

EXHIBIT H

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PRODUCTION OF TITANIUM OXIDE
PIGMENTS

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1
This invention relates to the production of pigment-useful titanium dioxide and to novel methods for obtaining that product. More particularly it relates to the production of TiO_2 pigments by the oxidation under controlled conditions of titanium tetrachloride while in the gaseous phase.

Titanium dioxide has been prepared in the laboratory by reacting titanium tetrachloride in the vapor phase with an oxygen-containing gas and by a so-called steam-splitting reaction. However, these prior oxidation processes lack technical importance and are neither adaptable to nor feasible for commercial exploitation. Thus, such methods entail a very difficult, costly and discontinuous type of operation, while the titanium dioxide resulting therefrom is decidedly lacking in essential pigment properties, e. g., its tinting strength is so poor and its particle size so coarse and of such wide, non-uniform distribution that it completely fails to meet the stringent requirements and demands of the trade with respect to TiO_2 pigments. Furthermore, these methods fail to afford a process in which the crystalline form of the titanium dioxide produced can be controlled at will, and require the use of large excesses of oxygen to convert the tetrachloride. This results in undesired contamination of the gaseous chlorine simultaneously formed with the TiO_2 to render such chlorine unfit for reuse in the process.

It has been found that the above and other disadvantages of prior vapor phase oxidation methods for TiO_2 preparation can be effectively remedied, and a principal object of this invention, therefore, is to provide novel methods and means for attaining that result. Particular objects of the invention include: the provision of a useful and efficient method for obtaining titanium oxide, through vapor phase oxidation of titanium tetrachloride, of controlled, uniform particle size and other necessary pigment qualities, including essential color, tinting strength, opacity, hiding power, etc., and which is directly useful as an excellent, high-quality type of pigment; the provision of a novel method for obtaining such pigment-useful titanium dioxide in either the rutile or anatase crystalline form and by an accelerated, controlled oxidation reaction; the provision of a process wherein the reaction

2
between oxygen and the titanium tetrachloride is effected in such manner that the use of large excesses of oxygen is effectively avoided and substantially complete conversion of the tetrachloride is obtained; and the provision of a process wherein the chlorine produced in the reaction is substantially free from oxygen and other impurities to become suitable for direct use and recycling in the process to obtain further quantities of the titanium tetrachloride reactant or otherwise. Further objects and advantages will become apparent from the following, more detailed description of the invention.

These and other objects are accomplished in this invention which comprises producing pigment-quality titanium dioxide, in either the rutile or anatase crystalline form, by decomposing titanium tetrachloride in the vapor phase under controlled oxidation conditions in the presence of small, regulated amounts of water vapor.

In a more specific and preferred embodiment, the invention comprises producing pigment-quality TiO_2 , more especially rutile, by reacting at an elevated temperature in the vapor phase and over a controlled time period relatively pure titanium tetrachloride with an oxygen-containing gas, and effecting said reaction in the presence of from 0.1% to 5% by volume (based on the total volume of gases) of water vapor to continuously form in situ of said reactants small amounts of an effective TiO_2 nucleating agent which promotes and insures production of a high-quality TiO_2 pigment.

In producing pigment-quality rutile in accordance with one preferred, practical adaptation of the invention, sufficient pure, vaporized, anhydrous titanium tetrachloride and an oxygen-containing gas, such as air, suitably enriched with from 1%-3% of water vapor, are separately and continuously introduced into an oxidation zone wherein their rapid, thorough admixture and reaction is effected at substantially constant temperatures ranging from 800-1200° C., with substantially complete oxidation of the titanium tetrachloride occurring as a result. Prior to introduction, either or both reactants are preheated to a temperature sufficient to insure the prevalence on their admixture and reaction of a temperature within the range mentioned. Any conventional corrosion-resistant type of reaction

2,488,480

3

vessel can be employed in the process, but such vessel should be of such design, construction and dimension that it will afford a continuous flow of the reactants and products within and through its oxidation chamber and permit of such control over the velocities, mixing rates, temperatures and retention times that, on the average, said reactants and products will remain in said chamber for only a limited, relatively short period of time, e. g., long enough to effect a substantially complete reaction but insufficiently long to permit undesired particle size growth of the TiO_2 to occur. Usually, a retention time of from about .1 to 1 second, using the indicated temperatures induces substantially complete conversion of the titanium tetrachloride to titanium dioxide.

The gaseous reaction products which contain the TiO_2 product in suspension, upon discharge from the oxidation chamber are subjected to quick cooling, such as by quenching, or otherwise, to reduce their temperature below $600^\circ C.$ and prevent any undesired growth taking place of the pigment particles by cementation or sintering of loosely-bound TiO_2 aggregates. One useful and effective method for accomplishing this rapid cooling comprises recirculating cooled product gases from the system and directly commingling them with the gaseous TiO_2 suspension as it issues from the oxidation chamber. The quantity of cooled products thus employed should be sufficient to drop the temperature of the pigment suspension preferably below $600^\circ C.$ in about 1 second and not to exceed 10 seconds' time. The rutile TiO_2 pigment can be recovered from such cooled gaseous products of reaction by means of conventional separatory treatments, including cyclonic or electrostatic separation, filtration through porous media, or the like. Said pigment will have an average particle size radius ranging from .05 to .5 micron, and preferably will range in average particle size radius from .1 to .25 micron. Such uniform, small particle size and the inherently high tinting strength, color, opacity, and other essential pigment properties possessed by the product render the pigment adaptable for use in all types of pigment application, including paints, enamels, finishes and other types of coating compositions, as a delusterant for rayon or other artificial fibers or silks, in printing inks, rubber, etc.

To a clearer understanding of the invention, the following specific examples are given, each being merely illustrative in character and not intended to limit the scope of the invention:

Example I

Liquid titanium tetrachloride was flash evaporated and preheated to $800^\circ C.$ in a corrosion-resistant tubular preheater and the preheated vapor admitted continuously at a rate equivalent to 100 parts by weight of $TiCl_4$ per hour to the upper portion of a vertical, corrosion-resistant reaction chamber maintained at a temperature of $1050^\circ C.$ Simultaneously therewith, air preheated in a similar fashion to about $800^\circ C.$, and to which sufficient water vapor had been added to give .95% H_2O content by volume, was continuously admitted through a separate inlet adjacent the $TiCl_4$ inlet to the upper portion of the reaction chamber. The metered, humidified air flow was maintained at a rate equivalent to 20 parts by weight of O_2 per hour. The separate inlets through which the reactants were admitted to the reaction zone were so arranged that the gas

4

streams entering the reaction chamber converged immediately to become rapidly mixed together in the upper portion of said chamber. Flow rates sufficient to provide an average retention time of gases and products in the reaction zone of about .5 second were utilized. The gaseous suspension of titanium dioxide reaction product, issuing from the bottom of the reaction chamber at a temperature of approximately $1000^\circ C.$, was quickly cooled by introducing sufficient cold chlorine gas therein to drop its temperature to $300^\circ C.$ in less than 2 seconds. The titanium dioxide pigment product was then separated and recovered in filter containers. The process was operated continuously with over 99% conversion of the titanium tetrachloride taking place. The titanium dioxide product was determined to be in the rutile crystal structure and possessed essential particle size uniformity and other pigment properties, as shown by its possession of a tinting strength value of 182, a color value of 19, and an average particle size radius of 0.17 micron.

Duplication of the foregoing example, except that air substantially free from moisture was employed, failed to result in a satisfactory final titanium dioxide product, being of lower refractive index (anatase) and having an average particle size radius of 0.60, a tinting strength value of 75, and a color value of 17. It was too coarsely crystalline, non-uniform, and deficient in essential properties to be useful as a pigment.

Example II

In the same type of apparatus as that employed in Example I, titanium tetrachloride vapor was preheated to about $865^\circ C.$ and admitted to the reaction chamber at a continuous rate of 100 parts by weight per hour. Oxygen gas, to which water, equivalent to .33% by volume of the total flow of reactants, had been added, was likewise separately preheated to $865^\circ C.$ and continuously admitted to the reaction chamber wherein it was rapidly admixed with the tetrachloride vapor. The metered oxygen flow was maintained at a rate of 19 parts by weight of O_2 per hour, and the flow rate of the total reactants was so controlled that their average retention time in the reaction chamber was .47 second. The temperature in the reaction chamber was maintained at about $1065^\circ C.$ and the gaseous, TiO_2 -containing reaction products, upon issuing therefrom, were cooled to below $600^\circ C.$ in less than 10 seconds by passing the reaction products so discharged at high velocity through cooled tubes. Thereafter, the pigment was removed from the gas stream by means of a glass cloth filter bag.

From this operation it was found that substantially complete conversion of the titanium tetrachloride to titanium dioxide resulted, with coincident formation of a gaseous product of about 94% Cl_2 by volume. The recovered titanium dioxide was in the rutile crystalline structure and exhibited excellent particle size uniformity, having an average particle size of 0.175 micron radius. Its tinting strength value was 179, its color was 23, and its hiding power was equal to the highest quality commercially obtainable rutile titanium dioxide pigments.

Duplication of this example, but without recourse to addition of water vapor to the oxygen, resulted in an anatase product which was too coarse in particle size and too poor in uniformity and other properties to be acceptable for such use as a pigment. Its tinting strength was but 88, its

2,488,439

5

color was 15, and its hiding power was wholly deficient.

Example III

In an apparatus similar to that used in Examples I and II, titanium tetrachloride vapor heated to 170° C. was admitted continuously at a rate of 1045 grams per hour to the oxidation chamber maintained at about 1000° C. by external heating. Air preheated to 170° C. and to which water vapor had been added to give a water content equivalent to 1.0% by volume was separately admitted to the oxidation chamber at a rate of about 640 liters per hour, measured at room temperature. The two gas streams were rapidly mixed in the upper portion of the oxidation chamber, and such flow rates of reactants were resorted to that the average retention time of reactants within the oxidation zone was about .99 second. The products of reaction, upon issuing from the lower portion of said chamber, were cooled in less than 10 seconds to below 600° C. Substantially complete conversion of the titanium tetrachloride was obtained with production of a high-quality anatase pigment having an optimum average particle size range and other essential pigment properties.

Duplication of this example, using the same flow rates and temperatures, etc., but employing moisture-free air, resulted in an extremely coarse-grained TiO₂ product wholly unsuitable for use as a pigment.

The TiO₂ pigment values given herein were determined in accordance with the methods described or referred to in U. S. Patents 2,253,651 and 2,046,054.

Although it is essential in producing pigment-quality TiO₂ under the invention that the temperatures, concentrations, and retention times resorted to must be controlled and correlated, it will be understood that the reactants, concentrations, volumes, ratios, temperatures, velocities, retention times, etc. used in the above examples are not to be taken as critical. Hence, due variation therefrom may be made without departing from the underlying principles and scope of the invention.

While air, humidified to the extent indicated, comprises a preferred type of useful oxygen-containing gas, other types and amounts of oxidizing gases containing free oxygen (O₂) and similarly moisture-enriched, can also be used, as can mixtures thereof. Examples of other useful gases include oxygen, oxygen-enriched air, or mixtures of oxygen or air with various inert gases.

Again, while I prefer to introduce the required concentration of water vapor into the reaction zone via the oxidizing agent, if desired other methods for insuring the presence of a sufficient H₂O concentration during the vapor phase reaction can be resorted to. Since it is essential and critical to the invention that the water vapor be present in controlled amounts, any method designed to introduce the required quantity (or lower the amount, if too high) into the oxidizing gas or reaction zone is contemplated as useful in practicing the invention. For example, the required amount of water vapor can be continuously added, either directly to the reaction zone itself, or as a component of the oxidizing medium being fed thereto. Alternatively, it may be introduced with either or both reactants, or by first mixing part or all of the gaseous reactants and then incorporating the desired quantity of water vapor therein prior to feeding the mixture into the reaction zone. Incorporation of the requisite

6

amount of water in the reactants being fed to the reaction zone can be effected in any desired manner, as by bubbling the oxidizing gas through the aqueous liquid body or by conveniently spraying it into the gas stream in the form of liquid or vapor (steam). For instance, a portion of the oxidizing gas can be saturated in this manner with water, in either the liquid or vaporized state, following which the saturated portion can be blended with the remaining dry portion of the reactant. Alternatively, the desired amount of water, in liquid or vapor state, or both, can be injected into or otherwise fed, intermittently or continuously, directly to the reaction zone to insure the presence of controlled amounts thereof during the oxidation reaction.

While water vapor in amounts ranging from .1-3% has been mentioned as preferred for use, other amounts ranging from, say, .05% to 5%, but not exceeding 10% (based on the total volume of gaseous reactants being fed to the reaction zone) can also be used, and comprise the contemplated practical limits of operation hereunder.

As noted, reaction zone temperatures ranging from 800-1200° C. are preferred for use herein, because optimum results have been found to accrue by reason thereof. If desired, higher or lower orders of temperature, say, from 800° C. to 1350° C., are also employable. These reaction zone temperatures can be readily obtained in a large scale or commercial type of operation by either separately preheating one or both reactants to an extent sufficient to insure on their admixture and reaction temperatures of the order indicated and are maintained by means of the heat generated from the oxidation reaction or through external heating of the reaction zone or vessel, whichever method is preferred. The temperatures mentioned above comprise those measured by a thermocouple extending through the walls of the reaction vessel and into the reacting gases.

Preheating the reactants can be effected by separately subjecting each to an equivalent heating temperature, or, if desired, the oxidizing gas may be preheated to a temperature above or below that to which the tetrachloride is subjected, whichever method is preferred. Any conventional equipment can be used in the preheating step, including any suitable type of electrical resistance apparatus or devices adapted to pass the reactants in direct or indirect heat exchange relationship with a heat-imparting medium. A useful type of heating apparatus comprises one in which the reactants pass over heat transfer surfaces heated directly by combustion of fuels or indirectly by circulation of a suitable heat transfer medium.

Normally, the titanium tetrachloride oxidation is effected under atmospheric pressures, but it may be carried out, if desired, under super or subatmospheric pressures. Similarly, any type or size of reaction vessel conforming to the scale of operation intended can be used in adapting the invention, equipment of such design and dimension as will permit a continuous flow of reactants through the reaction vessel, especially the oxidation chamber thereof, being preferred, whereby a continuous, as distinguished from a discontinuous or batch, type of operation, will be afforded. While a continuous type of process is preferred, the process can also be carried out as a batch or semi-continuous type of operation. The time of retention of reactants within the reaction zone is quite important and critical in the invention, especially in the production of pig-

2,488,480

ment-quality TiO_2 , as herein defined. In general, such retention time must not exceed about 5 seconds nor be less than about .01 of a second. A preferred time, to obtain an optimum quality pigment, ranges from .1 to 1 second.

As already noted, both anatase and rutile TiO_2 pigments can be produced in accordance with this invention.

In producing pigment rutile of optimum qualities, it is usually desirable to operate the $TiCl_4$ oxidation reaction under such combination of conditions that there will be employed

(a) a minimum moisture concentration in the reacting gases to insure formation of rutile crystal structure TiO_2 pigment;

(b) minimum preheating temperatures for the reactants and thorough, rapid mixing of such reactants;

(c) minimum retention time of reactants and products in the oxidation chamber sufficient only to effect substantially complete conversion of the $TiCl_4$ to TiO_2 and growth of the TiO_2 pigment particles to the desired size; and

(d) quickly cool the products from the oxidation after formation of the desired particle size TiO_2 to prevent over-growth of the pigment particles.

These variables are interdependent and optimum values, within the limits specified, for moisture content in the reacting gases, preheating and reaction zone temperatures and retention time in the oxidation chamber must be predetermined for a particular apparatus to obtain therefrom the desired particle size rutile pigment. The preferred relationship between these critical variables is dependent upon such factors as manner and speed of mixing of the reactants, size and shape of the oxidation chamber, etc., as well as upon the particle size desired in the pigment TiO_2 .

It has been found, as already indicated, that the temperature to which the reactants are subjected in the preheating operation has an important bearing upon the ultimate type, crystallinity, and character of the TiO_2 pigment. In producing anatase, it is usually desirable to employ lower preheating temperatures with resulting lower reaction chamber temperatures than are resorted to and necessary in the production of rutile. The preferred, most useful temperature will depend upon such factors as the scale of the involved operation, the size and shape of the reaction chamber, and the rapidity with which gas mixing is effected. In producing rutile, preheating temperatures adequate to insure a mixed gas temperature of at least $350^\circ C.$, and preferably above $400^\circ C.$, are usually necessary, while in anatase production preheating temperatures sufficient to afford a mixed gas temperature ranging from below $350^\circ C.$ to not lower than $100^\circ C.$ can be resorted to. While a preheating temperature of at least $350^\circ C.$ is suggested in rutile production, in general, and as already indicated, it will be found that as the size of a given operation increases, the amount or degree of preheating temperature required to effect such decreases. Hence, temperatures below that recommended and to as low as, say, $250^\circ C.$, may be employed.

The titanium tetrachloride reactant preferred for use herein comprises a high-purity material to insure production of a product exhibiting exceptionally high pigment whiteness and brightness characteristics. This reactant can be obtained from any convenient source, as for instance through the chlorination of a titaniferous

ore, such as ilmenite, followed by purification through careful fractional distillation to obtain the desired product. Examples of other utilizable titanium tetrachloride reactants comprise the pure, anhydrous titanium tetrachloride (freed of copper, vanadium, iron, and other impurities) contemplated in U. S. Patent 2,062,133, or the product which results from soya bean oil treatment disclosed in U. S. Patent 2,230,589.

Although chemically-equivalent concentrations of reactants are used herein and substantially complete conversion of the chloride to TiO_2 obtained as a result, in general I prefer to operate with amounts of oxidizing gas sufficient to provide about 10% excess oxygen over the theoretical so as to obtain a product gas containing about 30% Cl_2 by volume, when air is used as the source of oxygen, and 80-95% Cl_2 when gaseous oxygen is employed, with but small or minor amounts of O_2 and HCl . The use of oxygen-enriched air will produce chlorine concentrations intermediate between 30 and 90% Cl_2 gas in the oxidation products. However, the invention is not limited thereto, since it is susceptible of operation using either excess or deficient concentrations of the oxidizing or titanium tetrachloride reactant. In event an excess of the chloride is used, it can be separated from the oxidation products and reused in the system. Occasionally it may be desirable to operate the process with incomplete titanium tetrachloride conversion and such type of operation is likewise contemplated within the scope of the invention. Satisfactory titanium dioxide pigments have been produced hereunder with tetrachloride conversions as low as 50% of theoretical.

As already noted, in the commercial application of the invention any chlorine produced simultaneously with the titanium dioxide pigment can be conveniently recycled to produce more titanium chloride for oxidation. Consequently, a continuous, as distinguished from a non-continuous, type of operation is hereby afforded. The gaseous chlorine formed may be recycled directly from the pigment recovery operation or, if desired, may be concentrated prior to reuse in the chlorination operation. Such by-product chlorine can also be used for purposes other than chlorinating titaniferous materials, if that should be desired.

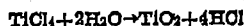
The products of reaction are most conveniently subjected to quick, rapid cooling by the recirculation of sufficient cooled product gases to instantaneously drop the temperature of the pigment suspension issuing from the reaction zone well below $800^\circ C.$, and preferably below $600^\circ C.$ Such cooling should be effected in less than 30, and preferably in less than 10, seconds' time. Other means for accomplishing cooling can be resorted to, such as quick quenching by spraying liquid chlorine into the oxidation products; impingement of the gaseous suspension on cold surfaces; rapid flow through cooled tubes, etc. Similarly, quenching with other gases, such as air, or with liquids other than chlorine can also be resorted to. The latter methods are less practical and hence are not preferred because undesired dilution may occur of the chlorine content of the gaseous products.

The precise manner by which the use and presence of the contemplated amounts of water vapor during the reaction induce production of the high-quality TiO_2 pigment obtainable hereunder is presently not clearly understood. It does appear, however, that under the controlled and regulated conditions of the reaction which prevail herein, the water vapor introduced into the reac-

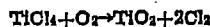
2,488,439

10

tion zone first forms extremely minute TiO_2 crystallites which are well dispersed throughout the gaseous mixture according to the reaction:



Control over the size, crystalline form, and number of these nucleating particles is effected by the amount of water present during the oxidation reaction and the temperature conditions under which they are permitted to form. Under the prevailing, controlled conditions of reaction, nuclear TiO_2 or oxychloride particles of such minute size, number and type form continuously in the reaction chamber to provide throughout the oxidation of the titanium tetrachloride a continuous, fresh supply of seeding material onto which the TiO_2 from such oxidation precipitates to build up or grow into TiO_2 particles of desired pigment dimension, uniformity and crystalline structure. Low temperatures favor the formation of anatase nuclei while high temperatures promote rutile formation, and the nucleating particles function as "centers" for subsequent growth by TiO_2 deposition in the same crystalline form as the "centers" by the oxidation reaction:



The average final particle size is then an inverse function of the number of nuclei, and the crystal variety (rutile or anatase) is determined by the type of seed crystallite formed in the first stages of the reaction. The present method of nucleation also serves to greatly accelerate the velocity of the oxidation rate at temperatures below 1000°C , which effect appears to be due to the large number of active "centers" present in the reacting mixture and resulting from the presence of controlled, small amounts of moisture. Hence, ultimate at-will production is assured of a high-quality TiO_2 pigment exhibiting either the anatase or rutile crystalline diffraction pattern on X-ray analysis. Quite surprisingly, this nucleating function and the production of a satisfactory TiO_2 product fails to exist when no control is exercised over the amount of H_2O present during the reaction, nor can a rutile type of product be obtained in the absence of such control and the combination therewith of the indicated temperature and reaction zone retention times.

In producing pigment-quality rutile, the nuclei formed or employed in the reaction zone preferably consist of minute, finely-divided rutile crystallites or particles. In the production of anatase, the nucleating particles may be either true anatase crystallites or particles, such as hydrated oxychlorides or the like, adapted to readily convert to anatase crystallites during the oxidation.

The nuclei employed herein are preferably formed, as shown in the examples, as the gases become mixed in the reactor. If desired, such nuclei may be formed externally of and prior to their admission into the oxidation reactor. The moisture or water vapor reacts with the chloride to form solid particles of titanium oxide or oxyhalide and the limitation of the amount of water admitted causes a suspension of solids which passes on as a gaseous fluid into the oxidation chamber, and which appear to serve as nuclei centers on which the titanium oxide grows. In forming the nuclei outside the reaction zone, a two-step operation may be resorted to, i. e., the nucleating particles of the desired crystalline form, size and number may be separately prepared and then dispersed in the reactant gases prior to the oxidation of any substantial quantity

of the titanium tetrachloride. In such instances the nuclei are formed in a first stage and continuously carried into a second stage for thorough incorporation in and admixture with the major reactants.

By the terms "pigment quality" or "essential pigment properties," as used herein and in the appended claims, is meant a TiO_2 product possessing satisfactory properties in respect to color, tinting strength, texture, particle size, and other requisite pigment properties which render the product commercially useful in coating compositions (paints, enamels, varnishes, finishes, etc.), pigmenting paper, linoleum; the production of shoe cleaner preparation or as a delusterant for artificial silks, nylon, etc. Such titanium dioxide is considered as being at least substantially equal to the quality obtained from a titanium sulphate process used in the production of either commercial anatase or rutile. Such properties as color, tinting strength, hiding power, texture, and particle size are referred to in the above-mentioned U. S. Patents 2,253,551 and 2,046,054. An additionally important property quite significant in the manufacture of rutile pigment is that commonly referred to as carbon black undertone. The effect of the addition of carbon black to a white paint is found to vary considerably and in some cases a gray of bluish undertone is produced while in other instances a gray of reddish undertone results. The paints may be identical in content of the carbon black and white pigment such as titanium dioxide, but yet appear quite different to the eye, due to the difference in undertone. This is considered as due to a difference in particle size and/or particle structure. The bluish undertone appears to be characteristic of pigments of small particle size, while the reddish undertone is characteristic of pigments of larger and less uniform particle size, although the structure of the pigment particle may also exert an influence. In order to give numerical gradings or values to this property, an arbitrary scale has been set up by assigning a grading of zero to a commercial pigment produced by the process of U. S. Patent 2,253,551, which shows excellent durability in outside house paints and other exterior coating compositions, but is relatively large in particle size and exhibits a reddish undertone. Another pigment produced in accordance with the process of U. S. Patent 2,224,987, having a relatively small particle size and exhibiting a bluish undertone, was given a rating of 100. These pigments serve as the basis for an arbitrary scale for rating by comparison the pigments produced by the present invention. The paint trade in general desires the pigment of bluish undertone, i. e., pigments rated in the upper part of the range or having numerical gradings in excess of about 50. It is obvious that some pigments may be graded over 100 if they are more blue in undertone than the based pigment rated 100.

The carbon black undertones of pigments best suited for optimum durability in exterior paints are in general rated low and are found to have ratings in the lower half of the indicated range. Such pigments are more chalk-resistant and therefore desired even though a sacrifice in pigment properties, such as tinting strength and hiding power, due to a growth in particle size, may have resulted. These superior pigments are adapted to exterior use and may be rated low in some pigment properties in order to provide the desired durability but would not be desired for

2,488,489

11

consumption in the manufacture of the highest quality interior finishes. It therefore follows that the optimum pigment properties for a given pigment depend, in some measure, on the type of application in which it is to be used.

I claim as my invention:

1. A process for producing a titanium oxide pigment which comprises reacting at an elevated temperature ranging from about 800-1350° C. and in the vapor phase titanium tetrachloride with an oxygen-containing gas in an oxidation zone, effecting said reaction within said zone over a reaction zone retention time period ranging from .01 to 5 seconds and in the presence of controlled, added amounts of water vapor ranging from .05% to 10% by volume, based on the total volume of gases being reacted, and recovering the resulting TiO₂ pigment.

2. A process for obtaining a titanium oxide pigment having an average particle size radius ranging from .05 to .5 micron and exhibiting an X-ray analysis the diffraction pattern of rutile, comprising reacting in the vapor phase in a reaction zone and over a reaction zone retention time period not to exceed 5 seconds at a temperature of at least 800° C. titanium tetrachloride and an oxygen-containing gas, effecting said reaction in the presence of controlled, added amounts of water vapor ranging from .05% to 10% by volume, based on the total volume of gases being reacted, and recovering the resulting rutile TiO₂ pigment.

3. A continuous process for producing pigment-quality titanium oxide which comprises reacting titanium tetrachloride with an oxygen-containing gas in the vapor phase and in a reaction zone maintained at temperatures above 1000° C., effecting said reaction over a reaction zone retention period of time ranging from .1 to 1 second, and in the presence of controlled added amounts of water vapor ranging from 0.1% to 3% by volume, based on the total volume of gases being reacted, promptly cooling the reaction products, and recovering the resulting TiO₂ pigment from the products of reaction.

4. A process for producing a titanium oxide pigment through the controlled vapor phase reaction of titanium tetrachloride with an oxygen-containing gas, comprising effecting said reaction at temperatures ranging from 800-1350° C. in the presence of from 0.05% to 10% of added water vapor by volume, based on the reactants, and in a reaction zone in which said reactants are allowed to remain for a period of from .01 to not to exceed 5 seconds, promptly removing the products of reaction from said zone and quickly cooling them to below 600° C., and then recovering the resulting TiO₂ pigment.

5. A process for producing pigment-quality titanium oxide through a controlled vapor phase reaction of titanium tetrachloride with an oxygen-containing gas, comprising effecting said reaction at a temperature above 1000° C. in the presence of from 0.05% to 10% by volume, based on the reactants, of added water vapor, in a reaction zone wherein the reactants remain for a period of from .01 to not to exceed 5 seconds, quickly removing and cooling to below 600° C. the products from the hot reaction zone after the reaction is substantially complete and before particle size growth of TiO₂ progresses outside the range of .1-.5 micron average radius, and then recovering the resulting TiO₂ pigment.

6. A process for producing pigment-quality rutile through controlled oxidation of titanium

12

tetrachloride, which comprises reacting in the vapor phase and at temperatures ranging from 800-1300° C. pure, anhydrous titanium tetrachloride and an oxygen-containing gas after the separate preheating of at least one of said reactants to a temperature sufficient to provide a gas temperature on their admixture of at least 400° C., effecting said reaction in the presence of from 0.05% to 10% of added water vapor, by volume, based on the total volume of gaseous reactants, and in a reaction zone wherein said reactants remain for a period of from .05 to not to exceed 5 seconds, cooling the reaction products immediately upon their discharge from said reaction zone to a temperature below 600° C., and thereafter recovering the TiO₂ pigment from said reaction-cooled products.

7. A process for producing pigment-quality rutile which comprises continuously reacting in the vapor phase TiCl₄ and an oxygen-containing gas in the presence of a controlled quantity ranging from .1 to 10% by volume, based on the total volume of gases being reacted of added H₂O, preheating at least one of said gases to a temperature sufficient to provide a gas temperature on their admixture of at least 350° C. but below 1000° C., effecting said reaction in a zone maintained by the exothermal heat of the reaction at a temperature of above 1000° C. and wherein the reactants are retained for a period of time ranging from about .01 to 5 seconds, promptly removing the resulting reaction products from said zone, cooling the same to below 600° C. within from 1 to not to exceed 10 seconds after such removal, and recovering the TiO₂ pigment therefrom.

8. A process for producing pigment-quality rutile which comprises continuously reacting TiCl₄ and an oxygen-containing gas in the vapor phase in a reaction zone maintained at a temperature above 1000° C., in the presence of an amount of added H₂O ranging from .1 to 10% by volume based on the total volume of gases being reacted and sufficient to effect a substantially complete reaction with development of essential properties in the TiO₂ reaction product within less than 1 second of retention time of reactants in said reaction zone, and then promptly removing the reaction products from said zone, cooling the same, and recovering the TiO₂ product therefrom.

9. A process for producing pigment-quality rutile which comprises continuously reacting TiCl₄ and an oxygen-containing gas in the vapor phase in a reaction zone maintained at a temperature above 1000° C., in the presence of an amount of added water vapor ranging from .1 to 10% by volume based on the total volume of gases being reacted and sufficient to effect a substantially complete reaction with development of essential properties in the TiO₂ reaction product within less than .2 of a second of retention time of reactants in said reaction zone, and then promptly removing the reaction products from said zone, cooling the same, and recovering the TiO₂ product therefrom.

10. A process for producing pigment-quality titanium oxide which comprises reacting in the vapor phase, and at temperatures above 1000° C., titanium tetrachloride with oxygen to which has been added an amount of H₂O equivalent to from .01% to 10% by volume, based on the total volume of gases being reacted, effecting said reaction within a reaction zone over a time period of reactant retention ranging from .01 to 5 seconds, cooling the resulting reaction products to a tem-

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perature below 600° C. within not to exceed 10 seconds from the time of their discharge from said zone, and then separating and recovering the resulting TiO₂ pigment from the cooled products of reaction.

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Country	Date
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Oct. 14, 1958

W. E. DUNN, JR.

2,856,264

CHARGING FLUIDIZING GAS INTO FLUIDIZED BED REACTOR

Filed April 9, 1954

FIG. 1.

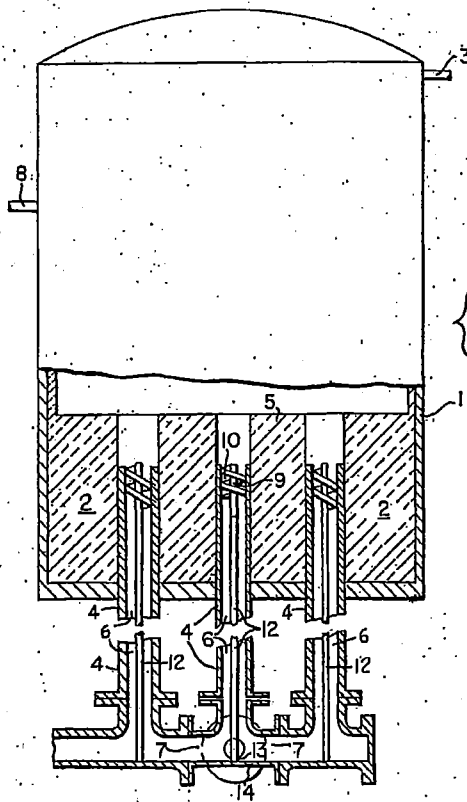


FIG. 2

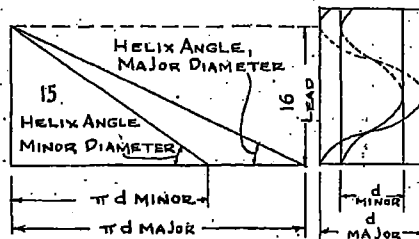
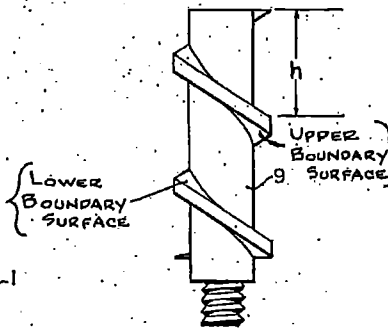


FIG. 3

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2,856,264

Patented Oct. 14, 1958

2,856,264

CHARGING FLUIDIZING GAS INTO FLUIDIZED BED REACTOR

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Application April 9, 1954, Serial No. 422,162

4 Claims. (Cl. 23-37)

This invention relates to novel methods and means for charging a fluidizing medium into a fluidized bed reactor. More particularly, it relates to an improved apparatus for effecting and insuring an evenly distributed flow of a fluidizing vapor into said reactor during its operational periods while preventing back-flow of solids at cessation of the fluidization, and which will allow unimpeded start-up on resumption of the fluidizing operation.

Fluidized solids processes such as those employed for chlorinating a titaniferous material in the presence of a carbonaceous reducing agent are most efficient when the entering gases are uniformly distributed over the entire cross-section of the chamber containing the solids being fluidized, so that maximum contact between gases and solids particles is assured. One most commonly used type of apparatus in large-scale operations comprises that containing a perforated plate or grate type bottom, with the grate serving as a distributor for the vapor charged. However, it is very difficult to construct this plate type of distributor of any material except metal, and if corrosive chemicals are present and elevated temperatures exist in the operation, no suitable metals are available for desired, prolonged satisfactory use. Resort to porous refractory plates can be made in some instances but are subject to disadvantageous, troublesome plugging. Furthermore, with grates having relatively large openings, portions of solid material tend to accumulate in certain areas of the plates to induce excessive flow in the remaining openings. Alleviation of this condition entails a costly and time-consuming operation. Recourse to other types of apparatus for introducing a fluidizing gas into a chemical reactor of this type has also proved to be unsatisfactory. Due to the relatively high temperatures of the reaction (850-1300° C.) and the corrosive nature of the reacting components, the bottom or floor portion of the reactor is usually quite thick and is made up of a refractory material. For this reason the gas entrance tubes are usually positioned vertically through the reactor floor. While good gas distribution can, at times, be obtained by positioning constricting orifices or the like below these vertical inlet tubes and outside the furnace or its lining, this is generally unsatisfactory because objectionable solids back-flow is encountered upon cessation of the normal upward flow of fluidizing gas. In consequence, objectionable plugging of these vertical tubes occurs and a costly shut-down and clean-out operation must be resorted to prior to resumption of the operation. This is particularly true in instances where the solids present become soft or sticky in nature. In an effort to overcome this, use of a short horizontal or nearly horizontal section of conduit, either within the chamber itself or somewhere closely adjacent to the surface of the floor to prevent the bed solids from falling back into the vertical entrance conduits, has been attempted. But such horizontal passages, when constructed of refractory material, are relatively fragile, readily break, and the section is very difficult to clean from within the reaction chamber, particularly where reaction

product stickiness develops. Again, where fragile horizontal outlet tubes break and solids drop into the vertical entrance tube, particularly during non-operation periods, plugging and poor gas distribution results. It is then only a matter of time when very poor distribution of the fluidization vapor takes place and a complete loss of reaction efficiency results.

It is among the objects of this invention to overcome these and other disadvantages which characterize prior fluidized bed reaction methods and apparatus. It is among the particular objects to provide an improved apparatus for introducing a fluidizing vapor through a plurality of reactor inlets and for maintaining solids in fluidized suspension therein, having means for automatically regulating the inlet pressure so that gas flow through the individual multiple inlets from a common source of vapor supply remains at all times essentially constant and uniformly distributed and further means for preventing solids back-flow into the vertical conduits of the chamber and consequent plugging thereof upon cessation of the upward flow of the fluidizing vapor. A further object is to reduce the rate of fouling at the constricting orifice from vapor-borne dust and liquid mists in the fluidizing gas. A further object is to provide an easy and accurate positioning of said apparatus within the conduit. An additional object is to provide easy removal of the constricting throat components for inspection and cleaning without requiring access thereto from the interior of the reactor. A still further object is to provide novel means for effecting easy resumption of the upward flow of the fluidizing vapor through the reactor after the bed particles have settled down over the inlets following cessation of the fluidizing gas flow. Other objects and advantages of the invention will be evident from the ensuing description and from the accompanying drawings wherein:

Fig. 1 is a sectional, side elevational view of one form of apparatus in which the invention can be practiced; and

Fig. 2 is a modified, preferred form of helix adapted for use in the invention.

Fig. 3 is a development of the spiral insert of Fig. 2, showing the graphic triangle which results from the unwrapping of one turn of the helical surface.

These and other objects are accomplished in this invention which comprises charging a fluidizing reactant medium into a fluidized solids reactor through a vertical inlet conduit provided with a serpentine helical passage having a helix angle within its lower boundary surface which is less than the effective angle of slide of the solids in said reactor and a cross sectional area smaller than the area of said conduit.

In a more specific embodiment, the invention comprises introducing a fluidizing reactant gas, particularly chlorine, into a reactor adapted to be maintained at temperatures ranging from about 800-1050° C. containing fluidized, finely divided titaniferous ore and carbonaceous reducing agent solids for reaction, through a serpentine helical passage formed within a vertical bottom inlet to said reactor, maintaining the greatest helix angle within the lower boundary surface of said passage less than the effective angle of slide of said solids, the cross sectional area of the helix smaller than the area of said inlet, and said boundary surface of a length equivalent to at least

$$\left[1 + \frac{h \cos A \cdot \sin B}{L \sin (A-B)} \right]$$

turns, wherein

h = the vertical height of the helical passage between a point on the radial line generating the upper boundary surface and a corresponding point directly below on the lower boundary surface

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B = the maximum helix angle at the lower boundary surface

A = the effective angle of repose of the solids

L = "Lead" of helical thread

In description, reference will be made to the preparation of titanium tetrachloride in a continuous type fluidization operation in accordance with the invention. Such product can be obtained by chlorinating at elevated temperatures (600° C.-1150° C.) the titanium values of a titaniferous material (ilmenite or rutile ores, TiO_2 concentrates, etc.) in the presence of a solid or gaseous reducing agent, including carbon, charcoal, coke, coal, etc. Examples of prior methods therefor include U. S. Patents 1,179,394, 1,528,319, 1,878,013, 2,184,884, 2,184,885 and 2,184,887. In a fluid bed chlorination the reactor bed suspension of, say, finely divided ilmenite ore and granular coke, together with partially reacted residual particles, such as furnace ash, is preferably at temperatures ranging from 800-1050° C., and in ebullient motion through the charging into the lower part of the reactor of a mixture of the reactant chlorine gas and other gases, such as nitrogen or oxygen oxides of carbon and a small amount of recirculated $TiCl_4$. As shown in Fig. 1, the apparatus can comprise reactor 1 of corrosion-resistant or other suitable metal, completely lined with a ceramic or other desired refractory material 2 protective against and resistant towards the corrosive effect of the highly heated reactant end product gases. An outlet 3 can be provided in the upper part of said reactor through which iron chloride and titanium tetrachloride products formed in the reaction can be exited to associated equipment (not shown) such as a condensing, separating or recovery system. Suitably disposed in the base portion of the reactor 1 is one (as shown) or a plurality of vertical inlet conduits 4. Within each of said conduits is a spiral insert 9 adapted to be accurately positioned within said conduit at or near the point of entrance of the latter into the reactor chamber and without attaining access to the interior of said chamber. Thus, as shown, said conduits extend just short (say within 3") of the inner or floor surface 5 of the refractory liner 2 and function by means of their passages 6 and inlets 7 to enable introduction into the reactor of chlorinating or other gaseous reactant and fluidizing agents from a source of supply (not shown) which communicates with said inlets 7. Such introduction can be effected at any desired controlled rate. A suitably valved inlet 8 communicating with a hopper or other source of titaniferous or and carbonaceous reducing agent supply (not shown) is provided in the upper portion of the reactor 1 through which a titaniferous material and said agent can be charged, either separately or in admixed state as desired, into the reactor and above its fluidized bed. Adjustably mounted or positioned within each of said vertical bottom conduits 4 is a removable, cylindrical, square-threaded spiral or helical insert 9 adapted to form a helix-shaped passage 10, the minor diameter helix angle of which is, as shown at 15 in Fig. 3, less than the angle of slide of solids to be retained within the reactor. The number of turns of the spiral is delineated by the length of the lower boundary surface of the helical passage. In the square-threaded spiral shown in Fig. 2, the length of the lower boundary surface of said helical passage is equivalent to at least

$$\left[1 + \frac{h \cos A \cdot \sin B'}{L \sin (A - B')} \right]$$

turns, wherein

h = the vertical height of the helical passage

B' = the vertical angle at the minor diameter of the helix

A = the effective angle of repose of the solids

L = "Lead" of the helical thread

The cross-sectional area of the spiral insert 9, is, as shown, less than the internal area of the conduit 4 and said insert can be screw-threadedly or otherwise fixedly se-

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cured to a metal support rod 12, the lower or base portion 13 of which rests upon a supporting element 14, the latter forming part of the walls of inlet 7.

In the operation of a device of the type described, the reactant fluidizing chlorine-containing gas mixture can be charged into the reactor from a conventional conduit and manifold system through the inlet 7 of the multiple vertical conduits 4 and passage 10 of the spirals 9. Simultaneously, a finely ground (capable of passing 50 mesh) mixture comprising about 1 part of powdered coke and about 5 parts of powdered ilmenite is fed from storage, either continuously or intermittently, through the inlet 8, the reactor having been previously heated to a temperature in excess of about 600° C. and within a range of from about 850-1050° C. by external heat application or by burning coke or other fuel therein. The gaseous feed rate is sufficient in velocity to effectively entrain the comminuted solids in fluidized or bubbling state within the reactor as distinguished from a violent or turbulent gaseous suspension, whereby a highly efficient solids-to-gas contact is maintained. During the reduction treatment such solids are not permitted to settle out to form a solid reacting mass. The gaseous products of reaction ($TiCl_4$ and $FeCl_3$) formed are discharged from the reactor 1 through the outlet 3 for passage to a cyclone or other separatory equipment (not shown), and thence to suitable condensing equipment for final separation and recovery.

By the provision and utilization of a plurality of the helix-shaped throats in the halogenating gas inlets, as herein contemplated, several advantageous results are realized. Thus, such throats serve as constricting orifices for the upward flow of entering fluidizing vapor during periods of reactor operation and prevent or stop bed solids from settling or flowing into the vertical multiple inlet conduits during periods of cessation of fluidizing vapor flow. Furthermore, the constricted throat being the same for all of the individual inlets causes a pressure drop between each of the constrictions and the main vapor inlet header ahead of the manifold to help equalize ebullition throughout the fluidized bed. As above noted, upon cessation of the operation and cutoff of vapor flows the fluidized bed settles down upon the reactor floor. In consequence, the multiple gas inlet conduit entrances, which, during periods of fluidized flow, are in contact with incoming feed gas at relatively low constant temperatures of, say, 100-300° C., become suddenly subjected to the higher temperature of the settling bed solids. The presence and contact of even small amounts of the reactant feed or product gases in these conduits would be very injurious due to their highly corrosive nature.

The actual size of the cross-sectional area of the helix-shaped passage in the spiral inserts will depend upon many factors, including gas flow, reactor operation variables, and the relative dimensions of the helix, etc. In general, this cross-sectional area would be less than $\frac{1}{2}$ that of the inlet conduit and in its preferred embodiment is of the order of $\frac{1}{4}$ of that area. Because of the small cross-sectional area and the consequent high velocity, this throat is generally self-cleaning. This is particularly advantageous if any solid or liquid which might be inadvertently deposited thereon due to presence of contaminants in the vapor stream or otherwise tends to become sticky. The spiral insert can conveniently consist of iron or steel or any other desired metal, although preferably it is composed of a corrosion-resistant metal such as nickel or bronze. Where the most corrosive conditions exist it may be fabricated of glass, silica or other ceramic material. The clearance between the cylindrical wall of the conduit and the outer boundary of the cylindrical spiral can be relatively slight and merely enough to allow passage of said spiral in and out of said conduit. Control of this clearance to a very accurate degree is not essential, although it is preferred that close tolerances be observed.

In its preferred embodiment, the spiral inserts em-

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ployed when positioned within the conduit will form a helix-shaped passage, the minor diameter helix angle of which is less than the effective angle of slide of the solids being retained within the reactor. In such adaptation the mixture of finely divided ilmenite ore, coke and furnace ash used has an effective angle of slide of 38-45° C. and an effective angle of repose within about the same range, with individual samples being about 2-3° greater than the effective angle of slide. With solids of this type, inlet conduits of about .8" inside diameter, a thread of about 1/8", and a minor helix angle of about 25° can be used, with the number of turns required for the removable square-threaded spiral insert being about 2±3 turns. Some variation in the effective angles of slide and repose will exist and consequently the minimum length of the passage must have some allowable variation for a given operation, particularly where the particles are continuously entering the reaction chamber, continually being reduced in size due to the reaction itself, and at the same time some particles are growing due to cementation reactions and the like.

While square-threaded cylindrical positionable spiral insert elements are preferred, other types and combinations of insertable elements are adaptable for use and to provide a serpentine helix-shaped passage for the upwardly flowing fluidizing gas and to prevent the undesired back-flow of solids from the reactor interior. These elements can be advantageously removable for cleaning without access from within the reactor and can be accurately positioned within the vertical conduit by means of rods or other suitable devices. If desired, the conduit wall can be provided with square-threaded rifling-like grooves which form with a removable cylindrical plug a helical-shaped passage. Alternatively, two or a plurality of insert elements can be utilized in each conduit and can be removed for cleaning from without the reactor. If desired, a cylindrical type plug and a helical spring-shaped element can be employed which, when positioned within the smooth, circular inner wall of the conduit, will form a helical-shaped passage. The critical dimensional requirements of these equivalent modifications of insert elements, forming a helical serpentine passage through which the fluidizing vapor can pass upwardly into a reactor and through the fluidizing solids, are substantially the same as for the preferred square-threaded type of spiral-shaped insert above referred to. That is, the passage which each forms within the vertical inlet conduit must have a helix angle at its minor diameter which is less than the effective angle of slide of the fluidized solids and the open cross-sectional area of said passage must be small compared to the cross-sectional area of the conduit.

The spiral passage insert of this invention can be employed in any process wherein a vapor is to be brought into contact with finely divided or granular solids. It is particularly useful in processes in which finely divided solids are fluidized by suspension in a gas. For example, an air elutriation of sand, ore, pigment, or other type of particulate solids may be advantageously suspended in air introduced into the separation chamber through a square-threaded cylindrical spiral of the type of the invention, allowing the entrance of the vapor from below, but preventing the back-flow of solids, and avoiding plugged inlets. While most useful in the case of multiple vapor inlet processes, the apparatus of the invention is also advantageously useful in a process requiring only one vapor inlet, positioned, for example, at the apex of a funnel-shaped bottom, of a reactor, elutriator, or other type vessel in which gas-suspended solids are required.

For convenience in cleaning and servicing, the insert element used is removable from the conduit. If desired, a complete unit, comprising the spiral insert and inlet tube, can be fabricated for use as a single removable unit. The positioning or supporting rod advantageously can be separable from the insert and removed from

the conduit after said insert has been positioned therein. The positioning rod when left in place will not interfere with gas flow, if constructed small in diameter in respect to the conduit.

When removing a spiral insert for cleaning, replacement, or other reason, during a period in which fluidizing gas has been cut off and the beds solids have settled down on the floor of the fluidizing chamber, a temporary, disposable plug can be inserted into the fluidizing gas inlet conduit, to retain the solids within the fluidizing chamber while the necessary servicing of the removable insert is being performed.

The effective angle of slide is the maximum inclination of a surface with the horizontal which allows solids to slide freely down an inclined surface and is a function of the characteristics of the inclined surface and material being retained, and in general is slightly less than the effective angle of repose.

The effective angle of repose of the granular solids is the inclination of a slant height of a cone of finely piled solids with the horizontal.

I claim as my invention:

1. A process for fluidizing solids within a vessel which comprises charging a fluidizing gas upwardly into said vessel through an inlet conduit and through a substantially vertical, helical, serpentine passage maintained in said conduit, said passage having a helix angle at its lower boundary surface which is less than the effective angle of slide of the solids being fluidized within said vessel, and the length of said lower boundary surface being equivalent to at least

$$1 + \frac{h \cos A \sin B}{L \sin (A - B)}$$

turns, wherein

h = the vertical height of the helical passage between a point on the radial line generating the upper boundary surface and a corresponding point directly below on the lower boundary surface

B = the maximum helix angle at the lower boundary surface

A = the effective angle of repose of the solids

L = "Lead" of the helical thread.

2. A method for fluidizing solids for reaction within a reaction vessel comprising charging a gaseous fluidizing reactant upwardly into said vessel and through a substantially vertical, helical, serpentine passage provided in the inlet conduit to said vessel, said passage having a helix angle at its lower boundary surface which is less than the effective angle of slide of the solids being fluidized in said vessel, and the cross-sectional area of said helical passage being small relative to the cross section of said conduit, and the length of said lower boundary surface being equivalent to at least

$$\left[1 + \frac{h \cos A \sin B}{L \sin (A - B)} \right]$$

turns, wherein

h = the vertical height of the helical passage between a point on the radial line generating the upper boundary surface and a corresponding point directly below on the lower boundary surface

B = the maximum helix angle at the lower boundary surface

A = the effective angle of repose of the solids

L = "Lead" of the helical thread.

3. A process for introducing a fluidizing vapor upwardly through a vertical inlet passage into a reaction vessel to maintain finely divided solids undergoing reaction in fluidized suspension, comprising charging said vapor through a spiral helical passage maintained in the upper portion of said inlet conduit, the helix angle at the minor diameter of the lower boundary surface of said passage is less than the effective angle of slide of the

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solids being fluidized and retained in said vessel, and the cross-sectional area of said passage being less than about one-half that of said inlet conduit, with the length of the lower boundary surface of said spiral being equivalent to at least

$$\left[1 + \frac{h \cos A \sin B'}{L \sin (A - B')} \right]$$

turns, wherein

h = the vertical height of the helical passage
 B' = the helix angle at the minor diameter of the helix
 A = the effective angle of repose of the solids
 L = "Lead" of the helical thread.

4. A method for charging a fluidizing gas into a reactor wherein finely divided solids comprising ilmenite ore and coke are reacted in fluidized state with chlorine at an elevated temperature to produce titanium tetrachloride which comprises passing said chlorine upwardly

8

into said reactor and through a plurality of vertical inlet conduits, and maintaining said solids in uniformly distributed fluidized suspension while preventing their back-flow into said conduits by providing in the upper extremity of each of the latter a square-sided, helix-shaped passage having a cross-sectional area of approximately one-fifth that of said conduit with the minor helix angle at the lower boundary surface of said passage being approximately 25° and the length thereof at least two turns.

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US005201949A

United States Patent [19]

[11] Patent Number: **5,201,949**

Allen et al.

[45] Date of Patent: **Apr. 13, 1993**

[54] **TiO₂ MANUFACTURING PROCESS**

[75] Inventors: **Alvin Allen, Claymont; Glenn R. Evers, Wilmington, both of Del.**

[73] Assignee: **E. I. du Pont de Nemours and Company, Wilmington, Del.**

[21] Appl. No.: **887,415**

[22] Filed: **May 20, 1992**

Related U.S. Application Data

[63] Continuation of Ser. No. 641,804, Jan. 16, 1991, abandoned, which is a continuation of Ser. No. 430,895, Oct. 31, 1989, abandoned, which is a continuation of Ser. No. 298,809, Jan. 18, 1989, abandoned, which is a continuation of Ser. No. 60,875, Jun. 12, 1987, abandoned, which is a continuation-in-part of Ser. No. 853,423, Apr. 18, 1986, abandoned.

[51] Int. Cl.⁵ **C09C 1/36**

[52] U.S. Cl. **106/436; 106/450; 423/613**

[58] Field of Search **106/436, 450; 423/613**

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Primary Examiner—Mark L. Bell
Assistant Examiner—Willie J. Thompson
Attorney, Agent, or Firm—David J. Gould

[57] **ABSTRACT**

Titanium dioxide pigment prepared by the high pressure (e.g., 10–200 PSIG) oxidation of TiCl₄ vapor is improved with respect to carbon black undertone, specific surface area, and gloss properties by the addition of a nucleant consisting essentially of a cesium substance which is present in the amount of about 8–2,000 parts per million, based on the weight of the TiO₂. The foregoing process is also used wherein the residence time of the reactants in the mixing zone of the reactor is about 1–16 milliseconds.

25 Claims, No Drawings

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TiO₂ MANUFACTURING PROCESS

This is a continuation of application Ser. No. 07/641,804, filed Jan. 16, 1991, which is a continuation of application Ser. No. 07/430,895, filed Oct. 31, 1989, which is a continuation of application Ser. No. 07/298,809, filed Jan. 18, 1989, which is a continuation of application Ser. No. 07/060,875, filed Jun. 12, 1987, which is a continuation-in-part of application Ser. No. 853,423, filed Apr. 18, 1986, all of which are abandoned.

BACKGROUND OF THE INVENTION

The preparation of pigmentary titanium dioxide by oxidizing titanium tetrachloride in the vapor state with an oxygen-containing gas is well known. Useful procedures therefore include those described in U.S. Pat. Nos. 2,488,439; 2,488,440; 2,559,638; and 2,833,627.

U.S. Pat. Nos. 2,488,439 and 2,488,440 also disclose that the addition of small, controlled amounts of water or hydrogenous water formers to the TiCl₄ or oxidizing gas reactants promotes nucleation and production of a high quality pigment having a high carbon black undertone or CBU. CBU is described in U.S. Pat. No. 2,488,440 (which is hereby incorporated by reference) and is a measure of particle size. The higher the carbon black undertone, the smaller the particle size and the higher the quality of the pigment for many applications. However, at increased oxygen concentrations and a corresponding allowable increase in reactor throughput, water becomes a less effective nucleant.

U.S. Pat. No. 3,208,866 discloses generally an improvement in the production of TiO₂ pigment by the oxidation of TiCl₄ which comprises utilizing a metal ion nucleant selected from the group consisting of sodium, potassium, lithium, rubidium, cesium, calcium, barium, strontium and cerium. In accordance with such patent, incorporating the nucleant results in improved bulk density and carbon black undertone. Such patent also discloses that potassium chloride is preferred and that cesium chloride is less active than potassium chloride.

U.S. Pat. No. 3,505,091 describes another improvement in the production of TiO₂ pigment by the oxidation of TiCl₄ which comprises conducting the reaction at a pressure of about 20-400 pounds per square inch gage, in the presence of AlCl₃. In accordance with such patent, the resulting TiO₂ exhibits improved resistance to chalking.

U.S. Pat. No. 3,640,745 discloses a process for producing agglomerated pigmentary TiO₂ by vapor phase oxidation of titanium halide in a reaction chamber at elevated temperatures in the presence of minor amounts of (1) an alkali metal, water soluble inorganic compounds of alkali metals or water insoluble organic compounds of alkali metals, (2) an auxiliary gas, and (3) minor amounts of water.

In modern processes for the production of TiO₂ by the oxidation of TiCl₄, potassium chloride is generally the preferred nucleant. Also in such modern processes, TiO₂ often is produced in reactors (1) operating at high pressures to reduce process equipment size and lower investment, and/or (2) having a short residence time of the reactants in the mixing zone of the reactor to increase product output. At such high pressures and/or short residence times, however, it appears that the effectiveness of potassium chloride (especially with respect to carbon black undertone, gloss and specific surface areas) can be reduced. In addition, this reduc-

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tion in effectiveness generally is apparent even if the concentration of potassium chloride is increased. Consequently, despite the above advances in TiO₂ production technology, there exists a need for a nucleant which produces increased TiO₂ carbon black undertone, specific surface area and gloss properties while operating at high pressures, short residence times of the reactants in the mixing zone of the reactor or both conditions. It should be noted that there is an increasing need for such TiO₂ pigment because modern end uses increasingly require these properties.

SUMMARY OF THE INVENTION

In accordance with this invention there is provided a process for producing pigmentary titanium dioxide which comprises:

- (a) reacting titanium tetrachloride and an oxygen containing gas in the vapor phase, at a reaction zone temperature of at least about 800° C., and at a pressure of at least about 10 pounds per square inch gage, in the presence of water vapor in the amount of about 50-100,000 parts per million, based on the weight of the TiO₂ under production, and a nucleant consisting essentially of a cesium substance wherein the cesium substance is present in the amount of about 8-2,000 parts per million, based on the weight of the TiO₂ under production, and
- (b) thereafter recovering the resulting titanium dioxide pigment.

There is also provided by this invention the foregoing process wherein the residence time of the reactants in the mixing zone of the reactor is about 1-16 milliseconds.

Additionally, there is provided in accordance with this invention, a process for producing pigmentary titanium dioxide which comprises:

- (a) reacting titanium tetrachloride and an oxygen containing gas in the vapor phase, at a reaction zone temperature of at least about 800° C. and at a residence time of the reactants in the mixing zone of the reactor of about 1-16 milliseconds, in the presence of water vapor in the amount of from about 50-100,000 parts per million, based on the TiO₂ under production, and a nucleant consisting essentially of a cesium substance wherein the substance is present in the amount of about 8-2,000 parts per million, based on the weight of the TiO₂ under production, and
- (b) thereafter recovering the resulting titanium dioxide pigment.

In accordance with this invention it has been found that the use of a cesium substance under the foregoing process conditions can improve carbon black undertone, specific surface area, and gloss compared to the use of potassium chloride. It also has been found that such improvement generally is evident even if the concentration of the potassium chloride is substantially increased. Moreover, it is believed that cesium can exhibit similar improvements, under the foregoing process conditions, when compared to other commercially used or commercially practical nucleants.

Finally, it has been found that the use of the cesium substance can permit higher TiO₂ output while still maintaining the desired or targeted level of CBU and/or gloss.

5,201,949

3

DETAILED DESCRIPTION OF THE INVENTION

The titanium tetrachloride and the oxygen containing gas are reacted in the presence of a nucleant consisting essentially of a cesium substance. By nucleant is meant any substance which can reduce the particle size of the pigment, such as a cesium substance or metals, oxides, salts or compounds of sodium, potassium, lithium, rubidium, calcium, barium, strontium, or mixtures thereof. By consisting essentially is meant that a nucleant other than a cesium substance can be present, provided that it is selected, and is present in such an amount that it does not negate or nullify the benefits of the cesium substance such as improved carbon black undertone, specific surface area and gloss. By cesium substance is meant any form of cesium or a mixture of various forms of cesium which can reduce the particle size of the TiO₂ pigment including cesium metal, cesium salts, cesium oxides and other compounds of cesium.

If a cesium substance is used with a nucleant other than a cesium substance, then such nucleant typically will not be present in an amount in excess of that specified hereinafter for the cesium substance. Preferably, such nucleant will be present in an amount less than that of the cesium substance.

Examples of cesium substances include cesium oxide, cesium halides (chlorides, iodides, bromides, fluorides), nitrates, phosphates, carbonates, sulfates, acetates, alcohulates, benzoates, hydroxides and oxides. Preferred is the use of cesium salts or water solutions of cesium salts such as cesium iodide, cesium chloride or cesium carbonate. Especially preferred are cesium chloride and cesium carbonate. Anions of the salt can be used which contribute color; however, they should not be employed where coloration is undesirable. Also, it is desirable that the cesium substance be substantially volatile at the reaction temperatures utilized for production of the TiO₂. Most preferably, the nucleant will consist of a cesium substance.

Procedures for adding the nucleants of this invention are described in U.S. Pat. No. 3,208,866 which is hereby incorporated by reference. Specifically, the nucleants are preferably added to or incorporated in the reactant oxygen gas stream being charged to the reactor, either as a finely divided solid, as a water solution, as a non-aqueous solution, as a molten salt, or as a colloidal dispersion. If desired, the nucleants may be charged directly into the reaction zone or to the mixed or mixing reactants just ahead of the actual flame of the reaction. Sometimes a third inert gas ("spacing gas") may be introduced into the reactor to prevent deposition of solids on the inlet area of the reactor. This spacing gas stream may be used as a carrier for the nucleants of this invention. Solutions of various nucleant salts of this invention can be sprayed into the gas stream and conveyed into the reaction as a mist. Also, they may be conveyed as fine solids or smoke. When the spacing gas is inert such as argon, it may carry the nucleant in elemental vapor form by suitable injection means or by use of any other desired means.

The use of water solutions of the soluble salts of the nucleants of this invention provides an excellent means of controlling product properties and compensating for variations in other process conditions. For example, the amount of a given salt solution used can be varied to hold the carbon black undertone value constant. To provide more accurate control without varying the

4

amount of water vapor used, two salt solutions of different concentration can be provided and blended as desired at constant water consumption. These solutions are usually made up with pure agents. However, the presence of other substances which are not deleterious can be tolerated. Mixtures of salts can also be effective. Naturally occurring solutions and brines which contain the nucleants of this invention and which are free of discoloring ions may be used if clear or clarified of silt and other debris.

The amount of the cesium substance present should be at least about parts per million, based on the weight of the TiO₂ under production. Preferably, the cesium substance will be present in an amount of at least about 10 parts per million and most preferably about 12 parts per million. The maximum amount of the cesium substance will be about 2,000 parts per million, based on the TiO₂ under production. Preferably, the cesium substance will be present in an maximum amount of about 1,000 parts per million and most preferably about 500 parts per million. Therefore, typical operating ranges include the following: about 8-2,000 parts per million, about 10-2,000 parts per million, about 12-2,000 parts per million, about 8-1,000 parts per million, about 10-1,000 parts per million, about 12-1,000 parts per million, about 8-500 parts per million, about 10-500 parts per million, and about 12-500 parts per million. An especially preferred range of cesium substance is about 8-200 parts per million, based on the TiO₂ under production. A more especially preferred range is about 20-200 parts per million, based on the TiO₂ under production. A very much preferred range is about 8-250 parts per million, based on the TiO₂ under production. The amount of the cesium substance is based on the weight of the cesium or the cesium component of the cesium salt, cesium oxide or cesium compound used.

Preferably, there is incorporated in the reaction zone vaporous AlCl₃ in the amount of about 0.1 to 10 percent, based on the weight of the TiCl₄. The method for incorporating the AlCl₃ is described in U.S. Pat. No. 3,505,091 which is hereby incorporated by reference.

The pressure for carrying out the reaction is at least about 10 pounds per square inch gage ("PSIG"). Preferably, the pressure will be at least about 15 PSIG and still more preferably at least about 20 PSIG. The upper pressure limit can be the operable limits of the process, e.g., up to about 200 PSIG. Preferably the upper limits will be about 100 PSIG and still more preferably about 70 PSIG. Therefore, typical operating ranges include the following: about 10-200 PSIG, about 10-100 PSIG, about 10-70 PSIG, about 15-200 PSIG, about 15-100 PSIG, about 15-70 PSIG, about 20-200 PSIG, about 20-100 PSIG, and about 20-70 PSIG.

The residence time of the reactants in the mixing zone of the reactor should be at least about 1 millisecond, preferably at least about 2 milliseconds, and most preferably at least about 3 milliseconds. The maximum residence time should be about 16 milliseconds, preferably about 14 milliseconds, and most preferably about 12 milliseconds. Typical ranges of residence times are about 1-16 milliseconds, preferably about 2-14 milliseconds, and most preferably about 3-12 milliseconds. By millisecond is meant 1×10^{-3} seconds. By mixing zone is meant the length of the reactor in which substantial mixing of the reactants takes place.

The residence time of the reactants in the mixing zone of the reactor is defined by the formula:

5

5,201,949

$$RT = \frac{3D}{V}$$

wherein RT=the residence time of the reactants in the mixing zone of the reactor, in seconds, D=the diameter of the reactor mixing zone in feet, measured at about the location where the reactants are first brought together, and V=the velocity of the reactants in feet per second.

The reaction temperature should be at least 800° C. Preferably, it should be about 800°-1800° C., and still more preferably about 900°-1700° C. An especially preferred range is about 950°-1500° C.

The water vapor should be present in an amount of about 50-100,000 parts per million, based on weight of the TiO₂ under production. Preferably, the water vapor will be present in an amount of about 0.1% to 3%, based on the weight of TiO₂ under production. Any water utilized as a solvent for the nucleant of this invention is considered in the total moisture added as water for nucleation. Any hydrogen-containing organic compound used as a liquid medium, such as benzene, burns to form water and also acts as the water of nucleation.

As mentioned previously, a spacing gas can be introduced into the reaction chamber. The spacing gas can be useful to prevent the deposition of solids on the inlet areas of the reactor and to control the reaction temperature. The spacing gas should be essentially chemically inert, i.e., it should not react with the reactants or the reaction product under the conditions under which the reaction is conducted.

Examples of suitable spacing gases include chlorine, nitrogen, carbon dioxide, noble gases, and recycle gas, i.e., gas withdrawn from the reactor outlet from which the titanium dioxide has been removed. The amount of the spacing gas should be about 1-100, preferably about 2-50, and most preferably about 5-25 mole percent, based on the titanium tetrachloride and the oxygen reactants.

U.S. Pat. No. 3,208,866 describes procedures for addition of the nucleant, reactors, and reaction conditions, as well as procedures for recovering and using the resulting TiO₂ pigment. Such patent is hereby incorporated by reference for such purposes.

The carbon black undertone ("CBU") values mentioned above and used to determine the values for the examples are described in U.S. Pat. No. 2,488,440 using a rating or value of 10 rather than 100 as used in such patent. Such patent is hereby incorporated by reference. A CBU value of 6 represents an acceptable quality pigment, with a preferred product exhibiting a CBU value of 8-16 or higher.

The specific surface area is defined as the surface area of one gram of pigment. It is defined by the formula

$$S = \frac{6}{Dia \times Den}$$

wherein

S=the specific surface area in square meters per gram

Dia=the average particle diameter in meters

Den=the density of the pigment in grams per cubic meters

The surface area can be determined by gas absorption or by determining the average particle size by use of an electron microscope and then using such particle size to calculate the surface area by use of the above formula. Additional information regarding determining the spe-

6

cific surface area is set forth in T. P. Patton, *Paint Flow and Pigment Dispersion*, 1979, John Wiley and Son, Inc. which is hereby incorporated by reference.

It has been found that the cesium substance of this invention is capable of increasing TiO₂ output while still maintaining the targeted or desired level of CBU. For example, to maximize output, a chloride process TiO₂ plant is typically operated with the use of KCl, and the output is increased until the CBU falls to the desired level. (Note that there usually is an inverse relationship between TiO₂ output and CBU.) At such point, output is maximized, and additional increases in output generally are not possible unless CBU is decreased or expensive new equipment is installed. However, at such point, it has been found that use of the cesium substance of this invention can permit increased product output while still maintaining the desired level of CBU. That is, if the cesium substance of this invention were added at such point, the CBU would increase and the output could then be increased until the CBU decreased to the desired level. It should be noted that such increase in output is highly commercially significant because (1) it is obtained without expensive capital investment, or equipment installations or modifications, and (2) modern chloride process TiO₂ plants operate at high rates (i.e. five or more tons per hour), and thus even minor percentage increases in output can result in substantially increased pounds of output. It should be noted that the use of the cesium substance of this invention can increase rate and still maintain the targeted or desired level of CBU whether or not the output is being maximized with KCl.

In a manner similar to that described in the immediately preceding paragraph, the cesium substance of this invention can increase TiO₂ output while still maintaining the targeted or desired level of TiO₂ gloss. Also, while certain process conditions can increase TiO₂ gloss, they generally decrease CBU. Under such process conditions, the use of the cesium substance of this invention can be beneficial to increase CBU.

It is believed that the use of the cesium substance of this invention can also extend the times between maintenance shutdowns and/or provide operating flexibility for chloride TiO₂ plants. For example, operation for extended periods of time can increase buildup of reactants, products, and by-products in the process equipment which can increase operating pressure. Also, desired reaction conditions may sometimes require or cause increased pressure. The increased pressure can be a problem by causing an adverse impact on TiO₂ CBU, surface area, and gloss, which can require (1) the output to be decreased to restore such properties, or (2) a plant shutdown to remedy the causes of the pressure increase. It is believed that under such conditions of increased pressure, use of the cesium substance of this invention could remedy some or all of such problems and thereby extend the times between maintenance shutdowns and/or provide for greater operating flexibility.

The following examples illustrate the invention. In the examples, the amount of cesium substance used is based on the weight of the alkali metal cation. Examples 1, 2, and 3 were run on separate days. It should be noted that on any given day, the CBU produced can vary, especially under industrial conditions. However, it is seen in all examples that the cesium substance produces improved results compared to the potassium nucleant.

7

5,201,949

EXAMPLE 1

TiCl₄ vapor containing vaporized AlCl₃ was heated and continuously admitted to the upstream portion of a vapor phase reactor of the type disclosed in U.S. Pat. No. 3,203,763. Other reactors which can be used are described in U.S. Pat. Nos. 2,833,627; 3,284,159; and 3,505,091. Simultaneously, preheated oxygen was metered through a separate inlet adjacent to the TiCl₄ inlet and was continuously admitted to the reaction chamber. A series of runs were made comparing various dosages of CsCl and KCl, each of which was introduced into the hot oxygen stream, in the form of an aqueous solution, just upstream of the mixing zone of the reactor. The amount of CsCl and KCl used is shown in Table I.

The conditions for the reactions were as follows:

TiCl₄—22,700 pounds per hour (about 385° C.)

O₂—4,700 pounds per hour (about 1530° C.)

AlCl₃—240 pounds per hour

Cl₂—600 pounds per hour

N₂—about 100 pounds per hour

H₂O—108 pounds per hour

CO₂—388 pounds per hour

Reaction Temperature—about 1350° C.

Pressure—56 pounds per square inch gage

Residence time of reactants in mixing zone of reactor—8.6 milliseconds

Production rate of TiO₂-Al₂O₃—5 tons per hour

The gaseous suspension of nucleated TiO₂-Al₂O₃ pigment formed in the reactor was separated from the gas stream at about 110° C. A substantially 100% conversion of titanium tetrachloride and aluminum chloride to their respective oxides, especially rutile in the case of TiO₂, was obtained with the resulting composite rutile pigment containing about 99% rutile and 1% Al₂O₃. The recovered raw titanium dioxide base was then tested for carbon black undertone and specific surface area.

The results of the reactions are summarized in Table I:

TABLE I

Run No.	Nucleant	Parts Per Million of Nucleant, Based on Weight of TiO ₂	Micromoles of Nucleant Per Gram Of TiO ₂	Average Carbon Black Undertone	Specific Surface Area (Square Meter/Gram)
1.	KCl	48	1.2	11.8	*
2.	KCl	31	0.8	11.5	6.5
3.	KCl	66	1.7	11.9	6.5
4.	CsCl	8	0.06	11.2	*
5.	CsCl	20	0.15	12.5	*
6.	CsCl	40	0.30	13.5	6.8
7.	CsCl	79	0.39	14.6	6.9
8.	CsCl	158	1.19	14.7	*

*Not measured

From the foregoing, the following is observed:

Comparing runs 2 and 6, at similar weight dosages (parts per million), CsCl produced 2 units higher CBU (13.5 vs. 11.5).

Comparing runs 1 and 8, at approximately equal mole dosages of CsCl and KCl, CsCl produced almost 3 units higher CBU (14.7 vs. 11.8).

Comparing runs 1 and 5, at 8 times less CsCl than KCl, on a mole basis, CsCl produced 0.7 higher units of CBU (12.5 vs. 11.8).

8

EXAMPLE 2

Using a procedure similar to that of Example 1, TiO₂ was produced using various dosages of CsCl and KCl. The conditions are summarized below:

TiCl₄—18,330 pounds per hour

O₂—4,700 pounds per hour

AlCl₃—176 pounds per hour

Cl₂—510 pounds per hour

CO₂—444 pounds per hour

H₂O—121 pounds per hour

Reaction Temperature—about 1350° C.

Pressure—53 PSIG

Residence time of reactants in the mixing zone of the reactor—10.7 milliseconds

Production rate of TiO₂/Al₂O₃—3.9 tons per hours

The results are summarized below

TABLE II

Run No.	Nucleant	Parts Per Million of Nucleant Based on Weight of TiO ₂	Micromoles of Nucleant Per Gram of TiO ₂	Average Carbon Black Undertone
1	CsCl	79	0.59	13.5
2	KCl	52	1.33	12.1

From the foregoing it is seen that approximately one-half the amount of cesium, on a mole basis, produced a CBU improvement of 1.4 units.

EXAMPLE 3

Using a procedure similar to that of Example 1, TiO₂ was produced using various dosages of KCl, Cs₂CO₃, and CsI. The conditions used are summarized below:

TiCl₄—23,220 pounds per hour

O₂—4,700 pounds per hour

AlCl₃—240 pounds per hour

CO₂—730 pounds per hour

CO₂—374 pounds per hour

H₂O—105 pounds per hour

Reaction Temperature—about 1350° C.

Pressure—54 PSIG

Residence time of reactants in mixing zone of the reactor—8.6 milliseconds

Production rate of TiO₂/Al₂O₃—4.9 tons per hour

The results of the reactions are summarized in Table III below:

TABLE III

Run No.	Nucleant	Parts Per Million of Nucleant Based on Weight of TiO ₂	Micromoles of Nucleant per gram of TiO ₂	Average Carbon Black Undertone
1	KCl	21	0.54	14.2
2	KCl	64	1.64	15.4
3	KCl	129	3.3	15.2
4	Cs ₂ CO ₃	100	0.75	16.9
5	CsI	119	0.90	17.1

From the foregoing, the following is observed:

Both Cs₂CO₃ and CsI produce improved carbon black undertone compared to KCl

Comparing runs 3 and 5, less than one-third the amount of cesium, on a mole basis, produced a CBU improvement of 1.9 units.

The invention claimed is:

1. A process for producing pigmentary titanium dioxide which comprises:

9

5,201,949

- (a) reacting titanium tetrachloride and an oxygen containing gas in the vapor phase, at a reaction zone temperature of at least about 800° C., and a pressure of at least 10 pounds per square inch gage, 5
- in the presence of water vapor in the amount of about 50-100,000 parts per million, based on the weight of the TiO₂ under production, and a nucleant consisting essentially of a cesium substance wherein the cesium substance is present in the amount of about 8-2,000 parts per million, based on the weight of the TiO₂ under production, and 10
- (b) thereafter recovering the resulting titanium dioxide pigment. 15
2. The process of claim 1 wherein the cesium substance is present in an amount of about 8-500 parts per million.
3. The process of claim 1 wherein the pressure is about 10-200 PSIG, the temperature is about 800°-1800° C., and the cesium substance is present in an amount of about 8-250 parts per million.
4. The process of claim 1 wherein the pressure is about 10-200 PSIG, the temperature is about 800°-1800° C., and the reaction is carried out in the presence of vaporous AlCl₃ in the amount of about 0.1-10% by weight, based on the weight of the titanium tetrachloride and the cesium substance is present in an amount of about 8-200 parts per million. 25
5. The process of claim 4 wherein a spacing gas is introduced into the reaction zone in the amount of about 5-200 mole percent, based on the titanium tetrachloride and oxygen reactants. 30
6. The process of claim 1 wherein the pressure is about 15-200 PSIG. 35
7. The process of claim 2 wherein the pressure is about 15-200 PSIG.
8. The process of claim 3 wherein the pressure is about 15-200 PSIG.
9. The process of claim 4 wherein the pressure is about 15-200 PSIG. 40
10. The process of claim 5 wherein the pressure is about 15-200 PSIG.
11. The process of claim 1 wherein the pressure is about 20-200 PSIG.
12. The process of claim 2 wherein the pressure is about 20-200 PSIG. 45
13. The process of claim 3 wherein the pressure is about 20-200 PSIG.
14. The process of claim 4 wherein the pressure is about 20-200 PSIG. 50
15. The process of claim 5 wherein the pressure is about 20-200 PSIG.
16. In a process for producing pigmentary titanium dioxide involving reacting titanium tetrachloride in the vapor state and an oxygen containing gas in the presence of water vapor and nucleant, the specific improvement comprising: 55
- (a) mixing and reacting the titanium tetrachloride and the oxygen containing gas with a residence time of 60 reactants in the mixing zone of the reactor of from about 1 to 16 milliseconds at a reaction zone temperature of at least about 800° C. and a pressure of

10

- at least 10 pounds per square inch gage, in the presence of water vapor in the amount of about 50 to 100,000 parts per million, based on the weight of the TiO₂ under production, and in the presence of an effective amount of a nucleant consisting essentially of a cesium substance to achieve improved CBU and improved specific surface area, wherein the cesium substance is present in the amount of about 8 to 2,000 part per million, based on the weight of the TiO₂ under productions, and
- (b) thereafter recovering the resulting titanium dioxide pigment characterized by improved CBU, gloss and specific surface area.
17. The improved process of claim 16 wherein the residence time of the reactants in the mixing zone of the reactor is about 2-14 milliseconds.
18. The improved process of claim 16 wherein the residence time of the reactants in the mixing zone of the reactor is about 3-12 milliseconds.
19. A process for producing pigmentary titanium dioxide which comprises:
- (a) reacting titanium tetrachloride and an oxygen containing gas in the vapor phase, at a reaction zone temperature of at least about 800° C., and at a residence time of the reactants in the mixing zone of the reactor of about 1-16 milliseconds, 5
- in the presence of water vapor in the amount of about 50-100,000 parts per million, based on the weight of TiO₂ under production, and a nucleant consisting essentially of a cesium substance wherein the cesium substance is present in an amount of about 8-2,000 parts per million, based on the weight of the TiO₂ under production, and
- (b) thereafter recovering the resulting titanium dioxide pigment.
20. The process of claim 19 wherein the residence time of the reactants in the mixing zone of the reactor is about 2-14 milliseconds.
21. The process of claim 19 wherein the residence time of the reactants in the mixing zone of the reactor is about 3-12 milliseconds.
22. The process of claim 19 wherein the TiO₂ nucleant is present in an amount of about 8-500 parts per million.
23. The process of claim 19 wherein the temperature is about 800°-1800° C. and the cesium substance is present in an amount of about 8-250 parts per million.
24. The process of any one of claims 19-23 wherein the temperature is about 800°-1800° C., and the reaction is carried out in the presence of vaporous AlCl₃ in the amount of about 0.1-10% by weight, based on the weight of the titanium tetrachloride.
25. The process of any one of claims 19-23 wherein a spacing gas is introduced into the reaction zone in the amount of about 5-200 mole percent, based on the titanium tetrachloride and oxygen reactants, the temperature is about 800°-1800° C., and the reaction is carried out in the presence of vaporous AlCl₃ in the amount of about 0.1-10% by weight based on the weight of the titanium tetrachloride. 60
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