a single crystal is more fully described and claimed in U.S. Patent Nos. 2,628,156 and 2,777,255 both of which are assigned to the same assignee as the instant invention. According to these patents, substantially pure strontium titanate powdered material is fed through an oxy-hydrogen flame onto a pedestal where the fused strontium titanate forms a boule. This boule after growing to a sufficient size is then annealed by heating in an oxidizing atmosphere at a temperature of 1000° C. to 1700° C. After annealing the boule is then subjected to a low temperature oxidizing heat treatment of 200° C. to 600° C. to improve the color of the boule. The product is then substantially transparent with only a slight trace of color. This single crystal is then cut into various sizes and shapes which are used primarily for optical objects such as lenses, prisms, gem stones and the like.

It is obvious that the extent to which these optical objects are used is dependent upon the color, transparency and clarity of the final product. In most instances for optical purposes it is desirable to obtain a material which appears colorless.

It is, therefore, an object of the instant invention to provide a process for treating a strontium titanate single crystal to produce a more nearly colorless product. Another object is to treat strontium titanate boules to produce more nearly colorless boules having a higher degree of transparency and clarity. These and other objects will become more apparent from the following more complete description of the instant invention.

Broadly, this invention contemplates a process for treating an annealed strontium titanate single crystal boule which comprises heating said boule in the presence of a nonreactive atmosphere at a temperature of 500° C. to 1000° C.

In carrying out the instant invention it is preferred to employ a strontium titanate single crystal boule which has previously been annealed at a temperature between 1000° C. and 1700° C. and which has been subjected to the oxidizing low temperature heat treatment described above.

Strontium titanate boules after the annealing treatment usually possess a pinkish color which is removed by the low temperature oxidizing heat treatment. Although it is not known it is believed that the pink coloration formed during the annealing step is due to slight physical defects in the crystal structure and that the low temperature oxidizing treatment removes these defects.

Subjecting these substantially transparent boules to the non-reactive heat treatments of the instant invention reduces the color of the boule still further until they appear

2

to be colorless. The effect of this treatment is best shown by the spectrophotometric curves.

In the drawing is shown three spectrophotometric curves of a strontium titanate boule: Curve A represents the strontium titanate boule after the annealing treatment; curve B represents the annealed boule after the low temperature oxidizing heat treatment; while curve C represents the boule after it has been heat treated in the non-reactive atmosphere of the instant invention.

It is obvious from the drawing that after the non-reactive heat treatment of the instant invention, the boule possesses a higher degree of transparency than before said heat treatment and in addition appears to be less yellow.

It also has been discovered that strontium titanate boules having a color and transparency equal to curve C may be produced by directly heat treating annealed boules to 500° C. to 1000° C. in the presence of the non-reactive atmosphere without previously treating the annealed boules with the low temperature oxidizing heat treatment. Such a procedure is adequate; however, if the low temperature oxidizing heat treatment is eliminated, the time of heat treatment under a non-reactive atmosphere should be somewhat lengthened.

The non-reactive atmosphere employed in the instant invention may be selected from any atmosphere which does not react with the strontium titanate crystal structure. Among those which have been successfully employed include argon, helium and other inert gases, nitrogen and steam. Another atmosphere which has also been successful is to heat treat the boule in a vacuum of less than 1.0 mm. pressure.

In carrying out the instant invention the annealed strontium titanate boule, whether or not it is subjected to the low temperature oxidizing heat treatment, is merely heated to 500° C. to 1000° C. in the presence of the non-reactive atmosphere and held at that temperature for ½ hour to 8 hours. After the heat treatment the boule is allowed to cool to room temperature.

In order to more fully illustrate the instant invention the following examples are presented:

Example 1

Using an oxy-hydrogen burner and passing substantially pure and finely divided strontium titanate feed material into a zone heated to 2075° C., a single crystal boule of strontium titanate 1 inch long and ½ inch wide was prepared in 2 hours. After forming, the boule was then annealed at 1500° C. for 25 hours, cooled slowly and then heated at 300° C. for 48 hours under an oxidizing atmosphere. The boule was then free from strains and possessed a substantially colorless appearance except for having a very slight yellow tone.

According to the instant invention, this boule was then heat treated under an argon atmosphere for 2 hours at 700° C. to reduce the yellow tone.

In order to show the effects of the heat treatment of the instant invention, spectrophotometric curves were run on the boule during the processing steps; curve A representing the boule after the annealing step; curve B after the low temperature oxidizing heat treatment and curve C after the non-reactive heat treatment of the instant invention. Curve C shows clearly that the boule treated according to the instant invention is less yellow and more transparent than it was before this instant non-reactive heat treatment.

Example 2

Another boule of equal size which had also been annealed at 1500° C. for 24 hours and cooled slowly to 900° C. was then held in a steam atmosphere for four and one-half hours at 900° C. It should be noted that

3

in this run the annealed boule was not subjected to the low temperature oxidizing heat treatment. The steam treated boule when cooled possessed a color and transparency equal to the boule previously obtained in Example 1.

Similar boules were treated in like manner except that other non-reactive atmospheres were used in place of argon. Steam, nitrogen, helium and a vacuum of 0.1 mm. pressure were singly employed and substantially identical improvements in the boules were obtained. The temperatures used during these treatments were between 500° C. and 900° C.

From the above description and by the examples shown it has clearly been shown that the non-reactive heat treatment of the instant invention produces boules which are more nearly colorless, less yellow and more transparent than the boules previously produced. The boules produced by the instant invention are therefore more useful for optical objects than those possessing inferior properties.

While this invention has been described and illustrated by the examples shown, it is not intended to be strictly limited thereto, and other variations and modifications may be employed within the scope of the following claims.

We claim:

1. Process for reducing the color and increasing the

4

transparency of an annealed strontium titanate boule which comprises heating said boule in the presence of a non-reactive atmosphere at a temperature of 500° C. to 1000° C.

5 2. Process according to claim 1 in which said non-reactive atmosphere is argon.

3. Process according to claim 1 in which said non-reactive atmosphere is nitrogen.

10 4. Process according to claim 1 in which said non-reactive atmosphere is helium.

5. Process according to claim 1 in which said non-reactive atmosphere is steam.

15 6. Process according to claim 1 in which said non-reactive atmosphere is a vacuum of less than 1.0 mm. pressure.

7. Process according to claim 1 in which the non-reactive heat treatment is carried out from 1/2 hour to 8 hours.

20 **References Cited in the file of this patent**

UNITED STATES PATENTS

2,628,156	Merker -----	Feb. 10, 1953
2,685,524	Merker -----	Aug. 3, 1954
25 2,777,255	Merker -----	Jan. 15, 1957
2,792,287	Moore -----	May 14, 1957
2,799,912	Greger -----	July 23, 1957