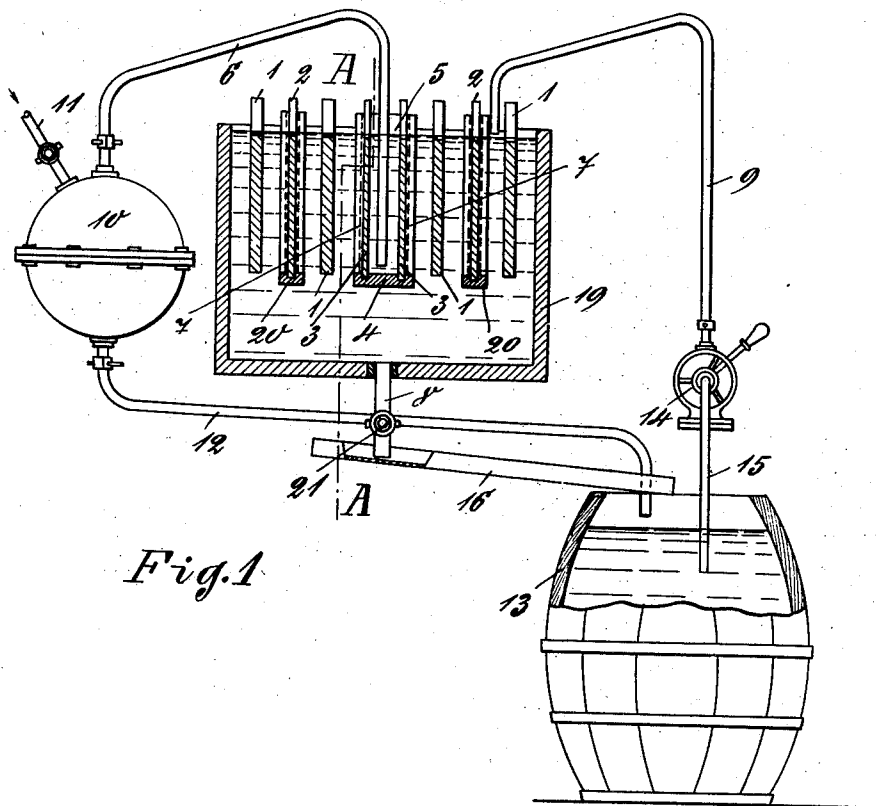
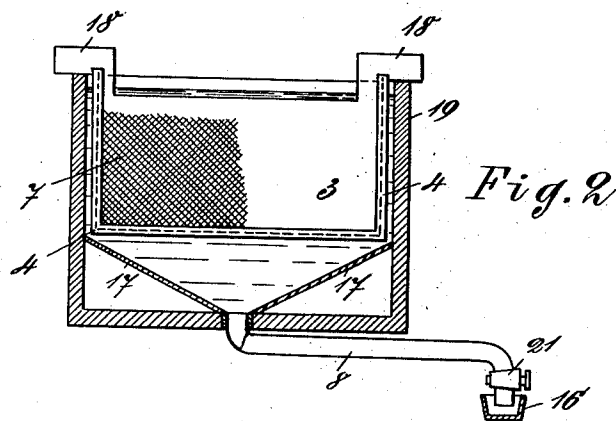


C. LUCKOW.
ELECTROLYTIC MANUFACTURE OF DIFFICULTLY SOLUBLE SALTS OF HEAVY METALS.
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Witnesses:
Karl Meiner
Carl Luckow

Inventor:
Carl Luckow.

UNITED STATES PATENT OFFICE.

CARL LUCKOW, OF COLOGNE, GERMANY.

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To all whom it may concern:

Be it known that I, CARL LUCKOW, a citizen of the Empire of Germany, residing at Cologne-on-the-Rhine, in the Empire of Germany, have invented a new and useful Electrolytic Manufacture of Difficultly-Soluble Salts of Heavy Metals, of which the following is a specification.

In my U. S. Patents No. 626,331 of June 6, 1899 (process of producing neutral chromate of lead); No. 627,002 of June 13, 1899 (process of producing white lead by means of electrolysis); and, No. 627,267 of June 20, 1899 (process of producing basic phosphate of copper by means of electrolysis) I have described processes of producing insoluble or difficultly soluble salts of heavy metals, the chief feature of which processes consists in that the electrolyte is a very diluted solution of a mixture of a "dissolving salt" with a "precipitating salt", principally from the class of the alkaline metals (inclusive of ammonium), and in that the "precipitating salt" is constantly regenerated by the continued introduction of fresh acid for replacing that consumed during the process.

My present invention relates to an electrolytic process for the manufacture of salts of heavy metals which are insoluble or difficultly soluble in the electrolyte, in which manufacture in contradistinction to the above mentioned processes the "precipitating salt" is completely consumed during the work and therefore requires to be constantly replaced in proportion to the consumption of its acid by fresh salt in a suitably diluted solution. This mode of working renders it necessary to avoid every undesirable percentage or injurious enrichment of the electrolyte with hydroxid of alkali (lye) in the manner, that the latter is always during the work extracted from the electrolyte in a diluted solution by means of a polar device, as it is produced. This is preferably effected by means of an electrolytic filtration and by removing the polar filtrate, *i. e.* the alkali lye, from the metallic conducting filtering bodies serving as cathodes, which I call "filtering cathodes". This new mode of working is suitable, for example when the silicic acid by reason of its difficult solution is replaced by silicates of alkali (water-glass), and is in all cases preferable, where the "precipitating salts" (alkali dichromates, alkali chromates, prussiates of potash, etc.) are cheaper than their acids (chromic acid,

ferrocyanic acids etc.), in order to render the manufacture more profitable. In other cases, where the "precipitating acids" are cheaper than their salts, it is of course preferable to turn the diluted solutions of the hydroxids of alkali running off from the "filtering cathodes" into diluted solutions of the "precipitating salts" by the introduction of the respective acids and to always add these salts to the electrolytes as they are consumed. The new manufacture moreover effects a considerable reduction of the consumption of energy or of the voltage required, the cathodes being constructed similar to the electrodes of storage batteries and serving as depolarizing means.

I will now proceed to describe my invention with reference to the accompanying drawing, in which—

Figure 1 is a diagram of a plant for carrying into effect the electrolytic manufacture of white lead; and Fig. 2 is a vertical cross section through the line A—A in Fig. 1.

Similar characters of reference refer to similar parts in both views.

In Figs. 1 and 2 I have for example illustrated a plant for carrying into effect a special mode of the new electrolytic manufacture, *viz.* the process of producing white lead. This plant is shown to comprise only one battery, but it will be understood, that the plant may comprise more than one storage battery with any number of cells each of any known construction. The anodes are denoted by 1 and the cathodes by 2, and all of them are shown to be suspended by means of projections 18 from the upper edges of a suitable vessel 19.

For carrying the new manufacture into effect, the following conditions require to be fulfilled:

1:—The anodes 1 are made from the heavy metal or an alloy of heavy metals which are to serve as bases of the products.

2:—The cathodes 2 are substantially constructed similar to the electrodes of storage batteries, for example they are ribbed plates, grates, box-plates etc., the respective metallic plates being filled or covered with fine grained or finely divided oxids capable of reduction to fungous metals, so that they can serve as depolarizing means for rendering the consumption of energy as economical as possible. The cathodes serving as filters for the caustic lyes, *i. e.* the "filtering cathodes," one or several of them in each cell, or

all of them in one cell or in special cells, are preferably made in several parts, for example they are double plates 3, 3 combined in narrow frames 4 like negative electrodes in storage batteries, so that they form boxes 5 of a small width for permitting the caustic lyes to store up in them and to flow off through siphons 6 or the like. The active masses of the "filtering cathodes" serve not only as depolarizing means but also and more particularly as filters for dividing as far as possible during the work the cations from the anions, the cations alone being permitted to enter their interiors 5. Where required, all of the cathodes 2 including the "filtering cathodes" 3, 4 may be for example inclosed with a wooden frame 20 and filtering cloths 7.

3:—The electrolyte is a diluted solution of a mixture of two or more salts (either single or double salts, inorganic or organic salts), more particularly of the alkali metals (inclusive of ammonium), it being essential, that at least one salt serves as "dissolving salt" (that is to say one the anion of which can dissolve the substance of the anodes 1 or form with the latter an easily soluble salt) and at least one salt serves as "precipitating salt" (that is to say one the anion of which can precipitate the substance of the anodes 1 or form with it a difficultly soluble salt). In order to enable the electrolysis to run a regular course, it is necessary that the electrolyte be a very diluted solution and that in the mixture the "dissolving salts" strongly overweigh the "precipitating salts." The reaction of the electrolyte may be weakly acid, neutral or alkaline. The temperature of the electrolyte may be cold, warm or hot. The substances withdrawn or separated from the electrolyte during the electrolysis are always or from time to time added as they are consumed. For enabling the cathodes to constantly act as depolarizing means, it is necessary to run off from time to time the electrolyte from the cells (for example through a discharge tube 8, a cock 21 or the like and a trough 16) down to the lower edges of the cathodes 2 and 3, 4 and to allow the fungous metal to which during the work the oxid had been reduced to burn with the oxygen of the air to oxid, which oxidation for example can be very well done during the night after every day. During the work the cations are divided from the anions by electrolytical filtration, the anions although by no means undissolved being prevented or at any rate greatly hindered from penetrating into the filtering bodies serving as cathodes, the filtering bodies permitting only the cations and the products of the electrolysis to enter them and to store up in them. The polar filtrate of the electrolyte, that is the caustic lye, is then permitted to gradually run off from the "filtering cathodes" 3, 4

(through a siphon 6 or the like), as may be required, and consequently "precipitating salt" in a diluted solution of suitable density is permitted to flow into the electrolyte (through a tube 9 or the like). In cases where it is possible or preferable, of course the exceeding diluted solutions of caustic lye running off from the "filtering cathodes" may be turned into diluted solutions of "precipitating salts" by the introduction of the respective acids, whereby the loss of the electrolyte in "precipitating salt" is compensated, as will be explained later on.

4:—The density of the current is preferably about from 25 to 75 amperes per square meter of the surface of the anodes, and the tension of the current is about from 1 to 3 volts per cell.

Following three examples will explain the new manufacture:

a. *Production of neutral chromate of lead (chrome-yellow).*—The anodes 1 consist of soft lead. The cathodes 2 are ribbed plates of soft lead or hard lead with active fillings of lead oxid (fungous lead); preferably all of the cathodes 2 including the "filtering cathodes" 3, 4 are inclosed with wooden frames 20 and filtering-cloths 7. The electrolyte is a diluted solution containing about one and a half per cent. of a mixture of about ninety five weight parts of chlorate of sodium and about five weight parts of dichromate of sodium calculated free from water. During the electrolysis dichromate of sodium and water are always added to the electrolyte, as they are consumed, and at the same time the soda-lye is run off from the "filtering cathodes"; any loss of chlorate of sodium is replaced.

b. *Production of Prussian blue and Paris blue.*—The anodes 1 consist of iron; the cathodes 2 are skeletons of iron with active fillings of iron oxid (fungous iron). The electrolyte is a diluted solution containing about one per cent. of a mixture of about ninety five weight parts of chlorid of potassium or sodium (kitchen-salt) and about five weight parts of ferrocyanid of potassium calculated free from water. During the electrolysis ferrocyanid of potassium or sodium and water are always added to the electrolyte as they are consumed, while the potash or soda-lye is extracted from the "filtering cathodes," and any loss of chlorid of potassium or sodium is replaced.

c. *Production of basic carbonate of lead (white lead),* see Figs. 1 and 2.—The anodes 1 consist of soft lead. The cathodes 2 are suitable skeletons of soft lead or hard lead with active fillings of lead oxid (fungous lead); preferably all the cathodes 2 including the "filtering cathodes" 3, 4 are inclosed with wooden frames 20 and filtering-cloths 7. The electrolyte is a diluted solution containing about from one to two per

cent. of a mixture of about from ninety to ninety five weight parts of chlorate of sodium and about from five to ten weight parts of carbonate of sodium (soda) calculated free from water. During the electrolysis the soda-lye is always extracted, as it is produced, from the "filtering cathodes" 3, 4 by means of a siphon 6 or the like and passed through a suitable receptacle 10 for carbonic acid introduced from some source through a tube 11, so that it is thereby turned into a solution of soda, which is conducted through a tube 12 into some reservoir 13 of any known construction. From the reservoir 13 the soda solution is sucked by means of some suitable pump 14 through the suction pipe 15 and is delivered through a tube 9 into the cell or cells in order to be added to the electrolyte.

17 denotes inclined plates for facilitating the collection of the product.

Of course the plant may be varied in various manners obvious to the expert.

I claim:

1. The herein described electrolytic manufacture of salts of heavy metals which are insoluble or difficultly soluble in the electrolyte, consisting in using anodes of a heavy metal, and cathodes of a similar metal with depolarizing fillings, a number of the cathodes forming boxes and serving as "filtering cathodes", in connection with an aqueous solution as electrolyte containing a small percentage of a mixture of "dissolving salt" and a "precipitating salt", both chiefly from the class of alkali metals (inclusive of ammonium), and in passing a current through said solution, the "precipitating salt" being always added, as its acid is consumed, and the hydroxid of alkali developed from the electrolyte and entering the "filtering cathodes" being therefrom extracted.

2. The herein described electrolytic manufacture of salts of heavy metals which are insoluble or difficultly soluble in the electrolyte, consisting in using anodes of a heavy metal, and cathodes of a similar metal with depolarizing fillings, a number of the cathodes forming boxes and serving as "filtering cathodes", all of the cathodes including the "filtering cathodes" being inclosed with

wooden frames and filtering-cloths, in connection with an aqueous solution as electrolyte containing a small percentage of a mixture of a "dissolving salt" and a "precipitating salt", both chiefly from the class of alkali metals (inclusive of ammonium); and in passing a current through said solution, the "precipitating salt" being always added, as its acid is consumed, and the hydroxid of alkali developed from the electrolyte and entering the "filtering cathodes" being therefrom extracted.

3. The herein described electrolytic manufacture of basic carbonate of lead (white lead), consisting in using anodes of soft lead, and cathodes of lead with depolarizing fillings of lead oxid, a number of the cathodes forming boxes for serving as "filtering cathodes", in connection with an aqueous solution as electrolyte containing about from one to two per cent. of an alkali chlorate in mixture with an alkali carbonate, and in passing a current through said solution, the alkali carbonate and water being always added to the electrolyte as they are consumed, and the lye developed from the electrolyte and entering the "filtering cathodes" being therefrom extracted.

4. The herein described electrolytic manufacture of basic carbonate of lead (white lead), consisting in using anodes of soft lead, and cathodes of lead with depolarizing fillings of lead oxid, a number of the cathodes forming boxes for serving as "filtering cathodes" and all the cathodes including the "filtering cathodes" being preferably inclosed with wooden frames and filtering-cloths, in connection with an aqueous solution as electrolyte containing about from one to two per cent. of an alkali chlorate in mixture with an alkali carbonate, and in passing a current through said solution, the alkali carbonate and water being always added to the electrolyte as they are consumed, and the lye developed from the electrolyte and entering the "filtering cathodes" being therefrom extracted.

CARL LUCKOW.

Witnesses:

LOUIS VANDORY,
BESSIE F. DUNLAP.