

No. 691,324.

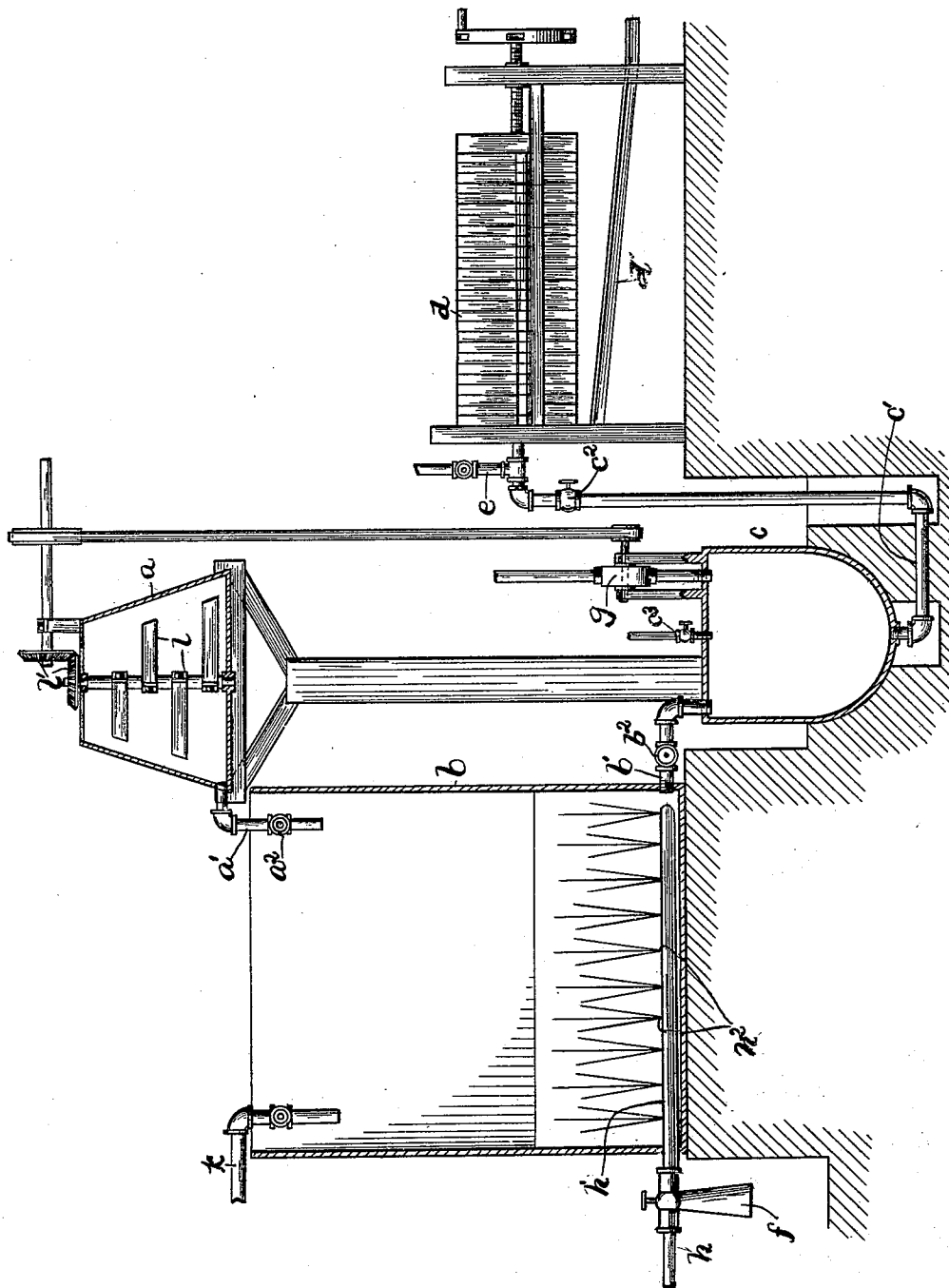
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A. S. RAMAGE.

PIGMENT AND THE PRODUCTION THEREOF FROM FERROUS LIQUORS.

(Application filed Sept. 10, 1900.)

(No Model.)



WITNESSES

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PIGMENT AND THE PRODUCTION THEREOF FROM FERROUS LIQUORS.

SPECIFICATION forming part of Letters Patent No. 691,324, dated January 14, 1902.

Application filed September 10, 1900. Serial No. 29,477. (No specimens.)

To all whom it may concern:

Be it known that I, ALEXANDER SYDNEY RAMAGE, a resident of Cleveland, in the county of Cuyahoga and State of Ohio, have
5 invented certain new and useful Improvements in Processes for the Utilization of Ferrous Liquors; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it pertains to
10 make and use the same.

My invention relates to a new and improved process for the utilization of ferrous liquors, especially waste iron-pickle liquor.

15 The object of my invention is to obtain a new chemical compound of great value in the arts, principally as a coloring material or pigment or as a base for such material.

My invention consists in treating ferrous
20 liquor in the manner hereinafter set forth, producing thereby a hydrated basic ferric oxid having the composition $\text{Fe}_2\text{O}_3\text{Fe}_2(\text{OH})_6$.

The ferrous liquor which I propose utilizing in carrying out my invention is usually a
25 waste product remaining after the pickling of iron and is obtainable in large quantities from wire-works, galvanizing-works, iron-plate works, and similar manufactories, or such liquor may be compounded in any suitable manner. This pickle liquor is usually
30 composed of ferrous sulfate or ferrous chlorid and may contain a small percentage of free acid. Some of these liquors are already utilized to some extent in the production of
35 copperas variously used in the arts and from which is produced Venetian red, iron oxid, &c.

My process consists, in general, in oxidizing the ferrous liquor preferably by blowing through it air or air and steam finely divided
40 and adding to the body of the ferrous liquor at any suitable time—as, for instance, during the process of oxidizing—an alkaline material—for example, a solution containing an alkaline-earth carbonate—to the point ap-
45 proximating neutrality and a comparatively large quantity of water, or the water may have been previously added in an amount at least equal in bulk to twice the original bulk of the ferrous liquor.

50 The accompanying drawing illustrates ap-

paratus suitable for carrying out my invention, in which b represents a tank adapted to hold the ferrous liquor to be treated. In the bottom of this tank b is arranged a pipe h' , having perforations h^2 , through which the
55 oxidizing agent is forced into the liquor. The pipe h' may be connected with a steam-supply pipe h and an air-intake f .

a represents a tank for holding the alkaline-carbonate solution, preferably located above
60 the level of the tank b . Let us suppose this tank b to be sixteen feet deep and seven feet in diameter. If the ferrous liquor has a strength of 28° Baumé, the liquor is run into the tank b to the depth of four feet, and this
65 quantity of liquor will practically contain four thousand five hundred pounds of copperas, ($\text{FeSO}_4, 7\text{H}_2\text{O}$.) Should the liquor be of another strength, such as 14° Baumé, then the liquor is run into the tank to a depth of
70 eight feet, and in similar proportion according to the strength of the liquor, so that the quantity of liquor taken into the tank at any time shall contain approximately four thousand five hundred pounds copperas.

The tank a is provided with an agitator l and is also provided with a pipe a' for conducting the contents of the tank a into the tank b . The pipe a' is preferably provided
80 with a valve a^2 .

c represents a closed tank located, preferably, below the level of the tank b , into which the contents of tank b drains through the pipe
85 b' , which is provided with a valve b^2 .

g represents an air-pump for creating an air-
85 pressure in the tank c . A pipe c' leads from the tank c to the filter d .

k represents a water-supply pipe for supplying water to the tank b .

In carrying out my process I proceed as
90 follows: The ferrous liquor is collected in a suitable tank, in which any free acid should first be neutralized. It is then led to the tank or converter b . Air or air and steam finely divided are preferably admitted to the pipe h'
95 through the pipes f and h , respectively, and the mixture is forced under pressure through the perforations h^2 into the body of the liquor, thoroughly oxidizing the same. As the oxidation of the ferrous liquor proceeds a sub-
100

stance or solution of a suitable alkaline reaction, preferably carbonate of soda, which has been previously placed in the tank *a*, is run into the ferrous liquor to the approximate point of neutrality. Instead of the solution of carbonate of soda carbonate of magnesia, carbonate of calcium, or carbonate of barium may be used. At the same time that the carbonate of soda is being added to the ferrous liquor, water, preferably at a boiling temperature, may be introduced through the supply-pipe *k* in such quantity that the bulk of the added water will preferably at least equal twice the original bulk of the ferrous liquor. This is on the presumption that 28° Baumé liquor has been used. Should a weaker liquor be used, the bulk of the added water must be such that at the close of the operation the contents of the tank will stand twelve feet deep or over. In other words, the dilution of the liquor must be in such proportion that at the close of the operation the liquid will stand in a tank of the given dimensions to about the depth of twelve feet when four thousand five hundred pounds of copperas has been taken.

In the case where it is important that the liquor be kept practically at the point of neutrality during the operation this may be done by continually testing the liquor—as, for instance, with Congo-red solution. As the operation proceeds a yellow precipitate is formed having the definite composition of



that is, a hydrated basic ferric oxid. Care has to be exercised that no soda or equivalent be added beyond the point of neutrality, as this would precipitate ferrous hydrate, which would be oxidized to ferric hydrate, thus contaminating the compound.

As an intermediate step in the process it will be seen that the ferrous liquor upon being blown throws down the basic ferric sulfate, and it is the function of the comparatively large mass of water used to hydrolize this sulfate into the basic ferric hydrate above described, or if the water be previously added, so that the blowing takes place in the presence of sufficient water to hydrolize the basic ferric sulfate, this salt will be hydrolized as formed with formation of basic ferric hydrate.

It is well understood that water in sufficient quantities exerts a strong decomposing influence on all such salts as are composed of a weak base combined with a strong acid or of a strong base with a weak acid, and such reactions are designated by the term "hydrolisis." (*Introduction to Physical Chemistry*: Walker, London, 1899, pages 278–282.)

Basic ferric sulfate formed by blowing the ferrous liquor is an example of the first class above mentioned and is therefore on the addition of sufficient water resolved into sulfuric acid and basic ferric hydrate. The acid is neutralized and set free by the gradual ad-

dition of sodium or other carbonate, thereby preventing the reaction from reaching an equilibrium and determining the complete decomposition of the basic ferric sulfate. It will thus be seen that the added water is the active precipitating agent and that the reaction is effected by hydrolysis.

To complete the process, the liquor after being treated in the tank *b* is run into the tank *c*, from which it is forced by air-pressure through the pipe *c'* into the filter *d*. The sulfate or chlorid solution runs off, and the hydrated basic ferric oxid which remains as a filtrate is collected and washed and dried at a low heat. The hydrated basic ferric oxid can be dried in its original state or calcined to produce the various shades of iron-oxid reds. The calcination will require little furnacing, producing shades surpassing those produced by the calcination of copperas and giving also an oxid which requires no levigation or grinding, being in a very fine state of subdivision and having no trace of acid or undecomposed sulfate.

If instead of carbonate of soda carbonate of magnesia be added to a ferrous-sulfate liquor, the resulting liquor would contain sulfate of magnesia, which could be crystallized and used as Epsom salts. If carbonate of calcium or carbonate of barium be used with ferrous-sulfate liquor, the same bright-yellow precipitate is obtained, but it contains all the calcium or barium as the sulfate of those metals. The product obtained by either of these methods would be about three times the quantity of the precipitate formed by treating the ferrous-sulfate liquor with carbonate of soda. A sample of this basic ferric hydrate when mixed as a paint was found to possess an absorption of oil three times as much as Rochelle, two and one-half times as great as standard French ocher, seven and one-half times that of white lead, and three times that of pure zinc oxid. It also had four times the covering power of white lead, twice the covering power of zinc-white, and from two to three times the covering power of the finest French ocher.

My process is equally adapted to the treatment of either a ferrous-sulfate or a ferrous-chlorid liquor. In both cases when an alkaline carbonate is used in carrying out my process the basic ferric oxid is obtained purer, as the sulfates and chlorids of alkalis remain in solution. If ferrous-chlorid liquor be treated with an alkaline-earth carbonate—such as barium, calcium, or strontium—then chlorids of these metals are obtained in solution and the pure basic ferric oxid is precipitated. The resulting liquor can be evaporated and utilized in the usual way or may be used for making blanc fixe in case a carbonate of barium has been employed or pearl-hardening if calcium carbonate has been employed. When ferrous-sulfate liquor is treated with an alkaline-earth carbonate, the basic ferric

oxid is mixed with the precipitated sulfate of the alkaline earth used.

What I claim is—

1. The process of preparing basic ferric hydrate from ferrous sulfate or chlorid liquors, which consists in blowing with air a mass brought to the condition described, and precipitating basic ferric sulfate or chlorid in the presence of a sufficient volume of water to hydrolize the basic sulfate or chlorid into the basic ferric hydrate.

2. The process of preparing basic ferric hydrate from ferrous-sulfate liquors, which consists in blowing with air a mass in a substantially neutralized condition and precipitating basic ferric sulfate in the presence of a sufficient volume of water to hydrolize the basic sulfate into the basic ferric hydrate.

3. The process of preparing basic ferric hydrate from ferrous sulfate or chlorid liquors, which consists in blowing with air a mass in a substantially neutralized condition by a gradual addition of an alkali carbonate or an alkaline-earth carbonate, thus precipitating basic ferric sulfate or chlorid in the presence of a sufficient volume of water to hydrolize the basic ferric sulfate or chlorid into the basic ferric hydrate.

4. The process of preparing basic ferric hydrate from ferrous-sulfate liquors, which consists in blowing with air a mass in a substantially neutralized condition by a gradual addition of soda-ash, thus precipitating basic ferric sulfate in the presence of a sufficient volume of water to hydrolize the basic ferric sulfate into the basic ferric hydrate.

5. The process of preparing basic ferric hydrate from ferrous-sulfate liquors, which consists in blowing with air in the substantially neutralized condition described, by a gradual addition of soda-ash in aqueous solution, thus precipitating basic ferric sulfate in the presence of a sufficient volume of water to hydrolize the basic ferric sulfate into basic ferric hydrate.

6. The process of preparing basic ferric hy-

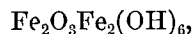
drate from ferrous-sulfate liquors which consists in blowing with air a heated mass in the condition described, thus precipitating basic ferric sulfate in the presence of a sufficient volume of water to hydrolize the basic sulfate into the basic ferric hydrate.

7. The process of preparing basic ferric hydrate from ferrous-sulfate liquors, which consists in blowing with air and steam, a mass in the condition described, thus precipitating basic ferric sulfate in the presence of a sufficient volume of water to hydrolize the basic sulfate into the basic ferric hydrate.

8. The process of preparing basic ferric hydrate from ferrous-sulfate liquors, which consists in blowing with air a mass in the condition described, thus precipitating basic ferric sulfate in the presence of a sufficient volume of water to hydrolize the basic sulfate into the basic ferric hydrate, filtering and washing the hydrate.

9. The process of preparing basic ferric hydrate from ferrous sulfate or chlorid liquors, which consists in blowing with air a mass brought to the condition described, thus precipitating basic ferric sulfate or chlorid in the presence of a sufficient volume of water to hydrolize the basic sulfate or chlorid into the basic ferric hydrate, filtering and washing the hydrate and drying the same.

10. As an article of manufacture, the light ferric hydrate, having the formula



the same being of a golden-yellow color, suitable for pigment, fine and velvety to the touch, absorbing more oil than standard French ocher, zinc-white or white lead, and also having more covering power than these pigments.

Signed by me at Cleveland, Ohio, this 19th day of July, 1900.

ALEXANDER SYDNEY RAMAGE.

Witnesses:

VICTOR C. LYNCH,
A. H. PARRATT.