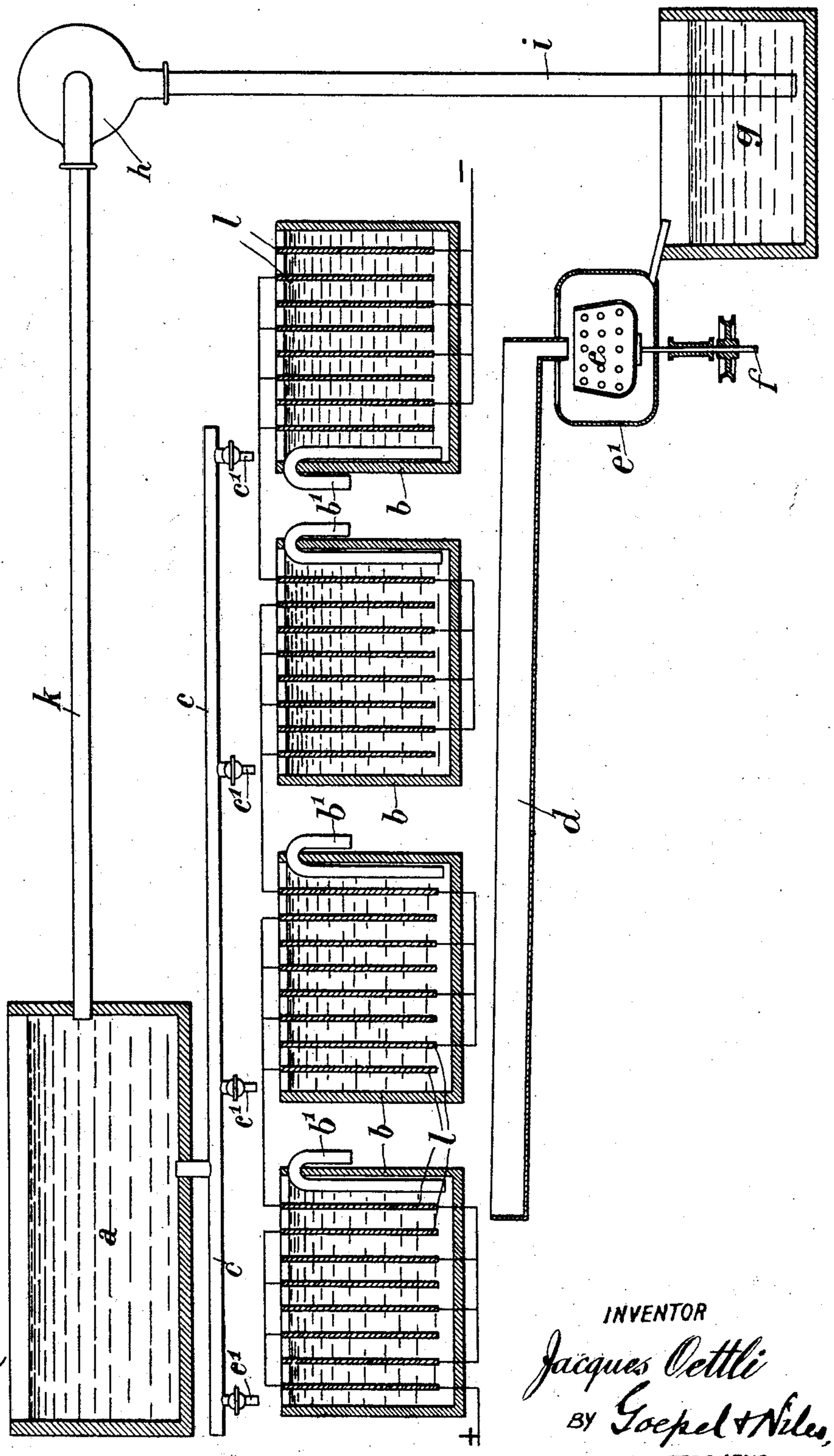
No. 771,024. PATENTED SEPT. 27, 1904.

J. OETTLI.

MANUFACTURE OF WHITE LEAD.

APPLICATION FILED JULY 6, 1903.

NO MODEL.



WITNESSES:
H. J. Sukrtier
J. Glaesser.

INVENTOR
Jacques Oettli
BY Goepel & Niles,
ATTORNEYS.

No. 771,024. Patented September 27, 1904.

UNITED STATES PATENT OFFICE.

JACQUES OETTLI, OF LAUSANNE, SWITZERLAND, ASSIGNOR TO THE FIRM OF SYNDICAT POUR L'EXPLOITATION DES INVENTIONS DU PROFESSEUR OETTLI, OF BERNE, SWITZERLAND.

MANUFACTURE OF WHITE LEAD.

SPECIFICATION forming part of Letters Patent No. 771,024, dated September 27, 1904.

Application filed July 6, 1903. Serial No. 164,265. (No specimens.)

To all whom it may concern:

Be it known that I, JACQUES OETTLI, professor, of Lausanne, Switzerland, have invented certain new and useful Improvements in and Relating to the Manufacture of White Lead, of which the following is a specification.

This invention has reference to an improved process for the electrolytic manufacture of white lead, and has for its object much more economical and simple means to this end than those which have been heretofore employed, while, moreover, the product obtained according to this invention is absolutely pure and of a very low price.

By means of the processes heretofore employed white lead may be produced in a powdery state, quite dry, and impalpable, and this product is liable to exert unpleasant and poisonous effects upon the workmen manufacturing or making use of such product.

In this improved process, which has the great advantage of avoiding the aforesaid inconveniences, white lead is obtained by means of lead electrodes and an electric current of relatively weak voltage, an electrolyte formed of a one-per-cent. solution of common salt and by carbonating the product of the electrolysis after having separated it therefrom. The white lead, absolutely pure, settles down in the form of a paste in the middle of the electrolyte if it has been carbonated in the bath itself. It is then extracted and introduced into a paint mill or grinder adapted to mix it with oil in order that it may be kept in the condition of a paste ready for sale.

It is important in the manufacture of white lead by means of this process to avoid the accidental formation of superior oxids of lead and by secondary reaction of oxychlorid of lead.

In order to obtain the desired result, it is necessary to observe the following conditions: The electrolyte is a one-per-cent. solution of common salt. This quantity must not be exceeded, experience having proved that a more concentrated solution gives rise to other compounds. The products of the electrolysis and of the secondary reactions are constantly the hydroxid of lead, ($PbOH_2$,) and the chlorid of sodium, (NaCl,) which is incessantly regenerated. Therefore the same electrolyte may always be used again, but mixed with water in order to obtain the above-mentioned degree of concentration in proportion to the absorption of the water by the chemical reactions. The water and lead are the only raw material used by the electrolysis. The hydrate of lead is then carbonated by the direct introduction of carbonic acid into the bath. The carbonic acid, or carbon which produces it, is the third raw material. There is no other, because the carbonation finishes the product in accordance with the following equations:

$$3Pb(OH)_2+2CO_2= (2PbCO_3+Pb(OH)_2)+2H_2O.$$

$$4Pb(OH)_2+3CO_2= (3PbCO_3+Pb(OH)_2)+3H_2O.$$

The electrodes are formed of plates of lead the submerged surfaces of which are of a size depending on the intensity of current.

A too great electrical density produces the formation of compounds of lead resulting from the oxidizing action of the chlorid—as, for instance, peroxid of lead, (PbO_2,)—and through them several oxychlorids of lead. The density which seems to be the most suitable is that of 1 amp. dm^2. It must in no case exceed 2 amp. dm^2.

Voltage: The chlorid of sodium must be decomposed. Its heat of combination is 96.2 cal., wherefrom is calculated the voltage $\frac{96.2}{23}=4.2$ volts, and on account of the exterior resistances, which may be easily reduced to a minimum, it amounts to five volts. Therefore there must be five volts in every tank whatever its size may be. It is preferable to make use of a series of ten tanks corresponding to a current of fifty volts, which seems to give satisfactory results. As to the water used in the tanks, the softer it is the better, and rain-water or the water of a lake or a river is preferable. The temperature of the electrolyte should not exceed that of the ambient air—

say about 15° C. A higher temperature would probably lead to the formation of superior oxids of lead and by secondary reaction of oxychlorid of lead, and this of course must be avoided. The aforesaid temperature may be easily maintained by means of a suitable circulation of the liquid. A distributing-tank causes the electrolyte to flow into the tanks from which the liquid is extracted in order that the white lead which it contains may be separated from it and to cause it to again circulate in the tanks by sending it back to the distributing-tank.

The following equations express the chemical reactions which are simultaneously accomplished. The tanks never contain any free chlorin, as has been ascertained by means of the reaction of the liquid on starched paper with potassium iodid.

$$2NaCl+Pb+2H_2O=PbCl_2+2NaOH+H_2.$$
$$PbCl_2+2NaOH=Pb(OH)_2+2NaCl.$$
$$4Pb(OH)_2+3CO_2=3PbCO_3+Pb(OH)_2+3H_2O.$$

The chlorin of lead which is produced at the anode is transformed at the moment of its formation and under the influence of the soda which is produced at the same time at the cathode into hydrate of lead, which falls to the bottom of the tank. The production is very rapid, and a deposit of hydrate of lead is formed on the anode and causes its polarization. In order to prevent this deposit and at the same time to use both electrodes, the current is reversed at very short intervals—every five or ten minutes. Experience has shown that this method gives very good results both as regards the quality and the quantity of the product obtained.

The current used is a continuous current not exceeding one ampere per square decimeter. For the purpose of preventing polarization the current is reversed at definite intervals by means of a suitable device.

The equations show that an evolution of hydrogen takes place, and as the quantity of this gas generated is considerable a very well-ventilated place for the operation should be provided.

It is preferable in order to prevent the liquid becoming heated to cause it to circulate. It may be collected in tanks in which one introduces carbonic acid, and after filtration it is caused to circulate again by means of a pump in the distributing-tank, from which it flows into the tanks.

The white lead is of better quality if the carbonation takes place just at that moment when the hydrate arises. Therefore it is preferable to effect this operation in the tanks of the electrolyte, on account of the hydroxid of lead being a base which easily absorbs carbonic acid. This manner of proceeding has the advantage of preventing the formation of superior oxids of lead and oxychlorids, which may also be the result of a too long absorption of hydrate of lead in a solution of common salt.

The introduction of carbonic acid into the tanks must be regulated, and the quantity of this gas must also be controlled. This controlling is not difficult. The hydrated oxid of lead is a base. Therefore the liquid of the bath becomes alkaline from the beginning of the electrolysis, turmeric paper becomes brown, and the red of litmus turns blue. Carbonic acid is introduced until the basicity of the liquid begins to disappear. The neutralization of hydroxid must, however, not be complete. The carbonation continues by itself during the following operations by means of the carbonic acid contained in the air.

The white lead settles down very quickly at the bottom of the tanks. The liquid is then removed by decantation, by sucking up by means of a siphon, or otherwise and is then caused to circulate again to be used for the electrolysis. The white lead is then thoroughly washed and separated from the remaining water by means of a filter-press or a centrifugal apparatus. The white lead obtained in this manner remains wet until it is prepared for sale. Consequently the dust, which is very injurious to health, is thus avoided. Drying should be done very slowly, the paste being first exposed to the open air, stretched on a large surface, and is then finished in drying-rooms by means of hot air having a temperature not exceeding 50° centigrade. For this purpose the lost heat resulting from the manufacture of carbonic acid by the combustion of the carbon may be employed.

The white lead is generally sold in the state of a paste—that is to say, ground with eight to ten per cent. of purified linseed-oil. The quality of white lead not only depends upon the process of manufacture, but also upon the quality of the lead employed. Badly-refined lead containing iron, copper, arsenic, antimony, or silver produce white lead of an inferior quality. Contaminations of copper are especially to be avoided, as paints made with white lead containing copper become very quickly yellowish. It is therefore preferable to use lead of first quality, which may be ascertained by chemical analysis.

If a density of 1 amp. dm^2 is made use of, there must be for a current of 1,000 amps. a surface of 1,000 dm^2=10 m^2 per tank. Therefore the lead cannot be used in the shape of pig-lead, but in plates the thickness of which, on account of the strong density of the lead, cannot be considerable. Assuming the plates to be 1 m^2, there must be ten per tank, and if such a plate has a thickness of 1 cm. it will weigh 115 kg., which will give for one tank more than a ton of lead—eleven and one-half tons for ten tanks—and working with a current of 40 KW. said plates will be worn out in

ten days; but practically they must be replaced in eight days, because they will become perforated at many points, which will influence the density of the current,

The worn-out plates are melted with new pig-lead and cast into plates of 1 cm. thickness. In order to facilitate manufacture, it would be preferable to use thinner plates, and in this case there would be an advantage in laminating the lead.

The tanks are preferably of wood, rendered water-tight and very carefully tarred to prevent the liquid from penetrating into the wood, any extraction from which, especially in new tanks, would injure the white lead, and it is therefore preferable to have them lined with lead.

The accompanying drawing shows, by way of example, a diagram of suitable apparatus embodying this invention.

In the drawing the said apparatus shows three series of four electrolytic tanks each; but in practice the said tanks are preferably grouped in three series of ten tanks, which are arranged in such a manner that two series work together and one series is out of use.

a is the electrolyte-distributing tank, containing a one-per-cent. solution of common salt, and *b* represents the electrolytic tanks.

c is a delivery-pipe provided above every tank *b* with a branch pipe *c'*, having a suitable tap. Each tank *b* is provided with a siphon *b'*, adapted to suck up from the bottom of the tank all the liquid containing the white lead and to conduct it into a channel *d*, opening into a hydro-extractor *e*, the shaft *f* of which is rotated by a suitable motor. The electrolyte flowing into the tank *e'* of the hydro-extractor then runs into the tank *g*, from which a pump *h*, actuated by a suitable motor, sucks it up through the pipe *i* and conducts it back through a pipe *k* to the distributing-tank *a*.

The lead electrodes *l* are preferably formed of plates of a thickness of 1 cm. and of 1 cm^2 of surface. They are connected together and with the electric circuit, as shown in the drawing, and said circuit contains, in the case of a distribution with continuous current, a reversing-commutator of any desired kind.

The white lead is collected in the condition of a wet paste in the hydro-extractor *e* and is then introduced into a paint mill or grinder, where it is mixed with oil, being then ready to be packed for sale.

I claim—

The process herein described of making white lead, which consists in electrically dissolving a lead electrode by a continuous current not exceeding one ampere per square decimeter, reversed at definite intervals, in an electrolyte formed of a solution of common salt of one per cent. and of a temperature of about 15° centigrade.

In testimony that I claim the foregoing as my invention I have signed my name in presence of two subscribing witnesses.

JACQUES OETTLI.

Witnesses:
Y. IMER,
L. H. MURICA.