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PROCESS FOR THE PRODUCTION OF FERROMAGNETIC CHROMIUM DIOXIDE
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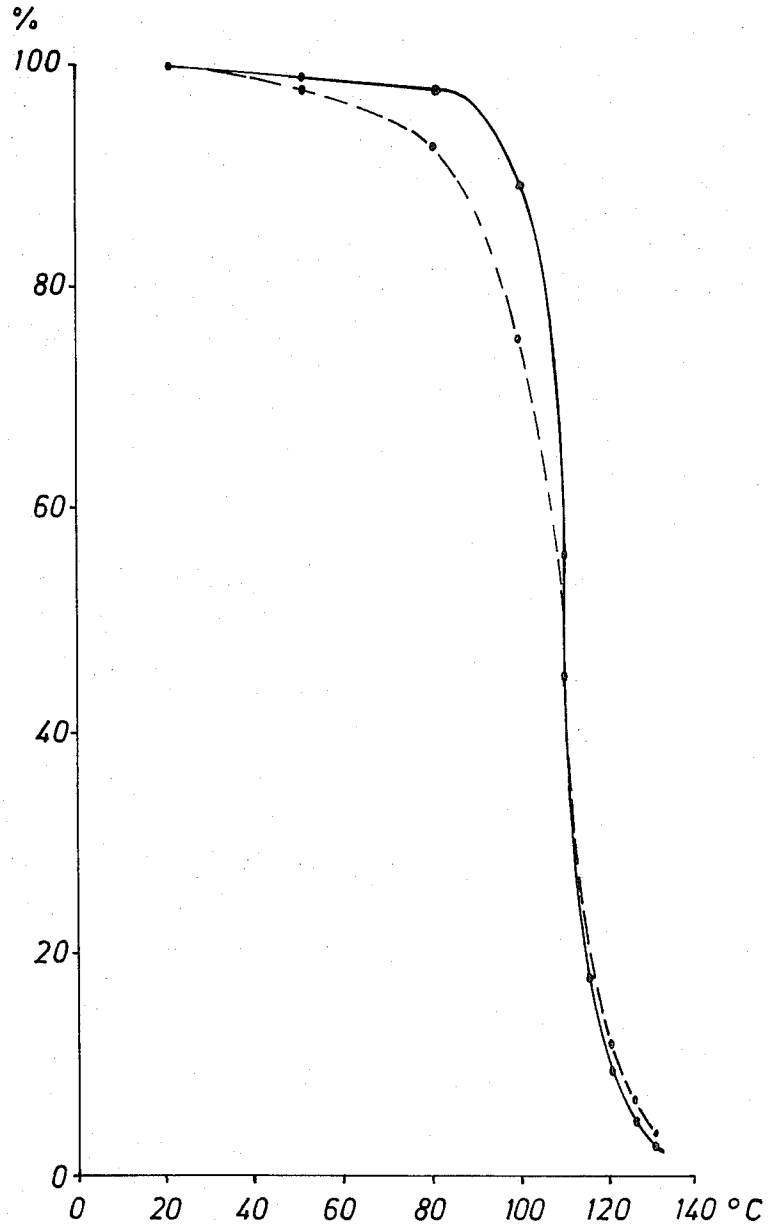

INVENTOR.

FRITZ RODI

BY Connolly and Hutz
their attorneys

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PROCESS FOR THE PRODUCTION OF FERROMAGNETIC CHROMIUM DIOXIDE

Fritz Rodi, Kaldenhausen, Germany, assignor to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany

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ABSTRACT OF THE DISCLOSURE

A method for the production of ferromagnetic chromium dioxide by dehydrating and tampering chromium oxide hydrate green which is obtained by reducing a chromium (VI)-solution with a reducing organic substance at a temperature of from 300° C. to 400° C. and at a pressure of from 250 to 350 kg./cm.². The obtained finely divided chromium oxide in which the average oxidation state of the chromium is in the range of from 3 to 4 is heated together with an oxidising agent under hydrothermal conditions at a temperature of from 50° C. to 400° C. and at a pressure of from 50 to 500 kg./cm.², optionally in the presence of a substance, which acts as a modifier.

This invention relates to a process for the production of high-grade ferromagnetic chromium dioxide for magnetogram carriers.

According to U.S. patent specification No. 2,956,955, chromium dioxide crystallising in the rutile lattice can be obtained in the pure form by the decomposition of chromic acid under hydrothermal conditions. The products thus obtained are in the form of coarse particles, the coercive forces being below 100 [oe.]; accordingly, they are unsuitable for numerous application, for example magnetic recording processes.

There has been no shortage of attempts to obtain chromium dioxide with improved magnetic properties. Thus, it is possible (according to British patent specifications Nos. 859,937 and 1,006,610 or U.S. patent specification No. 3,371,043) to control the particle size of the chromium dioxide particles and hence also their magnetic properties by adding small quantities of suitable modifiers. The manner in which the modified elements are introduced is a factor of crucial importance (U.S. patent specifications Nos. 3,117,093 and 3,371,043).

Finally, U.S. patent specification No. 3,278,263 relates to a process by which it is possible to produce chromium dioxide which is free from modifiers and has outstanding properties. Chromium oxides and chromium oxide hydrates, in which the average valency of the chromium is in the range of from 3 to 4, are oxidised into chromium dioxide under hydrothermal conditions. In the preferred embodiment of the process, a chromium oxide hydrate obtained from a chromium (III-salt) solution, for example a chromium(III)-nitrate solution, by precipitation with alkalis, for example ammonia, is used as a starting material for the chromium oxide employed. Chromium oxide hydrate produced in this way is dehydrated and tempered at a temperature in the range of from 200° C. to 1000° C. and thus converted into a chromium oxide with chromium in the average oxidation state of between 3 and 4. Chromic acid is preferably used as an oxidising agent for oxidation into chromium dioxide under hydrothermal conditions. Chromic acid is also converted into chromium dioxide under the reaction conditions so that an excess of the oxidising agent does not have any harmful effects.

This invention provides a process for the production of ferromagnetic chromium dioxide by heating finely divided chromium oxide in which the average oxidation state of the chromium is between 3 and 4, with an oxidising agent, optionally in the presence of a substance acting as a modifier, under hydrothermal conditions at a temperature of from 50 to 400° C. and at a pressure of from 50 to 500 kg./cm.², in which a finely divided chromium oxide is used which has been obtained by dehydrating and tempering a precipitated chromium oxide hydrate green, prepared by reducing a chromate or polychromate solution with an organic substance at a temperature of from 300 to 400° C. and under a pressure of from 250 to 350 kg./cm.².

More specially this invention relates to an improved process for the production of ferromagnetic chromium dioxide, wherein a chromate or polychromate solution is reduced by an organic substance at a temperature of from 300° C. to 400° C. and at a pressure of from 250 to 350 kg./cm.² to form chromium oxide hydrate green, wherein the resulting chromium oxide hydrate green is dehydrated and tempered to produce finely divided chromium oxide in which the average oxidation state of the chromium is in the range of from 3 to 4, and wherein the chromium oxide is heated with an oxidising agent under hydrothermal conditions at a temperature of from 50° C. to 400° C. and at a pressure of from 50 to 500 kg./cm.².

A certain type of chromium oxide hydrate green is obtained by reducing an aqueous chromate or polychromate solution, e.g. a solution of sodium chromate or soduim dichromate, under pressure with an organic substance and, for the purposes of the invention, this will be referred to as precipitated chromium oxide hydrate green. It has surprisingly been found that this precipitated chromium oxide hydrate green is eminently suitable as a starting material for the reaction to produce chromium dioxide. Substances with a reducing effect are used as the organic substances such as, for example, molasses, formaldehyde, formates, lignite powder. The reducing agent should be present in a quantity sufficient to guarantee a quantitative reaction of the dichromate into chromium oxide hydrate green.

Other known types of chromium oxide hydrate green, for example guignet green, are unsuitable (a comprehensive list of commercial chromium oxide hydrate green pigments can be found, for example, in H. Kittel, Pigmente, Stuttgart, 1960, pp. 293–297).

In order to obtain chromium dioxide with the required properties, it is advisable to dehydrate and temper the precipitated chromium oxide hydrate green before oxidation under pressure. The dehydration or tempering temperature may be in a range from 300 to 900° C. During this stage of the process, the extremely finely divided needle-shaped particles of the chromium oxide hydrate green are converted into isometric finely divided particles of chromium oxide. The chromium oxide thus prepared is distinguished by the uniform size of its particles and their limited tendency towards agglomeration, and thus meets the ideal requirements for conversion into chromium dioxide.

In a preferred embodiment of the process according to the invention, the chromium oxide prepared by dehydrating precipitated chromium oxide hydrate green is intimately mixed with water and chromic acid and treated under pressure. The ratio by weight of chromium oxide to chromic acid should be in the range from 1:1 to 1:5. If too little chromic acid is present, not all the chromium oxide used is converted into ferromagnetic chromium dioxide. If too much chromic acid is used, it is solely the chromium dioxide crystallising in the rutile lattice that

is formed, as shown by X-ray photographs, the particles, however, being too large and hence the magnetic values unsatisfactory. The quantity of water used can be varied within a wide range. A quantity of from 50 to 150% by weight of H_2O, based on the chromium oxide used, is favourable. The reaction temperature during the pressure treatment may be in a range of from 50 to 400° C., preferably of from 200 to 400° C. and the reaction pressure in a range of from 50 to 500 kg./cm.^{2}. Although higher temperatures and pressure can be used, they do not produce any improvement in the products and involve the use of fairly expensive pressure apparatus. The reaction time is not critical and can amount to a few hours.

By virtue of the process according to the invention, it is possible to obtain chromium dioxide free from modifiers with outstanding properties. If, however, particularly finely divided products are required, substances acting as a modifier may be added to the pressure-treated reaction mixture. In this way, it is possible to vary both the particle sizes and hence also the magnetic properties, over a relatively wide range and to adapt them optimally to a certain application. The overall interesting particle size range is readily accessible in this way.

The modifiers known from the literature referred to above may be used as modifiers, especially oxides and/or fluorides of manganese, cobalt, iron, niobium, ruthenium, arsenic, antimony, vanadium, tellurium and so on, of the kind described in British patent specifications Nos. 859,-937 and 1,073,483. It is preferred to use the oxide-forming compounds of tellurium and/or antimony. The tellurium may also be used in the elementary form or in the form of an alloy with antimony. A combination of a tellurium or antimony compound with an iron-containing compound may also be used. The TeO_2 or Sb_2O_3— content of the end product should not exceed 0.5% by weight. If a relatively large quantity of the modifier is used, the material becomes too finely divided and the magnetic properties deteriorate.

The remanent magnetising values for the chromium dioxide prepared as described in the foregoing are between 400 and 500 [gauss cm.^{3}·g.$^{-1}$]. The coercive forces are governed by the particle size and can readily be varied by adjusting the chromium oxide/chromic acid ratio and by adding modifiers, in a range of from 200 to 550 [oe.]. In this process, chromium dioxide accumulates in the form of needle-like particles. The length of the needles may be varied from 0.1 to 2 μm. and their width from 0.015 to 0.1 μm.

Since the chromium oxide used as the starting material obtained by dehydrating and tempering precipitated chromium oxide hydrate green has a favourable particle size distribution and a limited tendency towards agglomeration, the individual particles of the chromium dioxide obtained from it are also very uniform in shape and size. The process can be controlled so that as large a number of particles as possible is in the optimum particle size range.

The favourable particle size distribution has a beneficial effect upon a number of properties. Thus, unusually high print-through values of up to 60 [db.] were found on sound tapes that had been produced from the chromium dioxide obtained by the process according to the invention. The chromium dioxide has another qualitative feature: due to the relatively low Curie point of 126° C., the magnetic properties, for example the remanent magnetisation, are governed to some extent by temperature even at relatively low temperatures. This effect is undesirable because it is able to vary the characteristic of the tapes and can lead to disturbances during operation. Due to the favourable particle size distribution, the dependence upon temperature of the magnetic characteristics at temperatures of practical interest is minimal in the chromium dioxide produced in accordance with the invention.

The invention is illustrated by the following examples.

EXAMPLE 1

(a) Preparation of the precipitated chromium oxide hydrate green used as the starting material and conversion into chromium dioxide

200 to 220 litres/hour of a sodium dichromate solution containing 700 g./litre of $Na_2Cr_2O_7 \cdot 2H_2O$, 60 to 70 litres/hour of a 30% formaldehyde solution and 400 litres/hour of preheated water, were passed continuously through a pressure reactor of the kind described in FIAT Final Report No. 814, page 61. The pressure was kept at 300 kg./cm.^{2} and the temperature at 350° C. The chromium oxide hydrate green formed under these conditions was filtered through filter presses, washed and then dried.

The precipitated chromium oxide hydrate green was tempered for 2 hours at 700° C. in a rotating tubular oven. As a result it was converted with loss of water (20% weight loss) into α-Cr_2O_3 which was found by measurement to have a BET surface of 24 m.^{2}/g.

(b) Conversion into chromium dioxide

143.5 g. of Cr_2O_3 prepared from precipitated chromium oxide hydrate green as described above were stirred with a high speed stirrer into a suspension of 287 g. of CrO_3 in 110 ml. of H_2O accommodated in a refined steel beaker. A highly viscous mass was formed. The refined steel vessel was placed in an autoclave lined with Hastelloy C and the autoclave placed under a oxygen pressure of 70 kg./cm.^{2}. Its contents were then heated to 335° C. over a period of 90 minutes and kept at this temperature for 8 hours. After cooling, the autoclave was vented. The product was removed from the refined steel vessel, washed free of chromate with water and dried at 110° C.

The following magnetic data were determined:

Br/δ: 491 [Gauss. cm.^{3}·g.$^{-1}$], J_{Hc}: 374 [oe.]

(c) Producing a test tape

110 g. of CrO_2, 1.83 ml. of oleic acid, 60 ml. of a solution of a copolymer of polyvinyl chloride and polyvinyl acetate in ethyl acetate (120 g./l.), 115 ml. of butyl acetate and 251 ml. of ethyl acetate were mixed together and ground for 30 hours in a vibratory mill with 700 g. of glass balls (diameter 5 mm.). 24.9 ml. of a solution of a hydroxy group-containing polyester in ethyl acetate (60% by weight) were then added, followed by another 15 minutes' grinding. 3.68 ml. of a solution of a prepolymeric isocyanate (1:1) were then added to 100 ml. of the suspension thus prepared, and the lacquer applied by dip-coating to a 30 μm. thick polyester film. The CrO_2 coating was adjusted to 20 g./m.^{2}.

A print-through of 56 [db.] was determined on the tape in accordance with DIN 45 519.

COMPARISON EXAMPLE A

The use of chromium oxide hydrate according to U.S. patent specification No. 3,278,263 as starting material for the production of chromium dioxide.

(a) Preparation of the chromium oxide hydrate used as starting material and conversion into chromium oxide

A soluiton of 0.69 litre of 26% ammonia in 1.36 litres of distilled water was added with intensive stirring to 0.96 kg. of $Cr(NO_2)_3 \cdot 9H_2O$ dissolved in 6.03 litres of distilled water, the suspension diluted with 9.95 litres of distilled water and, after standing overnight, washed four times by decantation with 10 litres of distillated water. After filtering, the product was dried at 60° C. in a vacuum drying cabinet. The weight loss (water content) of the product during calcination amounted to 50%, the X-ray photograph corresponded to the statements of Schafer and Roy (Zeitschrift für anorg. und allg. Chemie, 276, 275 (1954)). Accordingly, the product corresponded to the chromium oxide hydrate described in U.S. patent specification No. 3,278,263.

Like the precipitated chromium oxide hydrate green in Example 1a, the preparation was heated for two hours at 700° C. in a rotating tubular oven. The chromium oxide obtained in this way had a specific surface of 19.8 $m.^2/g.$

(b) Conversion into chromium dioxide

Conversion into chromium dioxide was carried out under the conditions described in 1b. The following magnetic data were determined on the material:

Br/δ: 455 [Gauss. $cm.^3 \cdot g.^{-1}$], J_{Hc}: 384 [oe.]

(c) Producing a test tape

The test tape was prepared as described in Example 1c. A print-through of 49.5 [db.] was determined in accordance with DIN 45 519.

Following exactly the same procedure, the print-through obtained with precipitated chromium oxide hydrate green (Example 1) was 6.5 [db.] greater than that obtained with the chromium oxide hydrate obtained in accordance with U.S. patent specification No. 3,278,263.

The dependence of remanence upon temperature also has a more favourable trend in cases where precipitated chromium oxide hydrate green is used. In order to illustrate this, samples of the chromium dioxide preparations according to Example 1 and Comparison Example A were heated in stages to temperatures of from 22 to 130° C., magnetised to saturation, cooled to 22° C. and the remanent magnetisation determined. The remanent magnetisation at 22° C. after magnetisation at 22° C. was assumed to be 100%. As can be seen from the figure, the remanent magnetisation for the preparation according to Example 1 decreased more slowly with temperature than for the preparation according to Comparison Example A. Thus, the decrease in remanence at a magnetisation temperature of 100° C. amounted to 23% for the preparation according to Comparison Example A, and to only 10% for the preparation according to Example 1.

In the accompanying figure, the magnetisation temperature in ° C. was plotted on the abscissa and, on the ordinate, the remanent magnetisation at 22° C. in percent based on the remanent magnetisation, after magnetisation at 22° C. The solid-line curve shows the values obtained for the product according to Example 1, whilst the chain-line curve shows the values obtained for the product of Comparison Example A.

EXAMPLE 2

(a) Precipitated chromium oxide hydrate green according to Example 1a was tempered for two hours at 700° C. in a muffle furnace. After tempering, the product had a BET surface of 23 $m.^2/g.$

(b) Conversion into chromium dioxide was carried out as in Example 1b, except that the temperature was kept at 335° C. for only 4 rather than 8 hours. The chromium dioxide obtained in this way had the following magnetic properties:

Br/δ: 512 [Gauss. $cm.^3 \cdot g.^{-1}$], J_{Hc}: 396 [oe.]

(c) Producing a test tape

105 g. of chromium dioxide according to 2b, 1.75 ml. of oleic acid, 58.5 ml. of a solution of a copolymer of polyvinyl chloride and polyvinyl acetate in ethyl acetate (120 g./litre), 115 ml. of butyl acetate and 254 ml. of ethyl acetate were mixed together and ground for 30 hours in a vibratory mill with 700 g. of glass balls (5 mm. diameter). 22.8 ml. of a solution of a hydroxyl group-containing polyester in ethyl acetate (60% by weight) were then added followed by another 15 minutes' grinding. 3.68 ml. of a solution of a prepolymeric isocyanate (1:1) were added to 100 ml. of the suspension thus prepared, and the lacquer applied by dip-coating to a 30 $\mu m.$ thick polyester film. The CrO_2 coating was adjusted to 20 $g./m.^2$.

A print-through of 59 [db.] was determined on the test tape thus prepared in accordance with DIN 45 519.

EXAMPLE 3

143.5 g. of chromium oxide, prepared in accordance with Example 2b, and 1 g. of TeO_2 were stirred into a suspension of 287 g. of chromic acid in 110 ml. of water and the mixture heated in an autoclave under the conditions described in Example 1b.

Chromium dioxide with the following magnetic data was obtained:

Br/δ: 477 [Gauss $\cdot cm.^3 \cdot g.^{-1}$], J_{Hc}: 446 [oe.]

The average needle length was measured at 0.24 $\mu m.$ from photographs taken with an electron microscope, and at approximately 0.5$\mu m.$ for the preparations according to Examples 1b and 2b. The greater fineness in the division of the product caused by the addition of tellurium is also reflected in the greater coercive force.

EXAMPLE 4

143.5 g. of chromium oxide prepared in accordance with Example 2b and 1 g. of Sb_2O_3 were stirred into a suspension of 287 g. of chromic acid in 110 ml. of water and the mixture heated in the autoclave under the conditions described in Example 1b. The chromium dioxide thus prepared had the following magnetic data:

Br/δ: 459 [Gauss $\cdot cm.^3 \cdot g.^{-1}$], J_{Hc}: 468 [oe.]

COMPARISON EXAMPLE B

(a) Commercial guignet green (Reading Green and Marvell) was tempered for 2 hours at 700° C. in a rotating tubular oven. After tempering, the product had a specific surface according to BET of 24 $m.^2/g.$

(b) The reaction to form chromium dioxide was carried out as in Example 1b. The product was found to have the following magnetic data:

Br/δ: 285 [Gauss $\cdot cm.^3 \cdot g.^{-1}$], J_{Hc}: 184 [oe.]

A product of this kind is unsuitable on account of its poor magnetic properties. X-ray photographs show that the product contains Cr_2O_3 in addition to CrO_2.

Unlike precipitated chromium oxide hydrate green, guignet green is not suitable for use as a starting material in the production of chromium dioxide.

What I claim is:

1. A process for the production of ferromagnetic chromium dioxide, wherein a chromate or dichromate solution is subjected to the action of an organic substance at a temperature of from 300° C. to 400° C. and at a pressure of from 250 to 350 $kg./cm.^2$, said organic substance being a reducing agent for the chromate and dichromate under said conditions, to form chromium oxide hydrate green, wherein the resulting chromium oxide hydrate green is dehydrated at a temperature of 300° C. to 900° C. to produce finely divided chromium oxide in which the average oxidation state of the chromium is in the range of from 3 to 4, and wherein the chromium oxide is heated with chromic acid under hydrothermal conditions at a temperature of from 50° C. to 400° C. and at a pressure of from 50 to 500 kg./cm.2.

2. A process according to claim 1, wherein the finely divided chromium oxide is heated in the presence of a substance acting as a modifier in an amount such that the modifier oxide content of the end product of the oxidation of the chromium oxide does not exceed 0.5% by weight.

3. A process according to claim 2, wherein the substance acting as a modifier is tellurium or a compound thereof in an amount such that the modifier oxide content of the end product of the oxidation of the chromium oxide does not exceed 0.5% by weight.

4. A process according to claim 2, wherein the substance acting as a modifier is antimony or a compound

thereof in an amount such that the modifier oxide content of the end product of the oxidation of the chromium oxide does not exceed 0.5% by weight.

5. A process according to claim 2, wherein the substance acting as a modifier is a combination of tellurium or a compound thereof and an iron-containing compound in an amount such that the modifier oxide content of the end product of the oxidation of the chromium oxide does not exceed 0.5% by weight.

6. A process according to claim 2, wherein the substance acting as a modifier is a combination of antimony or a compound thereof and an iron-containing compound in an amount such that the modifier oxide content of the end product of the oxidation of the chromium oxide does not exceed 0.5% by weight.

7. A process according to claim 1, wherein the ratio of the chromium oxide to the chromic acid is in the range of from 1:1 to 1:5 by weight.

8. A process according to claim 7, wherein the chromic acid is mixed with water.

9. A process according to claim 8, wherein the quantity of water is from 50 to 150% by weight, based on the chromium oxide.

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TOBIAS E. LEVOW, Primary Examiner

J. COOPER, Assistant Examiner

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