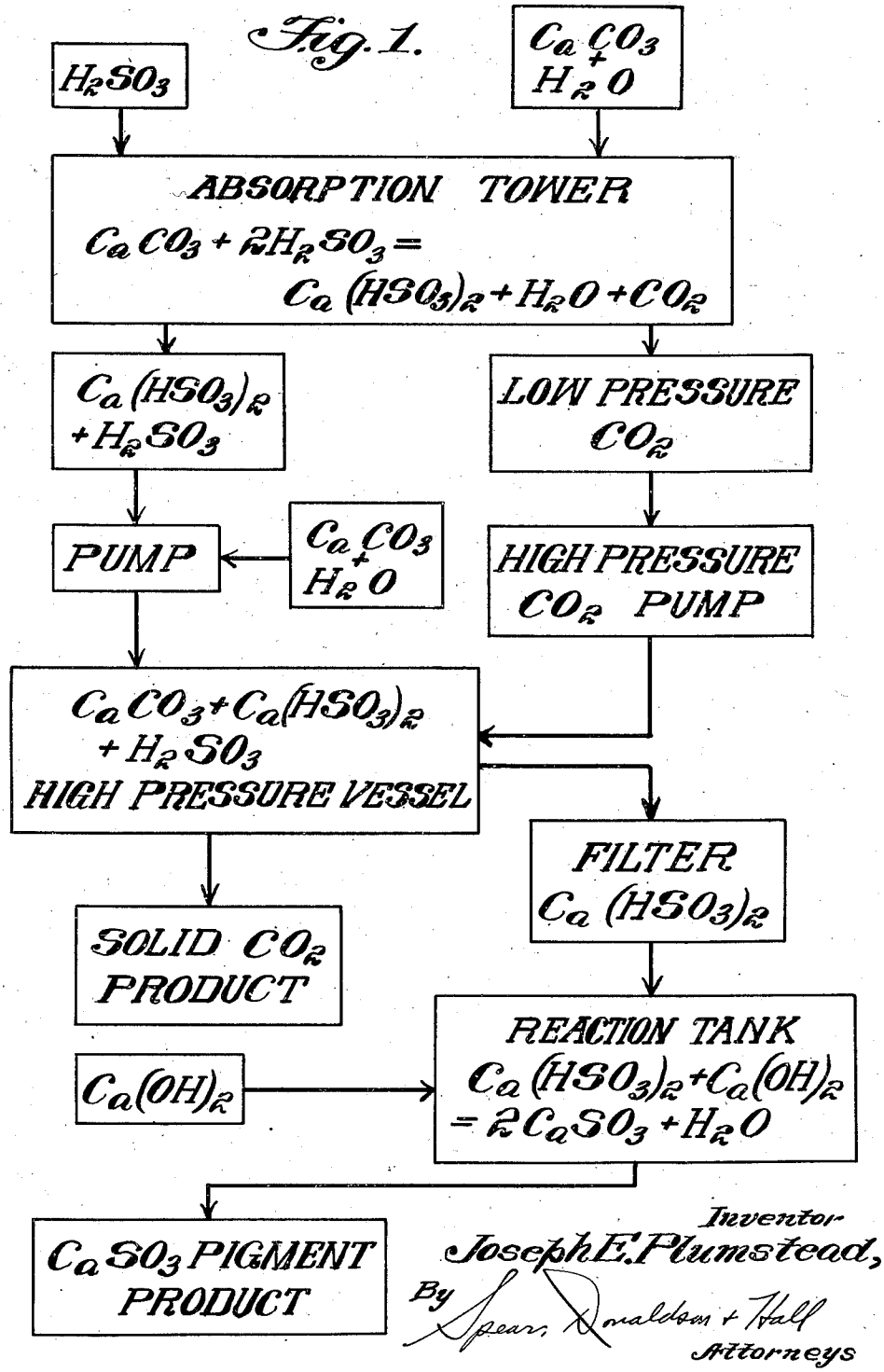
March 18, 1941. J. E. PLUMSTEAD 2,235,531

METHOD OF PRODUCING PAPER FILLER

Filed Sept. 4, 1931 2 Sheets-Sheet 1

Fig. 1.



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Fig. 2.

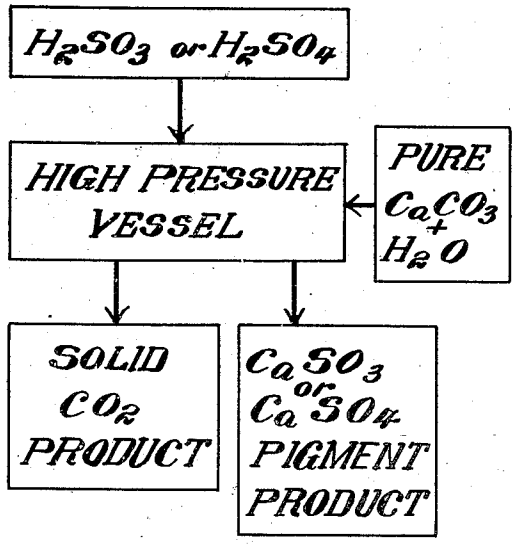


Fig. 4.

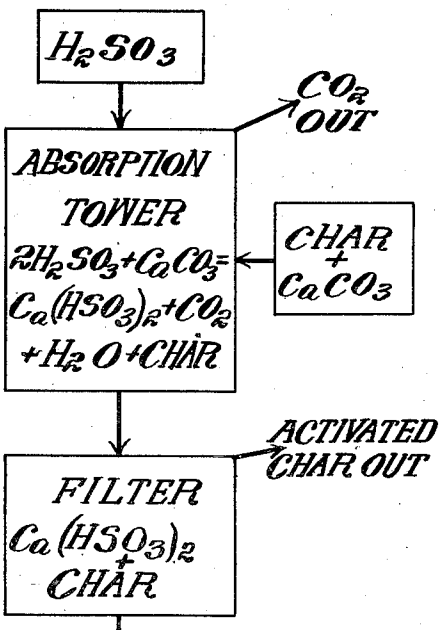
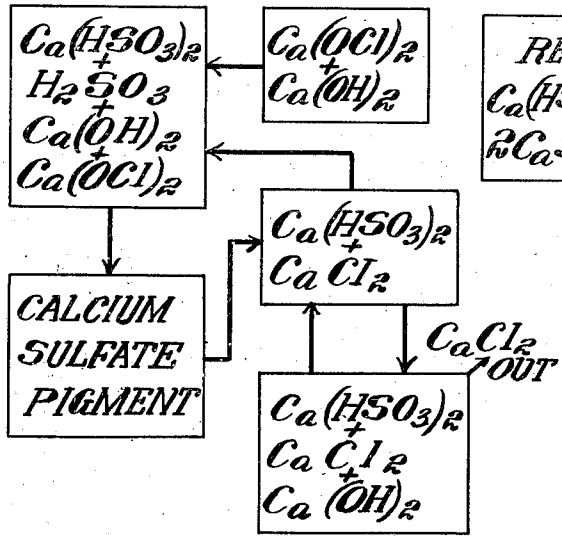
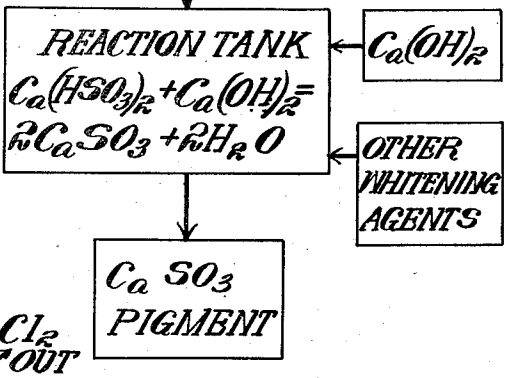


Fig. 3.





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Patented Mar. 18, 1941 2,235,531

UNITED STATES PATENT OFFICE

2,235,531

METHOD OF PRODUCING PAPER FILLER

Joseph E. Plumstead, Wilmington, Del., assignor, by mesne assignments, to West Virginia Pulp & Paper Company, New York, N. Y., a corporation of Delaware

Application September 4, 1931, Serial No. 561,241

14 Claims. (Cl. 23—122)

My present invention relates to an improved process of producing a sulfite or sulfate product particularly for use as a paper filler, although adapted for use as a pigment, disinfectant or reducing agent or other uses.

More particularly, the invention relates to a filler for use in paper making and to the method of producing the filler.

An object of the invention is to produce economically an effective paper filler for deterring aging or deterioration of the paper.

Another object is to provide a filler particularly valuable for paper made from mechanical or ground wood pulp, which filler has a white color and a reducing action which tends to produce a whiter paper from mechanical wood pulp and also tends to prevent the yellowing of such paper due to age and exposure to air and sunlight.

A further object is to produce an effective age deterrent paper filler by utilizing the materials available at the pulp and paper mills, thus effecting substantial savings.

Another object is the production of solid or liquid carbon dioxide as a part of the process of producing the paper filler, or substantially concurrently with the process of producing the paper filler.

Another object is to provide a process whereby a sulfate filler may be produced from bi-sulfite without requiring the use of hydroxide.

The drawings shown flow sheets or charts diagrammatically explanatory of the process. Figs. 1 and 2 show the simultaneous production of pigment and solid carbon dioxide. Figs. 3 and 4 show the filler production.

The invention consists in the process and product hereinafter described and particularly pointed out in the claims.

In carrying out my invention I have taken the calcium carbonate refuse remaining after the causticizing operation in a soda pulp mill and have treated this with sulfur dioxide until a solution of calcium bi-sulfite has been formed. This solution of bi-sulfite was filtered and clarified and then treated with enough milk of lime, calcium or magnesium hydrate, so that the resultant calcium or magnesium sulfite falls as a precipitate. This precipitate requires no washing and may be used either wet or dry as a paper making filler.

The reactions involved may be exemplified, as follows:

$$2H_2SO_3+CaCO_3=Ca(HSO_3)_2+CO_2$$

$$Ca(HSO_3)_2+Ca(OH)_2=2CaSO_3+2H_2O$$

This filler is particularly valuable for paper made from mechanical or ground wood pulp due to the fact that the reducing action of the calcium sulfite, together with its naturally white color tends to produce a whiter paper from mechanical wood pulp and also tends to prevent the yellowing of such paper due to age and exposure to air and sunlight.

If it is desired to convert the calcium sulfite filler into a calcium sulfate filler, the addition of calcium hypochlorite solution will accomplish the desired result and if the reactions are properly handled the calcium hydroxide in the hypochlorite solution will be utilized.

The oxidizing action of the hypochlorite on the calcium sulfite may be indicated as follows:

$$2CaSO_3+Ca(OCl)_2=2CaSO_4+CaCl_2$$

The reaction including the function of the calcium hydroxide may be indicated as follows:

$$Ca(OH)_2+SO_2+H_2O+Ca(OCl)_2+2CaSO_3=CaSO_3+CaCl_2+2CaSO_4+2H_2O$$

It is necessary in making up calcium hypochlorite solutions to have an excess of calcium hydroxide present to stabilize the hypochlorite. It is this calcium hydroxide which is used to form additional filler, either sulfite or sulfate, depending upon the amount of hypochlorite solution used. The calcium which is combined as calcium hypochlorite is not used as it goes to form calcium chloride which is soluble.

All of these steps in the process described are particularly apropos for pulp and paper mills inasmuch as the equipment for making the various chemicals is usually at hand. The sulfur dioxide would be available in a sulfite mill as also would be the limestone in case no soda mill calcium carbonate refuse or sludge were available. Calcium hypochlorite is usually manufactured and used by pulp mills.

The products resulting from my process and which are particularly adapted for use as age deterring paper fillers, are calcium sulfite, magnesium sulfite, and calcium sulfate. Magnesium sulfate is soluble in water and so would not be a pigment. Therefore, with this exception magnesium may be read into the specification and claims where calcium is specified, it being understood that calcium or an equivalent substance is intended, and that the claims are not to be restricted to calcium.

This pigment which among other uses may be used for a paper filler, may be produced by the use of a by-product lime, either carbonate as

hereinbefore indicated or hydroxide, to form a soluble bi-sulfite which may be filtered and clarified to free the lime from gritty and insoluble undesirable substances. The soluble bi-sulfite is formed from the by-product lime carbonate or hydroxide by treatment with sulfur dioxide gas.

The reaction of the sulfur dioxide on the carbonate of lime has been indicated hereinbefore. The reaction of the sulfur dioxide on the hydroxide is indicated as follows:

$$2SO_2+2H_2O+Ca(OH)_2=Ca(HSO_3)_2+2H_2O$$
$$Ca(HSO_3)_2+Ca(OH)_2=2CaSO_3+2H_2O$$

This shows how an excess of sulfur dioxide will react with the excess of calcium hydroxide in the hypochlorite solution to form calcium bi-sulfite.

Or the soluble bi-sulfite resulting from the treatment of the by-product lime carbonate or hydroxide with sulfur dioxide, may be filtered and clarified and then treated according to my present invention with a pure milk of lime suspension in such quantity or amount that a neutral or slightly acid or slightly alkaline, normal sulfite is formed.

The sulfite product which may as readily be produced with magnesium as with calcium may be used as a pigment, paper filler, disinfectant or reducing agent.

Also according to my process, calcium hypochlorite solution is used to react upon the bi-sulfite as produced in the first treating step with sulfur dioxide, as well as upon the sulfite as produced in the second treating step with milk of lime as hereinbefore indicated, in such a way as to react with the hypochlorite and to produce a sulfate product. The oxidizing power of the hypochlorite produces a quantity of calcium sulfate from the bi-sulfite or sulfite product, which quantity of calcium sulfate would be greater in weight, by reason of the calcium hydroxide in the hypochlorite solution, than the weight of calcium sulfate produced by the oxidization of the sulfite compound so acted upon. Equations indicating the reactions of the hypochlorite solution upon the sulfite have been hereinbefore set forth. The reaction of the hypochlorite and the bi-sulfite may be indicated as follows:

$$3Ca(HSO_3)_2+Ca(OCl)_2=$$
$$2CaSo_4+CaCl_2+Ca(HSO_3)_2+2H_2SO_3$$

In regard to the reaction of calcium hypochlorite upon bi-sulfite, this is a modification which might be used to produce calcium sulfate without the use of calcium hydroxide. If calcium hypochlorite solution were added to the calcium bi-sulfite solution the result would be a calcium sulfate suspension in an acid calcium bi-sulfite solution, which acid calcium bi-sulfite solution can be filtered from the calcium sulfate and be used again to react on additional calcium carbonate to form more calcium bi-sulfite, thereby entirely or partially obviating the necessity for the use of calcium hydroxide in the production of the calcium sulfate.

If additional sulfur dioxide is required, this of course, will be made up from the gas burner supply. The point intended to be conveyed is that the filtrate from the calcium sulfate filtering operation, after the addition of hypochlorite solution, will contain bi-sulfite of lime, not necessarily with an excess of sulfurous acid but this would probably be the case. In any case however this filtrate would be used for making up the next batch rather than to use fresh water for the purpose. The exact amounts of sulfurous acid and calcium bi-sulfite remaining in the filtrate would be determined by test and upon this test would rest the determination of the calcium carbonate or hydroxide addition.

The sulfate product may be used as a pigment, in paper making as a filler, either separately or mixed with some other pigment.

An important feature of the process lies in the complete dissolving of the lime so that it may be clarified and filtered, thus ridding the product of all gritty matters and insoluble substances which would be harmful in the use of the product as a paper filler or pigment. The use of a pure milk of lime or calcium hydroxide suspension for precipitation, a milk of lime which has been elutriated after slaking, is necessary in order to further assure and insure the purity and utility of the finished product.

I also contemplate the use of limestone in the first step as a substitute for the by-product lime.

The by-product lime may be the offal from the causticizing process, from the sugar industry, from the production of acetylene gas from calcium carbide and from various other industries where lime is used in process work and later discarded. The offal from soda pulp mill black ash operation contains carbon.

The reaction between sulfurous acid or calcium bi-sulfite and milk of lime is a rapid one for the greater part of the reaction. However, some of the milk of lime particles and some of the calcium sulfite particles may occlude sulfurous acid or calcium hydroxide, as the case may be, and cause a slowing up of the reaction toward the end. If the reaction is not properly balanced an inferior product will be obtained. Allowing the suspension to stand permits completion of the reaction.

My process further involves the production of a superior quality material by allowing the neutralized calcium sulfite water suspension to stand for sufficient time to insure completion of the reaction, and then throwing it back to a slightly acid reaction with the addition of any of the following: sulfur dioxide, iron free aluminum sulfate, or sulfuric acid or other suitable materials. I have also found that a material of superior quality may be produced by allowing the neutralized calcium sulfite water suspension to stand for sufficient time for completion of the reaction, and then throwing it to the alkaline side with a suitable material such as sodium aluminate. Usually much less than 1% of acid or alkali weight figured on total weight of chemical is used to throw the suspension slightly on the acid side or slightly on the alkaline side.

By shortening the mixing time of reacting the acid calcium bi-sulfite and calcium hydrate suspension, a white product has resulted according to the present process. In order to shorten the mixing time, the reacting chemicals are put together in the proper proportions as quickly as possible and after being put together are agitated and kept in contact with one another with sufficient time for completion of the reaction as explained above.

In regard to the term "proper proportion" these are strictly chemical reactions and proper proportions can mean only one thing, which is, that the raw materials must be tested for purity and combined, taking into consideration molecular weights and the determined raw material purity.

In regard to the statement "sufficient time to complete the reaction" the completion of the reaction is determined by tests and to run for one, two or three hours could not be specified ex-

cept by tests showing completion of the reaction. If the reaction is to be completed, the reacting chemicals must be in contact until the desired result is obtained. The physical state of the operation has a great deal to do with this speed of reaction completion. Temperatures, pressures and speeds of mixing and agitation influence the time required to complete the reaction.

Acid calcium bi-sulfite means that an excess of sulfur dioxide or sulfurous acid is absorbed in the calcium bi-sulfite solution. This may be a large excess or not as desired. Ordinarily there is about three times as much uncombined sulfur dioxide as combined.

A whiter product is also produced by reacting approximately proper chemical proportions of acid calcium bi-sulfite and calcium hydrate suspension without allowing any part of the final product of normal calcium sulfite to stand for any substantial time in a calcium hydrate suspension, nor in an acid calcium bi-sulfite solution, nor in a calcium bi-sulfite solution. In other words, a whiter product is produced by proportioning the reacting chemicals to complete the reaction properly and without permitting excess of either reacting chemical to act on the normal sulfite product.

By the action of the sulfur dioxide or sulfurous acid gas upon the water slurry of calcium carbonate, in addition to the calcium bi-sulfite product there is the product of carbon dioxide gas. This carbon dioxide product, according to my process is confined in a closed high pressure vessel and this carbon dioxide in the high pressure vessel builds up its own pressure to a point such that the discharge or release of the carbon dioxide gas into a vessel at a lesser pressure will result in solidification or liquefaction of the gas so discharged.

I may produce the solid carbon dioxide by pumping into a closed high pressure vessel a solution of calcium acid bi-sulfite and a suspension of calcium carbonate, and building up the pressure of the carbon dioxide gas to a point such that discharge of the gas into a vessel at a lesser pressure solidifies or liquefies the carbon dioxide.

Also by the use of sulfuric acid and calcium carbonate I may produce substantially simultaneously a calcium sulfate pigment product and solid or liquid carbon dioxide product, according to the following equation:

$$H_2SO_4+CaCO_3=CaSO_4+CO_2+H_2O$$

The solid or liquid carbon dioxide is produced as above suggested by building up pressure of the gas in a high pressure vessel and discharging it into a low pressure vessel.

A liquid pump is required for forcing in the chemicals but no gas pump is required for the carbon dioxide. Much smaller equipment will be required for handling a certain amount of acid and carbonate to produce a given quantity of solid or liquid carbon dioxide than would be required to handle this same amount of carbon dioxide if it were handled in gaseous form. In other words, the nascent carbon dioxide builds up its own pressure with a simultaneous formation of calcium bi-sulfite or calcium sulfite pigment or sulfate pigment,—a pressure sufficiently high that when it is released the carbon dioxide gas solidifies.

If a waste calcium carbonate is used,—a lime raw material which requires filtration in order to properly purify it,—then this cannot be used for a direct sulfate reaction nor can it be used for the direct production of calcium sulfite, where a clean product might be necessary, the clean sulfite being produced from the filterable bi-sulfite formed as indicated in Fig. 1. If, however, a pure clean calcium carbonate is used for the reaction, then a clean product may be obtained with the formation of calcium sulfate or with the formation of calcium sulfite within the pressure vessel.

It will therefore not be necessary to form the bi-sulfite except where raw material is used which needs to be purified. If it is desired to convert a pure calcium carbonate into calcium sulfite or sulfate it will not be necessary to go through the steps of bi-sulfite formation and filtration. But in the case of heavy limestone, it will be necessary to go to the bi-sulfite in order to remove a coat of calcium sulfite from the surface of the limestone to be reacted upon, in order to physically permit the reaction to continue. Also, although the sulfite may be formed in the high pressure vessel, it must go to the filtrable bi-sulfite in order to separate it from impurities in the waste lime carbonate used.

I am producing filler and carbon dioxide as two products. The filler may be used for its physical or for its chemical properties or for both purposes. In considering its physical properties, fineness, color and cleanliness are important. Chemically, calcium carbonate does not require going through the bi-sulfite stage for the formation of sulfite. If the calcium carbonate used in the reaction is sufficiently fine and sufficiently pure, a pure calcium calcium bi-sulfite solution and a pure calcium carbonate suspension may be mixed in the proper chemical proportions and produce thereby a pure calcium sulfite of a white color and fine texture, with the liberation of carbon dioxide. This reaction would be used:

(1) In the high pressure vessel in order to confine the carbon dioxide and build up its pressure.

(2) The reaction might also be used in case it would be desired to use a waste lime for absorbing all of the sulfur dioxide required for producing a certain amount of calcium sulfite and for furnishing one-half the calcium supply to produce this given amount of calcium sulfite and to use pure, finely divided calcium carbonate instead of calcium hydroxide for the other half of the calcium supply for the calcium sulfite production.

In a mixture of calcium carbonate and calcium bi-sulfite the acid radical in the calcium bi-sulfite is more loosely combined and has more affinity for the calcium in the carbonate than it has for the calcium sulfite, consequently the calcium bi-sulfite gives up its loosely combined acid radical which goes over to the calcium which is combined with carbon dioxide as calcium carbonate, with a liberation of carbon dioxide and the formation of calcium sulfite as follows:

$$Ca(HSO_3)_2+CaCO_3=2CaSO_3+H_2O+CO_2$$

Referring to Fig. 1, the excess of sulfurous acid in the acid calcium bi-sulfite solution will have to be large when pumped into the large closed high pressure vessel, if any great amount of carbon dioxide is to be generated. Some of the carbon dioxide gas generated at atmospheric pressure during the first stages of the acid calcium bi-sulfite reaction, may be forced into the reacting mass which forms carbon dioxide in

the high pressure vessel during the later stages of the reaction.

This step would not be necessary however in the formation of calcium sulfate from sulfuric acid and calcium carbonate in the closed high pressure vessel, as represented in Fig. 2.

Fig. 1 is a flow chart indicating diagrammatically the simultaneous production of sulfite pigment and solid carbon dioxide. As indicated in this chart, the sulfurous acid and calcium carbonate suspension are passed into reaction in the absorption tower, to produce calcium bi-sulfite and low pressure carbon dioxide which are drawn off as indicated. To this calcium bi-sulfite is supplied additional sulfurous acid, by-passed as shown from the source of supply or from any other source, and this mixture is delivered to the pump as shown. To the pump is also delivered calcium carbonate and water and the pump forces these materials into the high pressure vessel as indicated to produce the calcium bi-sulfite product which may be filtered off as shown, and the carbon dioxide product. The carbon dioxide gas builds up a high pressure in the vessel, and may be augmented by the low pressure carbon dioxide gas pumped at high pressure into the reacting mass in the high pressure vessel as indicated. The combined carbon dioxide gas under high pressure is then released from the high pressure vessel to solidify. The calcium bi-sulfite filtered off from the high pressure vessel is delivered to the reaction tank to which is also supplied calcium hydroxide, the reaction producing the desired calcium sulfate pigment.

In the formation of the calcium bi-sulfite in the absorption tower and in the high pressure vessel, this goes through the stages of calcium carbonate, then calcium sulfite, then calcium bi-sulfite, then acid calcium bi-sulfite. In other words, the sulfurous acid comes into the absorption tower in which there is calcium carbonate and water, thereby first forming calcium sulfite, then as more sulfurous acid comes in the bi-sulfite is formed and as still more acid comes in the acid calcium bi-sulfite is formed. The greater the excess sulfurous acid which may be present, the greater the amount of calcium carbonate which may be charged into the high pressure vessel separately, as indicated.

Fig. 2 is a flow chart showing the direct production of the sulfite pigment from pure calcium carbonate and sulfurous acid without the necessity of the intermediate formation of the bi-sulfite. This chart also shows the simultaneous production of the pigment and solid carbon dioxide. This chart also shows the production of calcium sulfate pigment by the action of sulfuric acid on the lime carbonate.

In regard to the pressure required for liquefying carbon dioxide, it will be understood that any gas which has been liquefied has a certain boiling point temperature under given pressure conditions just as water does and in order to give pressures for liquefaction would require a set of tables just as is shown in any mechanical engineer's hand book on steam. However, it may be stated in general that carbon dioxide sublimes passing directly from the solid to gas or from the gas to liquid at minus 78.2° C. under atmospheric pressure. It will depend upon the temperature of the cooling water used and the efficiency of the coolers as to what pressure, and consequently what temperature, will be required in any given case. Each case would require separate study in order to determine the extremes of summer and winter or seasonal cooling media temperature conditions.

Fig. 3 is a flow chart showing the production of the sulfate pigment by treatment of the acid calcium bi-sulfite—produced as shown in Figs. 1 or 4—with calcium hypochlorite and calcium hydroxide to produce the calcium sulfate pigment product, from which the calcium bi-sulfite and calcium chloride may be filtered off and returned to the process, as indicated. As shown, if the calcium chloride builds up too much, some of the filtrate may be withdrawn or by-passed as indicated, and treated in the regular way with calcium hydroxide and the calcium chloride washed out of the precipitated calcium sulfite which is returned to the process.

In the production of soda pulp there is carbon charcoal waste amounting to approximately 10% of the weight of the pulp produced. This charcoal contains about 10% of mineral substances, mostly calcium, which if treated by an acid would result in an activated char. I propose the mixing of this waste char with the waste lime sludge and the simultaneous acid treatment and activation of this char with the formation of filterable calcium bi-sulfite and an activated, adsorbent or absorbent carbon or char, which may be used as a decolorizing agent or for other well known purposes for which activated carbons are used.

Fig. 4 shows by way of flow chart, the production of the sulfite pigment or filler together with activated char. The sulfurous acid is delivered to the absorption tower and the calcium carbonate with waste char are also delivered thereto. The carbon dioxide gas produced by the reaction is passed off, and the bi-sulfite and char are filtered off and the activated char is passed out as a product. The bi-sulfite is treated in the reaction tank with calcium hydroxide and other whitening agents, to produce the calcium sulfite pigment product.

The invention also contemplates producing the calcium sulfite from the bi-sulfite by boiling the bi-sulfite which will give off SO_2 gas and will deposit the sulfite. In other words, instead of forming the bi-sulfite, filtering and then forming the sulfite by treating the bi-sulfite with calcium hydroxide as indicated in Fig. 1, the bi-sulfite may be formed, filtered, and then the sulfite thrown out from solution by boiling, and reclaiming the SO_2 gas.

That phase of the invention disclosed herein which relates to the product resulting from the addition of the improved pigment or filler material to pulp, and more particularly mechanical or ground wood pulp, has been divided from this application and will be made the subject matter of a separate, divisional application.

I claim:

1. The herein described method of producing a substance of improved qualities for use as a paper making filler or for other uses, comprising treating a suitable lime material with sulfur dioxide gas in the presence of water to produce calcium bi-sulfite solution, filtering and clarifying the calcium bi-sulfite solution to remove impurities, and treating the same with calcium hypochlorite solution so as to neutralize the lime in the hypochlorite solution and to oxidize the bi-sulfite to produce a calcium sulfate product.

2. The herein described method of producing calcium sulfate without requiring the use of calcium hydroxide, comprising adding calcium hypochlorite solution to a calcium bi-sulfite solution, to produce a calcium sulfate suspension in an acid calcium bi-sulfite solution, and filtering

the acid calcium bi-sulfite solution from the calcium sulfate product.

3. The method of producing a calcium sulfate pigment comprising treating calcium sulfite with calcium hypochlorite solution so as to neutralize the lime in the hypochlorite solution and to oxidize the sulfite to produce a calcium sulfate product.

4. The herein described method of producing a calcium sulfate pigment comprising treating acid calcium bi-sulfite solution with calcium hypochlorite and calcium hydroxide solution, producing a calcium sulfate pigment, filtering off from said sulfate pigment the excess bi-sulfite or sulfite and calcium chloride solution, and returning said excess filtrate to the initial reaction at the beginning of the process.

5. The method of claim 4 including by-passing a portion of the filtrate before returning it to the beginning of the process, and removing excess calcium chloride by treating the by-passed portion of the filtrate with calcium hydroxide and washing out the calcium chloride, and returning the precipitated calcium sulfite to the process.

6. The herein described process of producing a pigment comprising passing sulfurous acid and a mixture of waste lime sludge and char into reaction in an absorption tower or the like, producing carbon dioxide gas and calcium bi-sulfite, passing off the carbon dioxide gas, filtering out the calcium bi-sulfite and char, withdrawing the activated char from said bi-sulfite, passing the bi-sulfite into reaction with calcium hydroxide to produce the sulfite pigment which is withdrawn.

7. The herein described method of producing a substance of improved qualities for use as a paper making filler or for other uses, comprising treating a suitable lime material with sulfur dioxide gas in the presence of water to produce calcium bi-sulfite solution, filtering and clarifying the calcium bi-sulfite solution to remove insoluble impurities, reacting the filtered clear solution with a pure milk of lime suspension to precipitate a calcium sulfite product and allowing the calcium sulfite suspension thus formed to stand for sufficient time for completion of the reaction and then making it slightly acid with additional material.

8. The herein described method of producing a substance of improved qualities for use as a paper making filler or for other uses, comprising treating a suitable lime material with sulfur dioxide gas in the presence of water to produce calcium bi-sulfite solution, filtering and clarifying the calcium bi-sulfite solution to remove insoluble impurities, reacting the filtered clear solution with a pure milk of lime suspension to precipitate a calcium sulfite product and allowing the calcium sulfite suspension thus formed to stand for sufficient time for completion of the reaction, and then making it alkaline with additional lime material.

9. The herein described method of producing a substance of improved qualities for use as a paper making filler or for other uses, comprising treating a suitable lime material with sulfur dioxide gas in the presence of water to produce calcium bi-sulfite solution, filtering and clarifying the calcium bi-sulfite solution to remove insoluble impurities, reacting the filtered clear solution with a pure milk of lime suspension to precipitate a calcium sulfite product and allowing the calcium sulfite suspension thus formed to stand for a sufficient period to complete the reaction, and then making it alkaline with sodium aluminate.

10. The herein described method of producing a substance of improved qualities for use as a paper making filler or for other uses, comprising treating a suitable lime material with sulfur dioxide gas in the presence of water to produce calcium bi-sulfite solution, filtering and clarifying the calcium bi-sulfite solution to remove insoluble impurities, reacting the filtered clear solution with a pure milk of lime suspension to precipitate a calcium sulfite product, the proportions of calcium bi-sulfite and lime material being in approximately definite proportions whereby no part of the final product of normal calcium sulfite will be allowed to stand for any substantial time in any one of a group consisting of calcium hydrate suspension, acid calcium bi-sulfite solution, and calcium bi-sulfite solution to thereby increase the whiteness of the calcium sulfite product.

11. The herein described method of producing a pigment for use as a filler for paper making or other uses, comprising mixing waste carbon char with waste lime sludge and simultaneously treating the mixture with acid to activate the char and to form filterable calcium bi-sulfite, filtering and clarifying the calcium bi-sulfite solution and precipitating calcium sulfite by reacting said solution with pure lime milk suspension.

12. The herein described method of producing a substance of improved qualities for use as a paper making filler or for other uses, comprising treating a suitable lime material with sulfur dioxide gas in the presence of water to produce calcium bi-sulfite solution, filtering and clarifying the calcium bi-sulfite solution to remove insoluble impurities, reacting the filtered clear solution with a pure milk of lime suspension to precipitate a calcium sulfite product, and allowing the neutralized calcium sulfite water suspension thus formed to stand for sufficient time for completing the reaction, and then making it slightly acid with a material selected from the group consisting of sulfur dioxide, iron free aluminum sulfate and sulfuric acid.

13. The herein described method of producing a substance of improved qualities for use as a paper making filler or for other uses, comprising treating a lime carbonate material in the presence of water with sulfur dioxide gas producing carbon dioxide gas and calcium bi-sulfite solution, passing off the carbon dioxide gas, filtering and clarifying the calcium bi-sulfite solution to remove impurities, and treating the same with calcium hypochlorite solution so as to neutralize the lime in the hypochlorite solution and to oxidize the bi-sulfite to produce a calcium sulfate product.

14. The herein described method of producing a substance of improved qualities for use as a paper making filler or for other uses, comprising treating a lime carbonate material with sulfur dioxide gas in the presence of water, producing calcium bi-sulfite solution and carbon dioxide, passing off the carbon dioxide gas, filtering and clarifying the calcium bi-sulfite solution to remove insoluble impurities, treating the filtered clear solution with a pure milk of lime suspension to precipitate a calcium sulfite product and allowing the calcium sulfite suspension thus formed to stand for sufficient time for completion of the reaction and then making it slightly acid to slightly alkaline.

JOSEPH E. PLUMSTEAD.

CERTIFICATE OF CORRECTION.

Patent No. 2,235,531. March 18, 1941.

JOSEPH E. PLUMSTEAD.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 31, for the word "shown" read --show--; page 5, second column, line 67, claim 14, for "treating" read --reacting--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of June, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)