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(*Under International Convention.*)

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PROVISIONAL SPECIFICATION.

"Improvements in or relating to the Electrolytic Manufacture of Chlorates Perchlorates, Bromates, Iodates and the like"

I, PAUL EUGÈNE CHARLES CORBIN, Engineer, of Chedde, Haute Savoie, in the Republic of France do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of chlorates, perchlorates, bromates, iodates and the like and has for its chief object the production of these substances by the electrolysis of solutions of chlorides or chlorates or both with chromic acid in the greatest possible proportion or even in state of bichromate.

The remarkable action of chromic acid particularly when used in the form of chromates or bichromates, as an auxiliary means in the manufacture of chlorates or perchlorates by electrolysis, is well known owing to the experiments of Imhoff and especially of Müller & Broquet.

From practical experiments it has been shown that the preliminary addition of a small quantity of these salts to the solution of chlorides or chlorates to be electrolysed, has the effect of considerably increasing the electro-chemical re-action or yield (grammes of chlorates or perchlorates manufactured per ampère hour) either of chlorates or perchlorates as the case may be, without, however producing at the end of the operation, any material diminution in the initial quantity of chromic acid and consequently without the consumption of this substance.

It is also known, that, with the same amount of chromic acid, the increase of yield is substantially the same as when neutral chromate or bichromate is used.

Further it is known, that in the case of bichromate, the solution, originally red, becomes gradually yellow, and returns slowly to the red colour when the solution, after electrolysis, is allowed to stand.

These experiments however have only been carried out in laboratories and the public trials have only lasted for some hours. If it is intended to apply the result of these experiments to practical use the following conditions must be considered.

1. The cathodes should not be of platinum like the anodes but of a cheaper material, such for instance as iron, copper, brass, bronze, carbon *etc* which materials have the common quality of becoming attacked and more or less easily deteriorated in oxidising solutions.

2. The electrolysed solutions, after extracting by any convenient method the final product (*chlorate or perchlorate*), should be used again, either by stopping

the electrolysis when all the liquid has reached the maximum determined strength of perchlorate or chlorate, with the object of extracting the latter, and again submitting the mother liquors to electrolysis after having enriched them with the original substance (chloride or chlorate); or, on the other hand, when working continuously that is to say without interrupting the electrolysis by drawing off continuously or at certain intervals a quantity of liquid which, after having been deprived of the chlorate or perchlorate is enriched with the original substance, and again submitted to electrolysis.

Under these conditions of working, being the only commercial ones, nothing abnormal according to the method used can be remarked during the first days or first operations. The cathodes are maintained in good condition the liquids remain clear and of red-orange or yellow colour and the product is very high close to the theoretical amount which for instance, is about 0·76 grammes of potassium chlorate and 0·66 gr: of sodium chlorate per ampere hour, but this soon decreases and falls to a figure close to the usual figure in the process without chromic acid.

Further I have also discovered that the spontaneous and gradual return after electrolysis to the red colour of an originally red liquid, which in the course of the electrolysis slowly turns yellow, takes place slower and slower, and finally after a certain number of operations does not take place at all. This phenomenon is accompanied by a slow increase of the chlorometric strength as well as of the alkaline strength of the liquor which were both zero at the beginning of the operation. Thus the chlorometric standard is completed by reaching 6 to 7 gr. of active chlorine per litre and remains stationary even after electrolysis has been stopped. At this moment the yield which has progressively decreased becomes stationary at about 0·35 gr. to 0·45 per ampere hour in the case of chlorate of potassium for example instead of 0·70 gr. at the commencement.

The greater part of the cathodes of other material than platinum are slowly attacked and that more and more energetically during the electrolysis proper.

On interrupting the current by breaking the circuit a kind of violent ebullition takes place throughout the whole mass of the liquor and the cathodes when withdrawn appear to be strongly corroded over their entire surface.

Furthermore a general method of maintaining the electro-chemical yield at a maximum which at the same time allows the use of cathodes of such metal or alloy as is considered convenient. I have discovered that for this purpose it is sufficient to constantly maintain in a suitable manner the greater part of the chromic acid in the state of bichromate and not of neutral chromate.

The liquors remain clear and of a red-orange colour. If the current is broken whatever the temperature may be at the moment, no ebullition is observed, the cathodes of whatever the metal or alloy they may consist do not show any trace of alteration and if the liquor had turned slightly yellow since the last breakage of the circuit it becomes instantly orange-red and this state of things recurs indefinitely.

Thus, with a convenient amount of chromic acid, and by using always the same liquors and the same cathodes, a constant and very high yield is obtained, which can reach 90% of the theoretical amount, which result has never before been obtained. Moreover this increase of the relative amount of bichromate can be obtained either during the electrolysis in cases of continuous operation, or at the end of each operation in cases where the working is in successive operations.

The most simple process for maintaining the desired relative amount of bichromate consists in mixing the liquors with a very dilute solution of a mineral acid. The most convenient for this purpose is hydrochloric acid as it can only form chlorides and does not introduce foreign salts. The addition can be made either continuously or at certain intervals or at once after the stoppage of the electrolysis.

I have, moreover, observed that this addition which causes a troublesome liberation of chlorine gas when solutions of chlorides or electrolysed chlorates which do not contain chromates or bi-chromates are being operated upon, can be effected on the contrary very easily and without difficulty in the presence of these salts. Very considerable quantities of hydrochloric acid may indeed be introduced before liberating chlorine. In practice, however, a very small quantity is needed to renew the red colour, and in all cases the chromic acid can be entirely brought back to the state of bi-chromate—which is the best course to follow—without chlorine being liberated.

The constant maintenance of chromic acid in the state of bichromate has such an effect on the yield that it is possible in the case of very soluble chlorates, such as for example chlorate of sodium, to push the electrolysis far enough to decompose almost all the chloride and thus to succeed in saturating the liquor with chlorate of sodium at the temperature of the electrolysis, whilst maintaining a very rich yield, and this without forming an appreciable quantity of perchlorate, so that it is possible to continuously withdraw from the electrolyser a liquor saturated with chlorate of sodium at the desired temperature and allow it to deposit its chlorate by crystallisation in suitable cooling apparatus, on the one condition that the corresponding quantity of chloride is continuously supplied to the electrolyser, thereby enabling chlorate of sodium to be manufactured in exactly the same manner as chlorate of potassium instead of being obliged to effect an expensive and complicated concentration of the liquors containing it, as has been necessary up to the present time.

Thus, by my process, liquors containing only 130 to 150 grammes of NaCl as compared with 450 to 500 grammes of $NaClO_3$ at 70° C may be constantly withdrawn from the electrolyser whilst obtaining a constant electro-chemical yield of 0·55 gr of $NaClO_3$ per ampère-hour. Without the use of hydrochloric acid the yield falls under these conditions below 0·30 gr.

All that has above been stated about very soluble chlorates is moreover applicable to very soluble perchlorates, such as perchlorate of sodium, by replacing in the statement the word "chloride" by "chlorate" and the word "chlorate" by "perchlorate".

I have also established a remarkable fact in this connection *viz*: at the same time that by the addition of hydrochloric acid the neutral chromate is brought back to the state of bichromate the strength of the electrolysed liquor is decreased so that the amount of active chlorine never attains 1 gramme per litre during the electrolysis, and even if the addition of acid is made to the liquor coming from the electrolyser and while still hot, the active chlorine disappears completely in one or two hours, that is to say the chlorometric strength sinks to zero in the liquor when left to stand.

This is another very considerable advantage of my process which thus spontaneously supplies a non-oxidising liquor, and consequently suitable for use in the operations which the liquors have to subsequently undergo before returning them to the electrolyser, and which enables receivers or conduits of any material to be used for this purpose.

Finally all these principles and processes are applicable to all electrolytic operations where it is necessary to utilize the action of chromic acid, to increase the electro-chemical yield. Thus in the preparation of bromates, iodates, *etc.* the same results are obtained by using the hydrobromic hydriodic, *etc*, acids instead of hydrochloric acid.

Dated this 29th day of August 1901.

BOULT, WADE & KILBURN,
Agents for the Applicant.

COMPLETE SPECIFICATION.

Improvements in or relating to the Electrolytic Manufacture of Chlorates, Perchlorates, Bromates, Iodates and the like.

I, PAUL EUGÈNE CHARLES CORBIN, Engineer, of Chedde, Haute Savoie, in the Republic of France, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of chlorates, perchlorates, bromates, iodates and the like, and has for its chief object the production of these substances by the electrolysis of solutions of chlorides or chlorates or both with chromic acid

The remarkable action of chromic acid particularly when used in the form of chromates or bichromates, as an auxiliary means in the manufacture of chlorates or perchlorates by electrolysis, is well known owing to the experiments of Imhoff and especially of Foerster, of Müller and of Broquet.

From practical experiments it has been shown that the preliminary addition of a small quantity of these salts to the solution of chlorides or chlorates to be electrolysed, has the effect of considerably increasing the electro-chemical reaction or yield (grammes of chlorates or perchlorates manufactured per ampere hour) either of chlorates or perchlorates as the case may be, without, however producing at the end of the operation, any material diminution of the initial quantity of chromic acid and consequently without the consumption of this substance.

It is also known, that, with the same amount of chromic acid, the increase of yield is substantially the same as in the published laboratory tests when neutral chromate or bichromate is used.

Further, it is known, that in the case of bichromate, the solution, originally red, becomes gradually yellow, and returns slowly to the red colour when the solution, after electrolysis, is allowed to stand, at least according to the published laboratory tests.

These experiments however have only been carried out in laboratories and the public trials have only lasted for some hours. If it is intended to apply the result of these experiments to practical use the following conditions must be considered.

1. The cathodes should not be of platinum like the anodes but of a cheaper material, such for instance as iron, copper, brass, bronze, carbon *etc*: which materials have the common quality of becoming attacked and more or less easily deteriorated in oxidising solutions.

2. The electrolysed solutions after extracting by any convenient method the final product (chlorate or perchlorate) should be used again either by stopping the electrolysis when all the liquid has reached the maximum determined strength of perchlorate or chlorate, with the object of extracting the latter, and again submitting the mother liquors to electrolysis after having enriched them with the original substance (chloride or chlorate); or, on the other hand, when working continuously that is to say without interrupting the electrolysis by drawing off continuously or at certain intervals a quantity of liquid which, after having been deprived of the chlorate or perchlorate is enriched with the original substance, and again submitted to electrolysis.

Under these conditions of working being the only commercial ones, nothing abnormal according to the method used can be remarked during the first hours or first operations. The cathodes are maintained in good condition the liquids remain clear and of red-orange or yellow colour and the product is very high close to the theoretical amount which for instance, is about 0·76 grammes of

potassium chlorate and 0·66 gr: of sodium chlorate per ampere hour, but this soon decreases and falls to a figure close to the usual figure in the process without chromic acid.

Further, I have also discovered that the spontaneous and gradual return after electrolysis to the red colour of an originally red liquid, which in the course of the electrolysis slowly turns yellow, takes place slower and slower, and finally after a certain number of hours of working does not take place at all. This phenomenon is accompanied by an increase of the chlorometric strength as well as of the alkaline strength of the liquor which were both zero at the beginning of the operation. Thus the chlorometric standard is completed by reaching 6 to 7 gr. of active chlorine per litre and remains stationary even after electrolysis has been stopped the alkaline standard likewise attains a value 5 to 6 gr. of NaOH per litre or more and remains at that. At this moment the yield which has progressively decreased becomes stationary at about 0·35 gr. to 0·40 gr. per ampere hour in the case of chlorate or potassium for example instead of 0·70 gr. at the commencement.

The greater part of the cathodes of other material than platinum are slowly attacked and that more and more energetically during the electrolysis proper.

On interrupting the current by breaking the circuit a kind of violent ebullition takes place throughout the whole mass of the liquor and the cathodes when withdrawn appear to be strongly corroded over their entire surface.

Furthermore a general method of maintaining the electrochemical yield at a maximum which at the same time allows the use of cathodes of such metal or alloy as is considered convenient. I have discovered that for this purpose it is sufficient to constantly maintain in a suitable manner the whole or part of the chromic acid in the state of bichromate and not of neutral chromate, so that the liquid may never be alkaline.

The liquors remain clear and of a red-orange colour. If the current is broken whatever the temperature may be at the moment, no ebullition is observed, the cathodes of whatever the metal or alloy they may consist do not show any trace of alteration and if the liquor had turned slightly yellow since the last breakage of the circuit it becomes instantly orange-red and this state of things recurs indefinitely.

Thus, with a convenient amount of chromic acid, and by using always the same liquors and the same cathodes, a constant and very high yield is obtained, which can reach 90% of the theoretical amount, which result has never before been obtained. Moreover this increase of the relative amount of bichromate can be obtained either during the electrolysis in cases of continuous operation, or at the end of each operation in cases where the working is in successive operations.

The most simple process for maintaining the desired relative amount of bichromate consists in mixing the liquors with a very dilute solution of a strong mineral acid. The most convenient for this purpose is hydrochloric acid as it can only form chlorides and does not introduce foreign salts. The addition can be made either continuously or at certain intervals or at once after the stoppage of the electrolysis.

I have, moreover, observed that this addition which causes a troublesome liberation of chlorine gas when solutions of chlorides or electrolysed chlorates which do not contain chromates or bi-chromates are being operated upon, can be effected on the contrary very easily and without difficulty in the presence of those salts. Very considerable quantities of hydrochloric acid may indeed be introduced before liberating chlorine. In practice, however, a very small quantity is needed to renew the red colour, and in all cases the chromic acid can be entirely brought back to the state of bi-chromate which is the best course to follow—without chlorine being liberated.

The constant maintenance of the whole or part of the chromic acid in the state of bichromate has such an effect on the yield that it is possible in the case of very soluble chlorates, such as for example chlorate of sodium, to push the

electrolysis far enough to decompose almost all the chloride and thus to succeed in saturating the liquor with chlorate of sodium at the temperature of the electrolysis, whilst maintaining a very rich yield, and this without forming an appreciable quantity of perchlorate, so that it is possible to continuously withdraw from the electrolyser a liquor saturated with chlorate of sodium at the desired temperature and allow it to deposit its chlorate by crystallisation in suitable cooling apparatus, on the one condition that the corresponding quantity of chloride is continuously supplied to the electrolyser, thereby enabling chlorate of sodium to be manufactured in exactly the same manner as chlorate of potassium instead of being obliged to effect an expensive and complicated concentration of the liquors containing it, as has been necessary up to the present time.

Thus, by my process, liquors containing only 130 to 150 grammes of NaCl as compared with 450 to 500 grammes of $NaClO_3$ at 70° C may be constantly withdrawn from the electrolysor whilst obtaining a constant electro-chemical yield of 0·55 gr of $NaClO_3$ per ampere-hour. Without the use of hydrochloric acid the yield falls under these conditions below 0·30 gr.

All that has above been stated about very soluble chlorates is moreover applicable to very soluble perchlorates, such as perchlorate of sodium, by replacing in the statement the word "chloride" by "chlorate" and the word "chlorate" by "perchlorate".

I have also established a remarkable fact in this connection *viz*; at the same time that by the addition of hydrochloric acid the neutral chromate is brought back to the state of bichromate the chlorometric strength of the electrolysed liquor is decreased so that the amount of active chlorine never attains 1 gramme per litre during the electrolysis, and even if the addition of acid is made to the liquor coming from the electrolyser and while still hot, the active chlorine disappears completely in one or two hours, that is to say the chlorometric strength sinks to zero in the liquor when left to stand.

This is another very considerable advantage of my process which thus spontaneously supplies a non-oxidising liquor, and consequently suitable for use in the operations which the liquors have to subsequently undergo before returning them to the electrolyser, and which enables receivers or conduits of any material to be used for this purpose.

Finally all these principles and processes are applicable to all electrolytic operations where it is necessary to utilize the action of chromic acid, to increase the electro-chemical yield. Thus in the preparation of bromates, iodates, *etc.* the same results are obtained by using the hydro-bromic hydriodic, *etc.*, acids instead of hydrochloric acid.

It is impossible to give definite proportions of chromic acid and liquor, as they will vary considerably, for instance according to various conditions, such as the strength of current, volume and temperature of the liquor, &c, but, as an example I may state that I have obtained excellent results with a proportion of 10 or 12 grammes of chromic acid per litre of liquor.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. In the production of chlorates, perchlorates, bromates iodates and the like by electrolysis from solutions of chlorides or chlorates or the like or mixtures of the same in the presence of chromic acid as an auxiliary agent, maintaining the chromic acid during the whole electrolytic process wholly or partially in the state of bichromate and not only in the state of neutral chromate, substantially as and for the purposes described.

2. A practical form of carrying out the method according to Claim 1 consisting in adding to the liquid either continually or intermittently during the electrolysis or all at once after the electrolysis a small quantity of a diluted acid,

preferably hydrochloric acid, which converts the whole or a part of the neutral chromate present into bichromate, substantially as and for the purpose described.

3. The application of the described use of chromic acid to the manufacture of very soluble chlorates perchlorates bromates iodates and the like, especially the chlorates and perchlorates of sodium, whereby, at the first cast, constantly and indefinitely crystals of chlorate or perchlorate of the corresponding metal may be obtained by simply cooling the liquor coming from the electrolyser, without being obliged to concentrate these liquors, substantially as described.

4. The use of dilute hydrochloric acid (1) for the purpose of maintaining the chlorometric strength very low during electrolysis and (2) for the purpose of destroying very rapidly, without any other operation and without any liberation of chlorine gas, the chlorometric strength of the liquors coming from the electrolyser, for the purpose of using afterwards without difficulty the liquors, which have thus become non-oxidising, before sending them back to the electrolyser, and to enable receivers or conduits of any desired material to be used.

5. The application of the described process to all electrolytic operations where chromic acid is used as an auxiliary in order to increase the yield.

Dated this 25th day of April 1902.

BOULT, WADE & KILBURN,
Agents for the Applicant.

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