AMENDED SPECIFICATION

Reprinted as amended in accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the fourteenth day of September, 1949, under Section 11 of the Patents and Designs Acts, 1907 to 1946.

PATENT SPECIFICATION

605,983

Convention Date (Belgium): Feb. 27, 1943.

Application Date (in United Kingdom): Jan. 7, 1946. No. 623/46.

Complete Specification Accepted: Aug. 4, 1948.

(Under Section 6 (1) (a) of the Patents &c. (Emergency) Act, 1939, the proviso to Section 91 (4) of the Patents and Designs Acts, 1907 to 1942, became operative on Jan. 7, 1946).

Index at acceptance:—**Classes 1(ii)**, A9; **and 1(iii)**, D(9: x), G(1: 50).

COMPLETE SPECIFICATION

Manufacture of Alkali Chlorites

We, SOLVAY & CIE., a Body Corporate organized under the laws of Belgium, of 33, rue Prince Albert, Brussels, Belgium, 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:—

The invention concerns the manufacture of alkali chlorites by the intermediary of chlorine dioxide obtained by the action of hydrochloric acid on an alkali chlorate or an alkaline earth chlorate according to the reaction:—

$$2ClO_3^{1} + 4HCl = 2ClO_2 + Cl_2 + 2Cl^{1} + 2H_2O.$$

With a view to separating chlorine dioxide, it is known to bring the mixture of chlorine and chlorine dioxide into the presence of an excess of lime, in conditions such that the chlorine is absorbed and that the chlorine dioxide reacts as little as possible. This requires in practice the use of the lime in the powder state, a strict limitation of the quantity of water present and the use of a cumbersome and costly apparatus, necessitating constant supervision.

The process, according to the invention for the manufacture of alkali chlorite involving the action of hydrochloric acid on an alkali chlorate and/or alkaline earth chlorate, is characterised by causing the mixture of chlorine and chlorine dioxide so produced and entrained by air to undergo partial physical purification of the ClO_2 by being mixed with a concentrated solution of alkali or alkaline earth chloride and/or chlorate, whereby most of the chlorine dioxide and a little of the chlorine is absorbed, which mixture is then desorbed and further purified by being passed through a solution or milk of lime. In these conditions all the chlorine is fixed by the base, as also a quantity of chlorine dioxide, determined by the equation:—

$$Cl_2 + 4OH^{1} + 2ClO_2 = 2Cl^{1} + 2ClO_3^{1} + 2H_2O.$$

Due to the fact that there remains, in consequence of the physical purification, only a small fraction (less than $\frac{1}{10}$) of chlorine initially present, the quantity of chlorine dioxide thus sacrificed remains small and it is possible to accept deliberately this sacrifice in view of the surprising advantages that are obtained. In fact, contrary to what would be expected, the purification reaction indicated above is extremely rapid and only requires for its execution an apparatus of small dimensions. The chlorine dioxide is thereafter absorbed in a known manner by an alkali hydroxide and/or carbonate for the obtention of a mixture of the chlorite and chlorate, the latter being separated and re-used in the production of the chlorine dioxide.

The complete process of the manufac-

ture comprises the following operations:

1. Generation of a mixture of $ClO_2 + Cl_2$, containing air, by the reaction of gaseous or aqueous hydrochloric acid on a concentrated solution of alkali chlorates and/or alkaline earth chlorates which have been purified or partially purified of the chlorides formed as co-products of their manufacture, accompanied by an injection of air into the reaction solutions, intended to carry away the gaseous products as and when they are formed. There is produced in addition to the reaction above, the secondary reaction although to a more feeble extent:

$$ClO_3^1 + 6HCl = 3Cl_2 + Cl^1 + 3H_2O$$

2. Partial physical purification from chlorine of the gaseous products: this purification is obtained by absorption followed by desorption in a body of a concentrated solution of alkali or alkaline earth chloride and/or chlorate. By reason of the solubility of the ClO_2, much higher than that of Cl_2, only 5 to 10% of the chlorine generated is absorbed in the solution whilst more than 90% of ClO_2 is dissolved in the same solution. This latter is then desorbed by means of a current of air and gives back the gases in the proportion $\frac{Cl}{ClO_2} = \frac{1}{10}$ to $\frac{1}{15}$ in volume when initially this proportion was approximately $\frac{1}{1}$.

This partial physical purification eliminates an appreciable quantity of chlorine, so that the chemical purification (following phase) is made with a minimum loss of ClO_2.

3. Total chemical purification from chlorine of the desorbed gases by reaction of the latter with a solution or a milk of lime:

$$Cl_2 + 4OH^1 + 2ClO_2 = 2Cl^1 + 2ClO_3^1 + 2H_2O.$$

The ClO_2 which has not reacted with the chlorine and the lime, which may be about 80% of the dioxide initially produced, is perfectly free from chlorine.

4. Absorption of pure ClO_2 by a solution of alkali hydroxide and/or carbonate which may contain chlorate and chlorite coming from a previous operation, according to the reaction:

$$2ClO_2 + 2NaOH = NaClO_2 + NaClO_3 + H_2O$$
$$2ClO_2 + Na_2CO_3 = NaClO_2 + NaClO_3 + CO_2$$

5. Separation of the sodium chlorite and chlorate formed by crystallisation and, if desired, evaporation in such a manner as to recover separately the chlorite and the chlorate and finally to return this latter into the cycle.

The carrying out of the process according to the invention can be effected advantageously in the arrangement described below and illustrated in the attached diagram.

In a chlorinator (*a*) is introduced lime, water, chlorine and the unabsorbed gases coming from a previous operation. There is obtained a mixture of calcium chlorate and chloride which is freed in a known manner in (*b*) of all or a part of the $CaCl_2$ and conducted into a rectifying column or a scrubber (*c*) which also functions as a generator of ClO_2. This generator also receives a solution of chlorate led back from a later stage of the manufacture. The gaseous products (Cl_2 and ClO_2) are carried away by a current of air injected at the bottom of the generator and the gaseous mixture is introduced into an absorption tower (*d*) in which a part of the Cl_2 and most of the ClO_2 are preferentially absorbed by the purifying solution described above. The solution with absorbed gases is then transferred to a desorption tower (*e*) whilst the unabsorbed gases are directed to the chlorinator referred to above. In the tower (*e*) the solution is subjected to a jet of air which makes it give up the ClO_2 and the Cl_2 after which it is returned towards (*d*) and circulates intermittently. The mixture of gases which leaves the desorption tower contains little chlorine, relatively to its content of ClO_2. It can thereupon undergo a chemical purification by a milk of lime with a high yield of ClO_2. This operation is effected in a tower (*f*) which furnishes on the one hand a mixture consisting only of air and ClO_2 and, on the other hand, an aqueous solution of $Ca(ClO_3)_2$ and of $CaCl_2$ which returns towards (*c*). The mixture of air and ClO_2 enters at the base of a tower (*g*) fed with a solution of alkali carbonate and/or hydroxide: there is produced an alkali chlorite mixed with equi-molecular quantities of chlorate, these two compounds are separated in (*h*) by crystallisation and, if desired, by evaporation. The final product is recovered in a practically pure state, whilst the alkali chlorate returns to the generation of ClO_2. The mother liquors coming from (*h*) contain the alkali chlorite and chlorate and return into the tower (*g*). The air coming from this tower can be directed, as desired, towards (*c*) and/or towards (*e*).

The chemical purification of the ClO_2 which follows the partial physical purification, according to the invention, has

the advantage of obtaining by a simple process the complete removal of Cl_2 by an inexpensive base and of furnishing an alkali chlorite with a minimum of consumption of the alkali hydroxide or carbonate.

By way of example not limitative, there may be cited the manufacture of sodium chlorite because it is understood that there is manufactured by this method the other alkali chlorites without departing from the scope of the invention.

The gases carried away by the air injected at the base of the ClO_2 generator contain, per 1000 kgr. of $NaClO_2$ obtained, 1941 kgr. of ClO_2 and 2041 kgr. of Cl_2. They are made to bubble into the physical purifying solution which is then subjected to the action of a current of air: after desorption, the gases which contain 1747 kgr. of ClO_2 and 134 kgr. of Cl_2, are sent into a purification tower where they are brought into contact with a milk of lime containing 280 kgr. of $Ca(OH)_2$. There are formed 391 kgr. of $Ca(ClO_3)_2$ and 210 kgr. of $CaCl_2$ which return to the generation of ClO_2, whilst 1492 kgr. of ClO_2 are absorbed by a solution containing 885 kgr. of NaOH. This absorption furnishes 1598 kgr. of $NaClO_2.3H_2O$ and 1177 kgr. of $NaClO_3$ which are separated by crystallisation and evaporation. The $NaClO_3$ is directed into the ClO_2 generating tower whilst the hydrated sodium chlorite is dried and furnishes 1000 kgr. of anhydrous chlorite.

It is pointed out that the present invention consists in a novel combination of steps which *per se* are partly novel and partly old. There is a close interrelation between the novel and the known steps which gives rise to an advantage of great value in practice and amounts to a progress over the art.

Of publications which are relevant to the known steps we list the following:—

Martens—Annales de Chimie et de Physique, 1836, 66, pp. 306—307.

Schacherl — Liebig's Annalen der Chemie, 1876, 181—182, pp. 193—201.

Bray—Z. für Anorg. Chemie, 1906, 48, pp. 242—244.

Luther and MacDougall—Z. Physik, Chemie, 1908, 62, pp. 241—242.

Gmelin — Handbuch der Anorg. Chemie, 1927, vol. Chlor, p. 298.

Carlson and Gelhaar—Chem.-Zeitung, 1908, 32, p. 604.

Garzarolli — Liebig's Annalen der Chemie, 1881, 209, pp. 207—208.

British Specification No. 495,267 and United States Specifications Nos. 2,031,681; 2,036,311; 2,046,830; 2,108,976; and 2,169,066.

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

1. Process for the manufacture of alkali chlorite involving the action of hydrochloric acid on an alkali and/or an alkaline earth chlorate, characterised in that after the mixture of chlorine and chlorine dioxide so produced has undergone in a known manner partial physical purification by absorption in a concentrated solution of alkali or alkaline earth chloride and/or chlorate, the absorbed gases considerably poorer in chlorine are desorbed from the solution and brought into contact with a quantity of milk of lime just sufficient to cause all the chlorine present to combine according to the reaction:

$$Cl_2 + 2ClO_2 + 2Ca(OH)_2 = CaCl_2 + Ca(ClO_3)_2 + 2H_2O,$$

whereupon the residual chlorine dioxide is treated by an alkali carbonate or hydroxide and the chlorite and chlorate are separated in a known manner.

2. Process according to claim 1, characterised in that the chlorates entering into reaction with the hydrochloric acid are previously freed from all or a part of alkali and/or alkaline earth chlorides which are formed with the chlorates as co-products of their manufacture.

3. Process according to claim 1, characterised in that the unabsorbed gases from the partial physical purification of the ClO_2 are re-used for the manufacture of new quantities of alkali chlorate and/or alkaline earth chlorate, whilst the solution after absorption is subjected to a current of air which expels ClO_2 and Cl_2 which it contains, after which it is re-used in the absorption of new quantities of ClO_2 and of Cl_2.

4. Process according to claims 1 to 3, characterised in that, after separation of the products coming from the final absorption, the alkali chlorate separated from the alkali chlorite is directed towards the ClO_2 generating tower, whilst the mother liquors are returned to the final absorption.

5. Process of manufacture of alkali chlorite involving the action of hydrochloric acid on an alkali and/or alkaline earth chlorate, in substance as described above.

Dated the 7th day of January, 1946.

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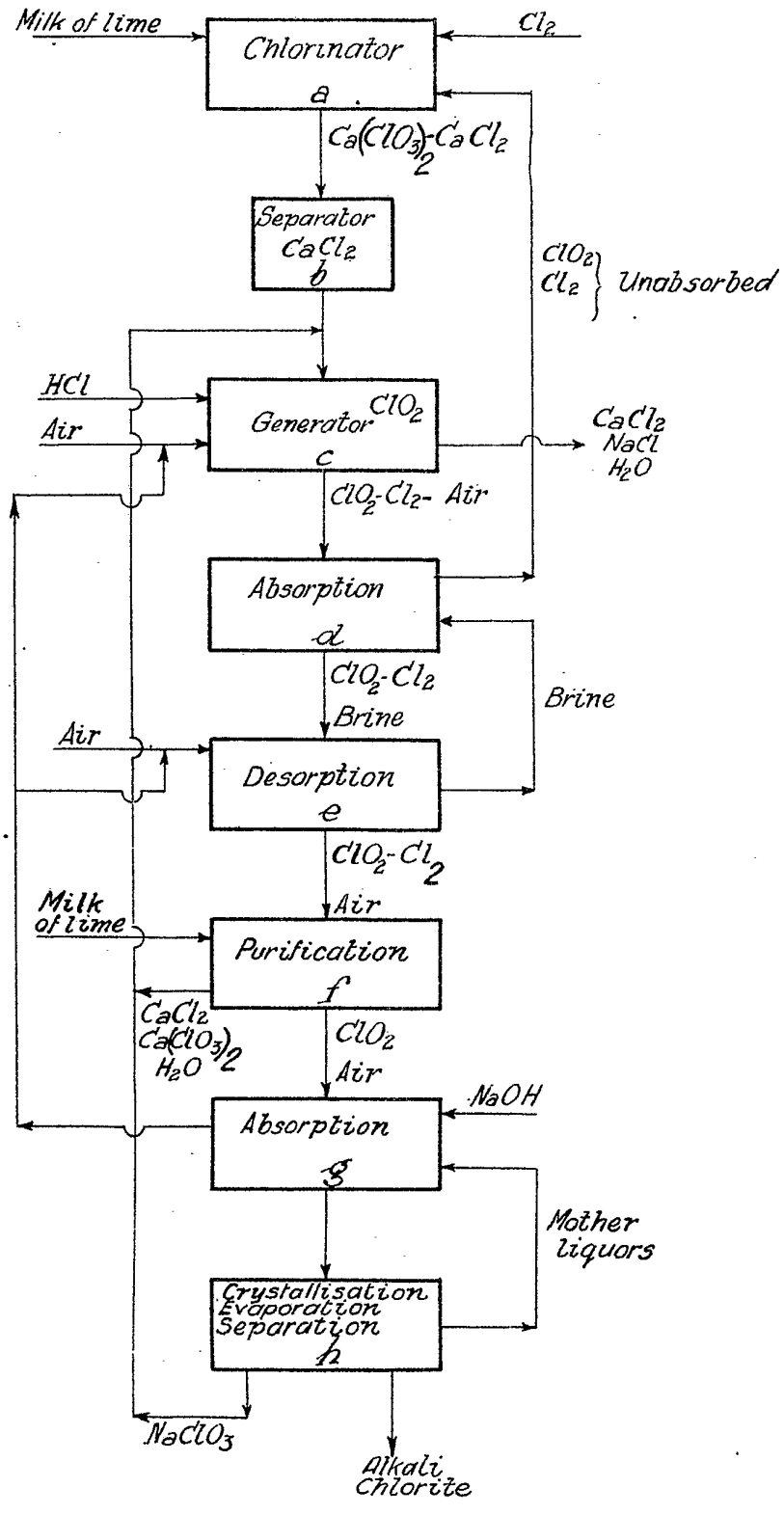
Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1949.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 2s. 0d. each (inland) 2s. 1d. (abroad) may be obtained.



[This Drawing is a reproduction of the Original on a reduced scale.]

H.M.S.O.(Ty.P.)