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PROCESS OF MAKING RED LEAD

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This invention relates to a process of making red lead (\(\text{Pb}_3\text{O}_4\)).

One of the objects is to provide a process by which red lead can be produced economically and in a form or condition highly suitable for certain uses such as for making paste for storage battery plates.

A further object is to provide a process by which red lead may be produced in continuous fashion and automatically in the sense that the material which is to be treated and oxidized to red lead is introduced preferably by a substantially continuous feeding operation at one end of a suitable retort and the finished product in very finely divided form is substantially continuously removed from the opposite end without requiring any hand manipulation or even any attention on the part of the operator at any point in the cycle of operation or course of treatment.

A still further object is to provide a process such that the reaction in the conversion of the raw material to red lead may be carried out at substantially atmospheric pressure with air and not an otherwise enriched gaseous mixture.

The above and other objects are attained by the present invention, which may be here briefly summarized as consisting in the steps of the novel process which will be more fully described below, the invention having special utility in connection with certain raw materials which or a portion of which are in a continuous fashion converted to red lead after a conversion to an oxide of lower order.

In the accompanying sheet of drawing, we have shown conveniently or diagrammatically a retort which may be used to advantage in carrying out the process, the single figure being a vertical sectional view.

In our improved process, the material operated on is oxidized to red lead by subjecting it to an oxidizing medium, preferably air, in the presence of heat (both the retort and the air itself being preferably heated) and to substantially continuous agitation, preferably by rotating the retort and therefore cascading the material being treated as it passes slowly from the inlet end to the outlet end of the retort. Specific conditions of heat, rate of rotation, length of the retort, and therefore the time of treatment, will vary with the particular material being treated. The material which we prefer to employ in the novel process is a finely powdered mixture of metallic lead and an oxide (lower than red lead), the mixture having an oxygen content (by weight) from approximately 3.58% to approximately 4.66% and does not spontaneously ignite in the air.

The gray oxide is preferably obtained by tumbling lead balls or pieces of lead in a rotating container under oxidizing conditions so that as the oxide is formed, it, as well as particles of the lead, will be ground off. The apparatus and the process utilized for obtaining the gray oxide in the manner just stated are preferably similar to the apparatus and process disclosed in U. S. Letters Patent No. 1,675,345, granted July 3, 1928, to Clarence A. Hall, where the oxidation is continued far enough to produce a product which does not spontaneously ignite in the air.

While the precise characteristics of the gray oxide, i.e., percentage of oxide, apparent density, etc., may be varied, and while no specific or definite characteristics of the kinds mentioned are essential to our invention, we prefer to use gray oxide, the color of which may be generally described as greenish gray, with an apparent density varying between 26 and 35 grams per cubic inch with an oxygen content in excess of 3.58% by weight, and of a fineness such that the major portion of the material will pass through a standard 250 mesh screen. Excellent results are obtained by us by using gray oxide having an oxygen content of approximately 4.66% by weight and with an apparent density of 32.5 grams per cubic inch and a true specific gravity of approximately 9.97, the fineness of this material being such that approximately 10% to 12% will be retained on a 300 mesh screen used serially with respect to the first mentioned screen. Gray oxide having these characteristics can be very readily produced by the apparatus and process described in said Patent No. 1,675,346. We might add that the degree of oxidation as well as the fineness of the gray oxide, affects ease of oxidation to red lead as well as the apparent density and fineness of the latter.

The \(\text{Pb}_3\text{O}_4\) content of the finished product will depend to some extent upon the characteristics of the raw material used as well as upon the particular raw material employed and to some extent upon the controllable factors of the process, such as the temperature employed, amount of air, rate of rotation, and time of oxidation. It is understood that what is termed "red lead" need not and generally does not have a \(\text{Pb}_3\text{O}_4\) content of 100%. With our process it is quite feasible to obtain red lead from gray oxide or the other
raw materials mentioned having a PbO content up to approximately 50%, but for storage battery use, we endeavor to and do actually obtain red lead having a PbO content of between 65% and 75%, the balance being principally PbO; but with the same raw materials, by varying the time of treatment, the temperature, the amount of air supplied, and such conditions, the PbO content can be varied considerably from that just mentioned.

Referring now to the drawing, the red lead is produced by our process preferably in a retort 10 which may be of cylindrical form as illustrated, and is supported to rotate on a horizontal or substantially horizontal axis by means of wheels 11 which or part of which may be used for rotating the retort. This retort is made from alloys which will maintain their strength at the elevated temperatures employed and will not oxidize as a result of any decomposition of red lead and the attendant evolution of oxygen.

The retort is preferably surrounded, for at least a portion of its length, with insulation 12 which may or may not be attached to the retort so as to rotate therewith. When the raw material becomes treated consists of metallic lead such as gray oxide described above, the insulation preferably does not extend the full length of the retort, as indicated in the drawing, but is omitted from a portion of the retort at its inlet end. This is for the purpose of preventing the temperature rising too high at this end of the retort since the oxidation to PbO in exothermic in its action, the heat of the reaction is high, and may require dissipation and therefore the cooling of the retort by allowing it to come in contact with the air at room temperature is desired at or adjacent to the inlet end where the major portion of the oxidation of the finely divided metallic lead of the gray oxide to litharge occurs. Means for positively cooling this end of the retort may be desired, as, for example, by use of an air blast.

The raw material which is indicated at 13 is, in this instance, supplied from a hopper 14 and is fed substantially continuously by a feeder 15 to a chute 16 which delivers into the inlet or right-hand end of the retort, the delivery being optional at the center thereof through an opening 17. The feeder 15 serves as a seal to prevent the passage up through the raw material in the hopper of the air which is supplied and passes lengthwise through the retort from the outlet end to the inlet end. The delivery chute has an outlet pipe 18 for the withdrawal of air just beyond the opening 17. This pipe of course may be connected to a suitable dust collector, if necessary.

The constant feeding of the fine material into the inlet end of the retort and the rotation of the latter cause the material in the retort to gradually move toward the outlet end and to pass out through the centrally arranged outlet opening 19. This passage of material lengthwise is brought about without requiring any positive feeding but occurs because of the material to seek its level. This is the case even though the retort is rotated on a horizontal axis, but it may be aided by tilting the retort though the tilting is not necessary. The rate of rotation of the retort is such that the material will move up along the side of the retort, and then dropped down or cascaded so to speak so as to obtain the maximum oxidizing effect.

The fact that the raw material is introduced into the retort near the center of the inlet end and that the finished product passes out near the center of the outlet end thereof, provides a substantial depth of charge in the retort and this condition enhances the cascading effect. The red lead which passes out through the opening 19 drops into a suitable delivery pipe or chute 20.

The retort is best its length and for this purpose electric heaters, indicated at 21, may be employed but other means of heating may be utilized. When gray oxide having the characteristics above described is employed, the heating elements preferably surround the retort for about one-half or two-thirds of its length, i.e., from the outlet end to or beyond the middle. This portion of the retort is maintained by the heating elements 21 at the best reaction temperature, which is approximately 850° F, at which the conversion from litharge to red lead takes place. However, the temperature may be varied from this temperature, in both directions, without affecting the process, but, if so, changes in the temperature from that just stated should be accompanied by corresponding changes in the rate of air flow, speed of rotation of the retort, or the rate of heating so as to produce the desired results. The temperature may be varied from approximately 800° F to approximately 900° F without materially affecting the results, but the temperature should not be below the reaction temperature of red lie, nor too high to break up the red lead or sinter it. Likewise, at the inlet end where the temperature is considerably lower, as, for example, at a suitable point between room temperature and 400° F, there may also be some variation in the temperature, depending upon the materials used. The desirable temperature is one wherein the finely divided metallic lead is oxidized to litharge rapidly but yet not fast enough either to fuse the lead or sinter the litharge which is produced directly from the metallic lead. It might be added that by controlling the temperature from the outlet end where the red lead is delivered to the inlet end where the raw material is supplied, sintering at all points in the cycle of operations can be avoided and the final product need not be ground but remains in a finely divided condition.

The oxidized material is suitable for use as occurring at the center thereof through an opening 22 which may surround the tubular outlet opening 19, as illustrated. This air is heated preferably by electric heating elements indicated at 23, as this method of heating allows an accurate temperature control. The air is supplied at a temperature the side of the retort and the temperature at which the retort is maintained at its outlet end by the heating element 21 (or other means) as it is not intended that the heated...
air either add to or subtract from the heat supplied by the heating means. Of course the air is supplied in sufficient volume to furnish the necessary oxygen for the oxidizing steps of the process plus the necessary excess of oxygen to exceed the decomposition pressure of Fe₃O₄. It will be understood, of course, that while our process works satisfactorily with the use of air as the oxidizing medium, any other available suitable oxidizing gas or mixture may be employed. However, other means for heating the air may be employed, as by a countercurrent of air next to the retort in a spiral coil or equivalent device.

In operation, the raw material 13 is supplied from the hopper and fed continuously to the rotating retort which, as explained above, is heated at least at its outlet end and is supplied with a suitable volume of heated air which passes through the retort contrariwise to the general direction of flow of raw material from the hopper. The rotation of the retort causes a constant agitation or cascading with a gradual feed toward the outlet end, with the result that the material is, by the action of the heat and the oxidizing medium, together with the agitation, converted to red lead which passes substantially continuously through the outlet opening 19. This continuous feeding of the raw material and the continuous formation of red lead are believed to be novel when the raw material consists of a mixture of metallic lead and an oxide below red lead. However, the process is particularly novel, important and effective when the raw material is gray oxide, especially the fine gray oxide produced in the manner and having substantially the characteristics mentioned above in describing the preferred raw material. In this event, the conversion of the fine metallic lead to litharge takes place before the material reaches the zone heated for conversion to red lead and then, before the material reaches the outlet, the conversion to red lead takes place. This result is obtained without disturbing the fine powdered condition of the material. That is to say, the red lead has substantially the fineness of the fine gray oxide as is desired for storage batteries and possibly other uses. A further advantage of this fineness in the gray oxide lies in the fact that it greatly facilitates the conversion to red lead since the surface of each particle exposed to the oxidizing action of the air is practically the maximum.

Having thus described our invention, we claim:

1. The process of making red lead from a material in the form of a finely divided powder composed in part of metallic lead and largely of an oxide of lead lower than red lead, which comprises passing the material lengthwise through a single continuous heated rotating retort so that the material will be cascaded and thus agitated, passing an oxidizing medium through the retort, and maintaining the temperature in the retort at the outlet end thereof and for a distance toward the inlet end at a relatively high temperature suitable for the formation of red lead and at the same time maintaining adjacent the inlet end of a lower temperature suitable for the conversion of the metallic lead of the powder to litharge without fusion of the lead.

2. The process of making red lead from a finely divided material consisting of gray oxide substantially as described, which comprises passing the material lengthwise through a single continuous heated rotating retort so that the material will be cascaded and thus agitated, passing an oxidizing medium through the retort, and maintaining the temperature in the retort at the outlet end thereof and for a distance toward the inlet end at a relatively high temperature suitable for the formation of red lead and at the same time maintaining adjacent the inlet end a lower temperature suitable for the conversion of the metallic lead of the powder to litharge without fusion of the lead.

3. The process of making red lead from a material in the form of a finely divided powder composed in part of metallic lead and largely of an oxide of lead lower than red lead, which comprises passing the powder lengthwise through a single continuous retort, causing the powder as it passes from one end of the retort to the other to be agitated, passing an oxidizing medium through the retort, heating the retort and maintaining within the retort at the outlet end and for a distance lengthwise thereof toward the inlet end a temperature high enough for the formation of red lead and at the same time maintaining adjacent the inlet end a lower temperature suitable for the conversion of the metallic lead of the powder to litharge without fusion of the lead.

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