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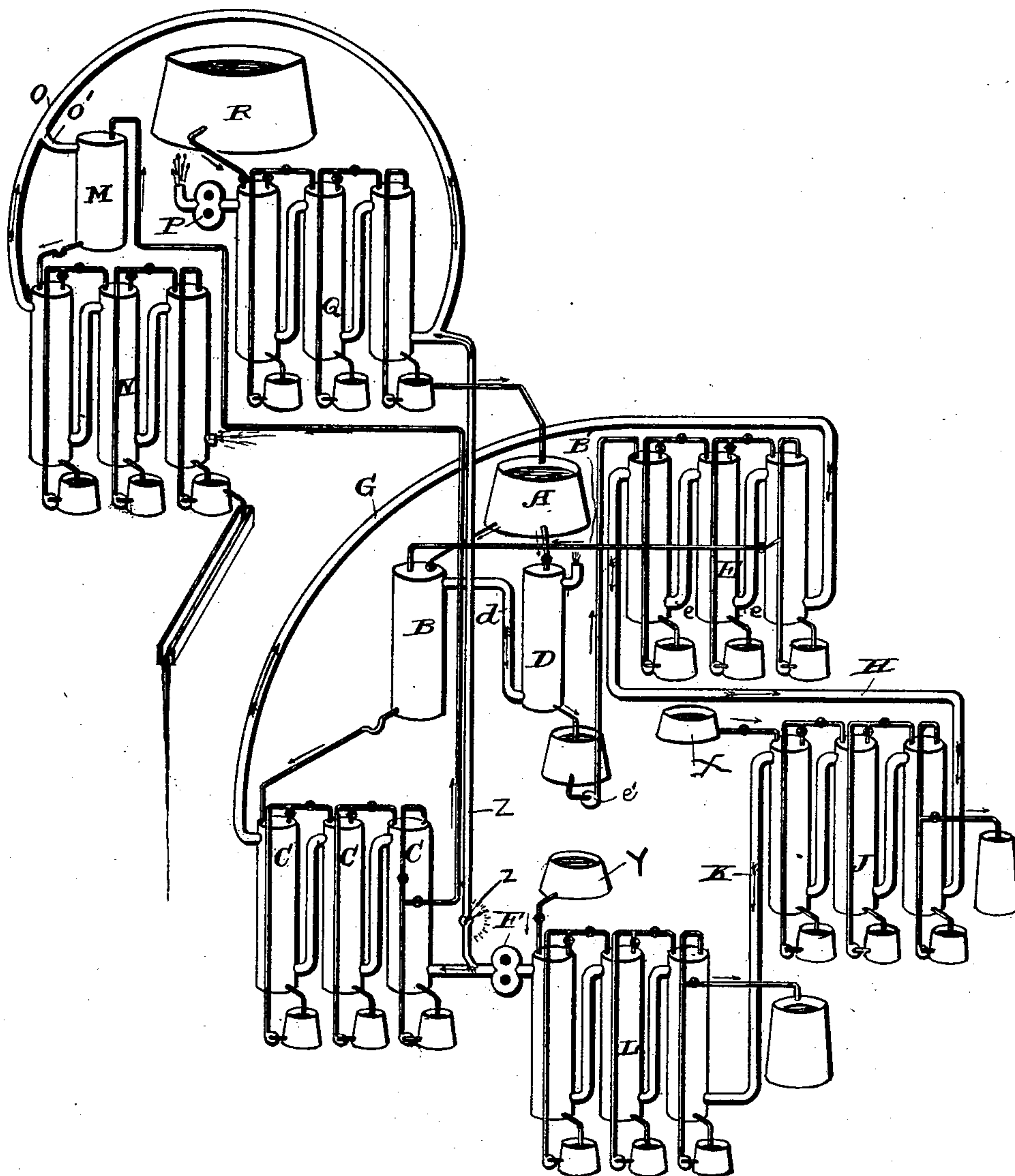
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H. H. DOW.

PROCESS OF EXTRACTING BROMIN FROM BRINE.

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(No Model.)



WITNESSES:

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PROCESS OF EXTRACTING BROMIN FROM BRINE.

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Application filed December 7, 1900. Serial No. 39,042. (No specimens.)

To all whom it may concern:

Be it known that I, HERBERT H. DOW, a citizen of the United States, and a resident of Midland, county of Midland, State of Michigan, have invented a new and useful Improvement in Processes of Extracting Bromin from Brine, of which the following is a specification, the principle of the invention being herein explained and the best mode in which I have contemplated applying that principle, so as to distinguish it from other inventions.

My invention consists in an improved process for more completely extracting bromin from natural bromid brines and the production of a bromid nearly or entirely free from chlorin. Said process consists of a series of steps hereinafter fully described.

The annexed drawing and the following description set forth in detail one mode of carrying out the invention, such disclosed means constituting but one of various ways in which the principle of the invention may be used.

In said annexed drawing is represented a diagrammatic view of a form of apparatus used in my improved process.

In said apparatus, A represents a brine-reservoir of a main system, which reservoir is supplied with brine from an auxiliary system. These two systems and their connection with each other will now be described.

The brine is permitted to flow from the said reservoir A into an oxidizer B. The oxidation may be accomplished by any one of various means explained in my reissued United States Letters Patent No. 11,232. From the oxidizer the brine flows into a series of blow-out towers C, no special form of tower being required, many forms of apparatus for bringing liquids into contact with gases being familiar to technical chemists. Lunge-plate columns or coke-towers are common examples of apparatus that may be employed for this purpose.

Part of the brine from the reservoir A is permitted to flow through a tailings-tower D, which is connected by means of a gas-passage *d* with the oxidizer B. The brine after passing through the tailings-tower is pumped by any suitable means, such as a pump *e'*, into a

purifier E, consisting of a series of towers of construction similar to that of the blow-out towers and in which the gas may be brought into intimate contact with the brine flowing therethrough.

From the purifier the brine is pumped through a pipe B' into the oxidizer B, so that it is seen all of the brine from the reservoir A eventually passes through the oxidizer B. A blower F forces a current of air through the blow-out towers C, from whence it emanates through a suitable duct G and passes into the purifiers E, which are connected with each other by suitable ducts *e*. A duct H leads from the purifying apparatus to a second system of purifiers J of a construction similar to that of purifiers E. Said purifier J is connected by means of a duct K with the absorbers L, also of similar construction to blow-out towers C. Said absorbers are connected with the blower F, which forces air into the blow-out towers C, as shown. It is thus seen that a closed system of air circulation is established, the above-described apparatus constituting the main system used in my improved process.

From the blow-out towers C the brine is pumped into an oxidizer M of the auxiliary system, from whence it flows into a system of blow-out towers N of a construction similar to that previously described, and from which the brine, which, as will be hereinafter fully described, has been almost completely divested of bromin, flows into the waste.

An air-duct O leads from the blow-out towers and forms an exit for air, which is drawn through such towers by means of exhaust-blower P, as will presently be seen. Said duct passes into a system of absorbers Q of a construction similar to that previously described in the main system. A connection is also formed from the blower F to the absorbers Q through the connection Z, in which is located a regulating device *z*.

A second brine-reservoir R is connected with said absorbers, the brine from such reservoir flowing through said absorbers and from them into the reservoir A of the main system.

The oxidizer M is provided with a duct O', which connects with the duct O. The ex-

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haust-blower P is connected, as shown, with the absorbers Q. Oxidizer M, blow-out tower N, absorbers Q, and blower P and their connections constitute the auxiliary system of the apparatus.

In order to set free all of the bromin in the brine as shown in the process described in my reissued Letters Patent of the United States No. 11,232, dated April 12, 1892, it would be necessary to overoxidize it—that is, oxidize it to such an extent that some free chlorin exists in the brine. The complete subsequent blowing out of the bromin from the brine would entail the simultaneous blowing out of the chlorin present due to such overoxidation, a condition which could not be allowed to exist contemporarily with the economical manufacture of bromid and bromates, as is well understood. In order to recover practically all of the bromin from the brine treated, with a contemporary expenditure of oxidizing energy equivalent to the bromin content only, my improved process is carried out in the following manner:

The brine on leaving the reservoir A, as above stated, enters the oxidizer B, where it is oxidized sufficiently to set only part of the contained bromin free, together with a certain amount of chlorin. The brine then leaving said oxidizer enters the blow-out towers C, through which a current of air is forced by the blower F, such air passing out of the blow-out towers laden with free bromin and chlorin. From the blow-out towers such bromin and chlorin laden air enters the purifiers E, through which, as previously described, is flowing a supply of brine from the main reservoir A, which has previously passed through the tailings-tower D. The bromin and chlorin laden air passing through the purifiers E comes into contact with the brine flowing therethrough and is almost completely depleted of free chlorin by the substitution of the latter for the bromin in the bromid present in the brine, the chlorin in the air being thus utilized to liberate the bromin. We have found in practice, however, that such chlorin is not completely absorbed from the air.

The nearly-chlorin-free air coming from the purifiers E passes through the second set of purifiers J, through which a strong bromid solution (provided from a suitable source, such as the receptacle X) is caused to circulate, where the last trace of chlorin is removed by the substitution of such chlorin for the bromin in the bromid solution, such bromin being liberated and passing out through the duct K, together with the free bromin previously formed. Such bromin-laden air then passes into the absorbers L, which may contain any suitable material, the latter being provided from a suitable source of supply, such as the receptacle Y, which will combine with the bromin, as explained in my above-mentioned Letters Patent.

As above described, the air after having been depleted of its bromin in the absorbers

L is again blown through the blow-out towers C, the same process as before described then being repeated in the main system.

The brine in the tailings-tower D is used only to absorb the gases passing from the main oxidizer-vent *d*, such gases consisting mainly of bromin, formed by oxidation and air. The brine leaving this tower may contain considerable free bromin and is thence conducted to the purifier and blown out to such a point that the amount of bromin in the air and in this brine are in equilibrium.

The brine that leaves the main system from the blow-out towers C contains some free bromin which has not been blown out by the air-current. It also contains some combined bromin that was not oxidized in the main system oxidizer B. In fact, it is necessary to leave quite an amount of combined bromin in the brine at this stage, as the bromin that is blown out contains less chlorin if some bromid be present. This brine after being discharged from the main system passes to the oxidizer M in the auxiliary system, where it is oxidized to excess in order that all the combined bromin may be converted into free bromin, chlorin being set free by such oxidation, it being practically impossible to set all the bromin free without setting free some chlorin. From said oxidizer M the brine then passes through the blow-out towers N, where practically all the bromin is extracted with a considerable proportion of chlorin. This bromin and chlorin laden air is then passed through the air-duct O into and through the absorber Q, where this chlorin and bromin are removed by being absorbed by brine, as hereinafter explained, which passes therethrough and is discharged into the reservoir A of the main system.

All natural brines that contain bromid are extremely impure, in many cases containing besides the chlorid of sodium, calcium, magnesium, potassium, lithium, also carbonate of iron. In other cases they contain dissolved hydrogen sulfid and also traces of iodids, and as is well known oil is frequently associated with brine in natural deposits. By my improved process the brine is not evaporated, is not even heated, but is worked in the cold without any preliminary process whatever for the bromin it may contain—an obvious economical advantage. Any impurities that have a reducing action on bromin will of necessity have to be oxidized before the bromin itself can be set free. It is therefore of great economical value to oxidize as far as possible with atmospheric air, and if this oxidation is then supplemented by the action of waste gases that contain traces of chlorin or bromin a further economical effect will result. The great importance of the feature will be understood when it is considered that natural brines contain in almost every case very much less than one-tenth of one per cent. of bromin, and hence an enormous amount of brine must be handled in

order to secure a limited amount of bromin, and if this brine, as pumped, contains only traces of reducing material, and if such material is not removed by such preliminary oxidation such reducing material may consume more oxidizing energy than is consumed in the extraction of the bromin itself after such preliminary oxidation has taken place. In other words, when the oxidation is conducted solely with chlorin or its equivalent and not by air several times the amount of chlorin may be consumed than would be the chemical equivalent of the bromin produced. As these bromid-containing brines are always more or less impure, they are not adapted for the manufacture of salt, and if salt be made from such brines the impurities seriously complicate the process and deleteriously affect the quality of the salt manufactured. It is therefore very desirable to extract the bromin without incurring the necessary expense which the manufacture of salt—that is, the evaporation of the brine—involves. By the described process bromin is extracted without the production of salt, and hence without the application of heat.

The hydrogen sulfid and other impurities are not added or required for the express purpose of absorbing chlorin, but are necessary evils that originally exist in the brine, which must be gotten rid of before free bromin can exist in the brine; but to the extent that they absorb free bromin in the air with which it is blown they have value. I am therefore able to use the natural brine as an absorbent material in the towers Q.

The hydrogen-sulfid gas contained in the natural brine, which flows into the absorbers Q, will hence unite with the free bromin in the chlorin and bromin laden air, which passes therethrough from the blow-out towers N.

The natural-salt brines from the reservoir R entering the top of the absorbing-towers Q come into contact with air which, entering at the bottom of such towers, has been, as will presently be explained, made practically pure, and hence more or less of the gases dissolved in the brine will be removed. As the brine descends a little lower the hydrogen sulfid that has not been removed by the pure air, as well as any other substances capable of oxidation by bromin and which have remained in the brine, is attacked and destroyed by the oxidizing action of the dilute bromin and chlorin. As the brine descends still lower and becomes free from reducing agents the chlorin in the air will set some bromin free, and the bromin itself, to a limited extent, will become dissolved in the brine, the latter passing to the main system, in which the bulk of the bromin is set free and is blown out. Such above-described union of the hydrogen sulfid and the bromin forms additional bromid, which hence makes it subsequently necessary to resort to additional oxidation in the oxidizers to recover such combined bromin, such additional oxidation being proportional

to the amount of hydrogen sulfid present. Such hydrogen sulfid is, however, blown out to a greater or less extent by the air at the top of absorber Q, and hence is partially removed before it enters the oxidizing-towers or the oxidizing zone of the auxiliary absorber. The amount of additional oxidation required to set the bromin free which has combined with the sulfid is hence greatly reduced.

Carbon dioxid, which may be present in the brine, is likewise removed, and is therefore prevented from retarding absorption in the absorption-towers J when alkaline hydrate is used as an absorbent material to produce a bromid.

It is thus seen that the excess of oxidizing agent in the form of chlorin gas which has been necessarily expended in the auxiliary oxidizer M in order to remove the last traces of bromin is used to set free in the untreated brine the amount of bromin equivalent to the excess of oxidizing agent employed, and I am in this manner enabled to use again and again such excess of oxidizing energy first supplied to the system and, as before stated, to recover practically all the bromin from the brine treated.

It is evident that a second auxiliary system might be added by taking the exhaust-brine from the first auxiliary system, oxidizing and blowing it and absorbing the bromin from the bromin-laden air in natural or unoxidized brine, then subsequently substituting this brine for the natural-brine supply in the auxiliary system, thus making what might be called a "triple-extraction" system instead of a compound system. It is also evident that the process might be carried to a fourth or fifth stage. The compound system described is, however, preferable.

The use of the brine in the purifiers E, and the consequent utilization of the bromid contained therein for absorbing the chlorin, does away with the necessity of employing a large quantity of expensive alkaline bromid for this purpose and prolongs the life of such alkaline bromid as is used in the purifiers J by performing a large part of the work of extracting chlorin which would otherwise devolve upon such purifiers.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the steps herein disclosed, provided the step or steps covered by any one of the following claims be employed.

I therefore particularly point out and distinctly claim as my invention—

1. The steps in the process of manufacturing bromin from bromid-containing brines, which consist in bringing unoxidized bromid-containing brine into contact with air and subsequently into contact with air containing a free halogen.

2. The steps in the process of manufacturing bromin from bromid-containing brines,

which consist in bringing unoxidized bromid-containing brine into contact with air and subsequently into contact with air containing chlorin.

5 3. The steps in the process of manufacturing bromin from bromid-containing brines, which consist in bringing unoxidized bromid-containing brine into contact with air and subsequently into contact with air containing
10 bromin and chlorin.

4. The steps in the process of extracting bromin from bromid-containing brines, which consist in oxidizing the brines short of the bromid content, blowing out the free bromin,
15 and then oxidizing the remaining brine to excess of the bromid content.

5. The step in the process of manufacturing bromin, which consists in bringing unoxidized bromid-containing brine into contact
20 with air containing a free halogen which has been liberated in such process.

6. The step in the process of manufacturing bromin, which consists in bringing unoxidized bromid-containing brine into contact
25 with air containing chlorin which has been liberated in such process.

7. The step in the process of manufacturing bromin, which consists in bringing unoxidized bromid-containing brine into contact
30 with air containing chlorin and bromin which have been liberated in such process.

8. In a process of extracting bromin from bromid-containing brines, the method of removing traces of chlorin from dilute bromin
35 and chlorin mixtures, which consists in treat-

ing said mixtures to contact with a natural brine-containing bromid, and then to contact with a more concentrated bromid solution comparatively free from chlorin.

9. The process of extracting bromin from 40 bromin-containing brines, which consists in removing a portion of the bromin, subjecting untreated bromid-containing brine to the action of chlorin and bromin set free by excessive oxidation of brine from which such portion 45 of the bromin has already been removed whereby the amount of bromin in such untreated brine is increased and practically all the bromin in the previously-oxidized brine is
50 recovered.

10. The process of extracting bromin from bromid-containing brines which consists in oxidizing the brine, blowing out the bromin and chlorin so formed with air, treating the bromin and chlorin laden air with bromid-containing brine whereby most of such chlorin is 55 removed, subsequently absorbing the remaining chlorin whereby chlorin-free air is obtained, oxidizing the brine recovered from the blowing-out process to excess and treating un- 60 oxidized brine with the chlorin and bromin formed by such excessive oxidation whereby the amount of bromid in such brine is increased.

Signed by me this 5th day of December, 65
1900.

HERBERT H. DOW.

Attest:

E. E. CROWELL,
A. E. MERKEL.