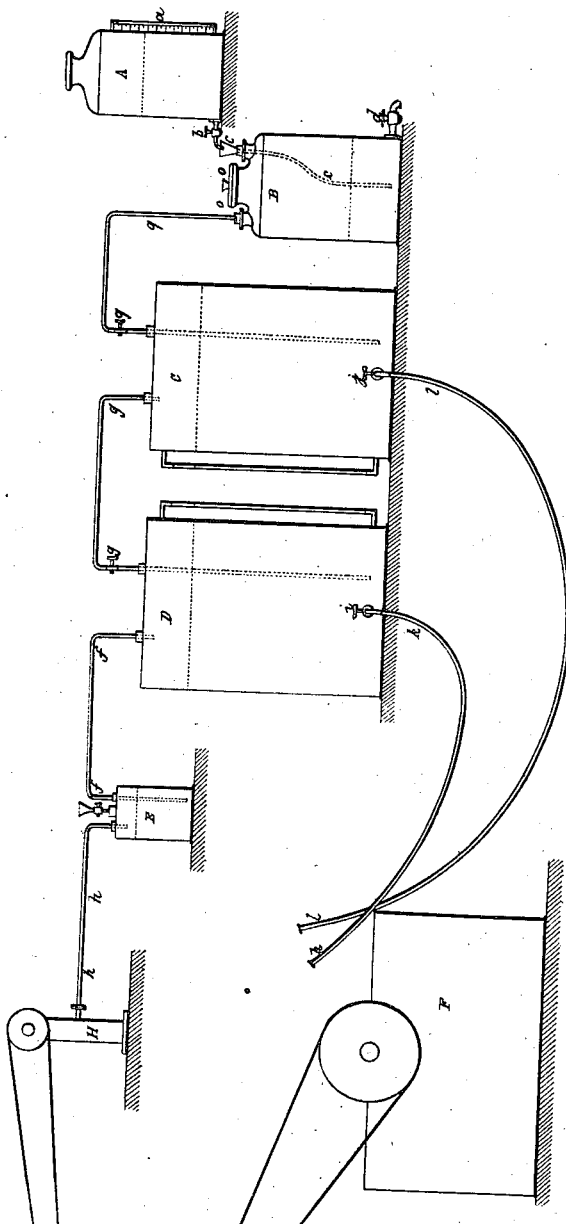


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Manufacture of Bleaching Liquids.

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PLACE.

IMPROVEMENT IN THE MANUFACTURE OF BLEACHING-LIQUIDS.

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October 14, 1878; patented in France, February 9, 1878.

To all whom it may concern:

Be it known that I, THOMAS SIMON, Comte de Dienheim-Brochocki, of Paris, France, engineer, have invented Improvements in the Manufacture of Liquids for Decolorizing and Bleaching; and I do hereby declare that the following is a full, clear, and exact description of the same, reference being had to the annexed sheet of drawings, making a part of the same.

This invention relates to the manufacture of chlorozone on a commercial scale, and to the applications of the same for bleaching fibers, fabrics, paper-pulp, and other materials.

In bleaching with chlorine in the ordinary manner the material to be treated is brought into direct contact with the bleaching agent, whether it consists of dry chlorine gas or an aqueous solution of hypochloride of lime. In the first case the chlorine destroys the coloring-matter by combining with its hydrogen, forming hydrochloric acid, ($\text{Cl} + \text{H} = \text{HCl}$) which, as fast as it is formed, acts destructively upon the ligneous matter, and the mass is not entirely bleached without being destroyed to a great extent. In the other case the hypochlorous acid of the chloride of lime, which is to act by its oxygen and chlorine, is, however, too intimately combined with its base to have any great tendency to combine with the hydrogen of the coloring-matter, and it is only by the addition of acid which displaces it from its base that it is rendered active. The result is, first, a loss in hypochlorous acid, which escapes from the mass, owing to the more or less energetic action of the decomposition of the hypochlorite; second, an immediate injurious effect upon the fiber caused by the acid added; third, a more or less slow destructive action due to the lime, which becomes encrusted in the pores of the fibers in the form of insoluble salts, incapable of being entirely removed by washing.

As regards the alkaline hypochlorites known in commerce under the name of "bleaching-liquid," or "Labarraque's fluid," they are also attended with objections in bleaching which render their employment difficult. Whether weak or concentrated relatively to their rich-

ness in decolorizing power, they are always very alkaline, and consequently too corrosive, and bleach with difficulty without the aid of an acid to stimulate the reaction and neutralize the excess of alkali. The concentrated product being only obtained by a long, objectionable, and dangerous process, its cost is necessarily very high.

The following are the two methods known and used in commerce for the manufacture of these hypochlorites: first, saturation of an alkaline lye (carbonate or oxide) by a current of gaseous chlorine, obtained by manganese according to a suitable formula; second, double decomposition of the solution of chloride of lime combined with that of an alkaline carbonate.

In the first case the operation of manufacture requires twenty-four hours. The base should be considerably in excess in the solution; otherwise decomposition will certainly take place. It is difficult to give the product a chlorometric power exceeding 35° to 30° Baumé, which leaves about one-third of base in excess. Beyond this limit the chlorous saturation becomes difficult, the heating of the material, notwithstanding refrigeration, is unavoidable, and its more or less rapid decomposition ensues. The product, moreover, is most unstable, and loses very rapidly the greater portion of its decolorizing power. It is dear, very caustic, and with difficulty transported during the summer season. Its formula is as follows: $2\text{NaO} + 2\text{Cl} = \text{NaO}, \text{ClO} + \text{NaCl}$.

In the second case, neither the chloride of lime nor the alkaline carbonate being soluble at a cool temperature and necessary in this case beyond a restricted limit, the product obtained by their double decomposition is still poorer in decolorizing principle than the product obtained by the method above referred to. The operation itself, though simple in principle, becomes long and tedious on account of the many washings of the precipitates. It furnishes a product of twenty-five chlorometric degrees, containing in its solution a sensible quantity of chloride of calcium, which in the bleaching operation is found again in the form of carbonate or sulphate of lime, according to

the mode of treatment adopted. Here again, as in the preceding case, the product is too alkaline, most unstable, and too costly.

Different results, and at a much more advantageous rate, may be obtained in bleaching with chlorozone, produced by a simple, rational, and inexpensive operation. The chlorozone may be acid or alkaline, liquid or solid. It is obtained in the cold by saturating a caustic alkaline lye by a current of hypochlorous acid in conjunction with a current of air.

It is well known that by decomposing the hypochlorite or chlorate of an alkali or an alkaline earth by an acid or an electric current, free hypochlorous acid or chlorine is evolved, according to circumstances.

Example.— $(\text{CaO}, \text{ClO} + \text{CaCl}) + 2\text{A} = 2\text{CaO}, \text{A} + 2\text{Cl}$, (chlorine); $(\text{CaO}, \text{ClO} + \text{CaCl}) + \text{A} = \text{CaO}, \text{A} + \text{CaCl} + \text{ClO}$, (hypochlorous acid); $(\text{MO}, \text{ClO}_5) + 3\text{HCl} = \text{MCl} + 3\text{HO} + 3\text{ClO}$, (hypochlorous acid.)

It is also known that the oxygen of the air in the nascent state combines with chlorine gas and forms hypochlorous acid, and that water at the ordinary temperature dissolves two hundred times its volume thereof. It is also known that a current of hypochlorous acid passing in excess through the alkaline solution (oxide, carbonate, or chloride) converts these salts into chlorates.

Starting from these premises, if, on the one hand, hypochlorous acid be produced by the decomposition of a hypochlorite or chlorate by means of an acid in conjunction with a current of air, and if, on the other hand, an alkaline solution, such as of soda, for example, be saturated with this gas, it is evident that the product obtained will be the chlorozone in question, which is acid or alkaline, according to the proportion of the equivalents of the base in solution, and of the hypochlorous acid by which it is saturated.

According to theory, the result of this reaction should be a pure alkaline hypochlorite, which is a very unstable salt; but owing, however, to a continuous action under the influence of a constant current of air, the final product of the operation is a triple salt, and, according to circumstances, conforms to one of the following formulas:

Acid chlorozone: $\text{NaO} + \text{XHO} + (200 - \text{XCIO}) = \text{NaO}, \text{ClO}_5 + \text{XHO} + 199 - \text{XCIO}$.

Alkaline liquid chlorozone: $(4\text{NaO} + \text{XHO}) + 4\text{ClO} = (\text{NaO}, \text{ClO}_5 + 2\text{NaO}, \text{ClO} + \text{NaCl}) + \text{XHO}$.

Both may have a very high decolorizing power.

It is evident that if the current of air drawn in during the manufacture be shut off, and if the quantity of decomposing acid be halved, chlorine gas will be evolved, and not hypochlorous acid. The final product will then be a common hypochlorite.

Example.— $(\text{CaO}, \text{ClO} + \text{CaCl}) + 2\text{A} = 2\text{CaO}, \text{A} + 2\text{Cl}$, $2\text{Cl} + 2\text{NaO} = \text{NaOClO} + \text{NaCl}$.

The alkaline chlorozone, marking 40° Baumé and one hundred to one hundred and twenty

chlorometric degrees, becomes easily crystallizable at a low temperature; but the crystals obtained are melted easily by the least heat. Its employment is on that account impracticable. The contrary is the case if the chlorozone be solidified by the absorption of its excess of water by means of a hydrometric alkaline salt. In this case neither the too-low temperature nor the maximum chlorometric richness of the chlorozone are necessary.

Dried carbonate of soda, for example, added to the chlorozone in proportions varied according to the density of the liquid at a temperature of + 6° to + 8° centigrade, forms a compact mass capable of being molded and granulated, and the harder as the temperature of the operation was lower. It only softens at a persistent heat of 20° centigrade. Hardened anew by lowering the temperature, it resists ambient heat better, and loses none of its decolorizing qualities if it is kept protected from air-currents, light, and humidity. The liquid alkaline chlorozone, marking 30° Baumé and fifty chlorometric degrees, is very stable, and may be kept several months. It is therefore easily transported. With an equal quantity of base and chlorine, the decolorizing power of chlorozone is double that of an alkaline hypochlorite of commerce obtained, as before mentioned, by a current of chlorine.

Example.—Chlorozone: $4\text{NaO} + 4\text{ClO} = (\text{NaO}, \text{ClO}_5 + 2\text{NaO}, \text{ClO} + \text{NaCl}) + \text{XH} = (4\text{NaCl} + 8\text{HO}) + \text{X} - 8\text{H}$. Hypochlorite: $4\text{NaO} + 4\text{Cl} = 2(\text{NaO}, \text{ClO} + \text{NaCl}) + \text{XH} = (4\text{NaCl} + 4\text{HO}) + \text{X} - 4\text{H}$.

Its use is valuable for dyers and bleachers of linen, as, besides its decolorizing power, it possesses, owing to its alkaline base, saponifying qualities.

As regards acid chlorozone, it should be used immediately after being made, so that it is necessary that it should be manufactured on the spot. It is chiefly intended for bleaching raw vegetable matters, such as paper-pulp, cotton, linen, hemp, and other fibers. Compared with chloride of lime, it should be observed that chlorozone, with an equal quantity of chlorine and three-fourths less base, will take up three times as much hydrogen from the coloring-matter as the chloride of lime.

Example.—Chloride of lime: $2(\text{CaO}, \text{ClO} + \text{CaCl} + \text{A}) + \text{XH} = 2(\text{CaO}, \text{A} + \text{CaCl} + \text{HO} + \text{HCl}) + \text{X} - 4\text{H}$. Chlorozone: $(\text{NaO}, \text{ClO}_5 + 3\text{ClO}) + \text{XH} = \text{NaCl} + 9\text{HO} + 3\text{HCl}) + \text{X} - 12\text{H}$.

In the first case there is 4H and in the second case 12H taken from the coloring-matter, as shown by the following reaction: $(\text{NaO}, \text{ClO}_5 + 3\text{ClO}, \text{HO}) + \text{XH} = (\text{NaO}, \text{ClO}_5 + 6\text{HO} + 3\text{HCl}) + \text{X} - 6\text{H} = (\text{NaCl} + 9\text{HO} + 3\text{ClO}) + \text{X} - 6\text{H} = (\text{NaCl} + 12\text{HO} + 3\text{HCl}) + \text{X} - 12\text{H}$.

The apparatus employed in the manufacture of chlorozone is most simple, inexpensive, and requires but little room. It is composed, first, of a hypochlorous-acid-gas generator, a closed vessel of about one hundred and fifty liters capacity; second, of two saturators, also closed, of about two hundred liters capacity;

third, of an air-pump or exhauster working by a jet of steam or current of water. The whole of these apparatus are connected together by a system of tubes, fixed and arranged as hereinafter described.

The accompanying drawing represents, by way of example, only the apparatus which is employed in preparing the bath, the decomposing agent being a liquid acid.

A is the receiver to contain the acid, provided with a graduated gage, *a*, for indicating the quantity of liquid in the receiver, and also that which has passed out, and a cock, *b*, for regulating the flow.

B is a receiver for the hypochlorite or chlorate, to be decomposed by the acid supplied from the vessel A, and introduced at the center of B in a fine stream through a pipe, C, which also gives admission to air. The mouth O O of the vessel, through which it is charged, is hermetically sealed, and the vessel is provided with a cock, *d*, for emptying it. This vessel is the generator of the hypochlorous acid. The next two portions of the apparatus, C D, are saturators, containing the alkaline solution, and consist simply of vats or other vessels hermetically closed. Next in order to these is a small glass bottle, E, also closed, and filled to three-fourths of its capacity with water colored with indigo-blue. Lastly, H is the air-pump. F is the bleaching-vat, provided with an agitator.

It will be evident that when it is desired to use a gaseous acid—carbonic-acid gas, for example—it would be supplied in the usual way.

The vessels B C D E are, like a Woulfe apparatus, placed in communication with each other by pipes *g g f*, which rise from the top of each vessel and dip down nearly to the bottom of the next, and finally connected by a pipe, *h*, with pump H, which draws air through the whole series of apparatus.

Suppose it is desired to form a bath of chlorozone containing one thousand liters of hypochlorous acid or two thousand decolorizing units, and that the elements for its production are chloride of lime and hydrochloric acid. The vessel A is charged with eighty kilograms of hydrochloric acid diluted with water to about 12° Baumé, and vessel B is charged with twenty kilograms of chloride of lime at one hundred chlorometric degrees. The vessels C D are charged with a solution of three kilograms of soda in five hundred liters of water, (two hundred and fifty liters in each vessel;) and, lastly, the bottle E is filled with water colored with indigo-blue. The cock *b* of vessel A is then opened and the acid allowed to flow out slowly, and the pump H set in motion rather slowly, in order to avoid pumping out the gas.

Instead of a pump, an exhauster may be used, working with a jet of steam or water, like a Giffard injector, and vessel A may be replaced by an electric battery, whose poles are placed in vessel B.

The draft of air through the generator and

saturators has the advantage, first, of assisting the production of hypochlorous acid in the generator by a portion of its oxygen, which goes to produce this reaction; second, of moderating the chemical reaction in the generator; third, of preventing any leakage of gas in the apparatus, as well as any possible explosion of the apparatus, by reducing the pressure of the gases to a minimum; and, fourth, of facilitating the completion of the reaction by which the hypochlorous-acid gas is produced in the generator, and the extraction from the generator of the last traces of the said gas.

The hypochlorous acid, in traversing the liquid contained in the vessels CD, saturates them in unequal proportion, C receiving the maximum and D the minimum degree of saturation. The base held in solution in the former is transformed into chlorate and that in the second into hypochlorite of soda. The excess of hypochlorous-acid gas will only be absorbed by the water of the solution in the first saturator. The operation lasts about one hour. If the blue liquor in E be quickly decolorized, it shows that gas is being drawn out with the air, and that the exhaust should be moderated. When saturation is complete—that is to say, when the whole of the acid has run out from vessel A—the exhaust is stopped, after which the contents of the apparatus C D are discharged through cocks *i j* and india-rubber pipes *k l* into vat F, containing the materials to be bleached, which have previously been suitably scoured and washed with acids and water.

The chemical action of this bath upon the coloring-matter is very rapid, being almost instantaneous, but never injurious, as it is principally due to the action of nascent oxygen, as is shown by the following reaction, (the water used for the solution being understood:)

$$\begin{aligned} (\text{NaO}, \text{ClO}_5 + 3\text{ClO} + \text{HO}) + \text{NaO}, \text{ClO} + \text{HO} + \text{XH} &= (\text{NaO}, \text{ClO}_5 + \text{NaO}, \text{ClO} + 5\text{HO} + 3\text{HCl}) + \text{X} \\ \text{X} - 6\text{H} &= (\text{NaCl} + \text{NaO}, \text{ClO} + 8\text{HO} + 3\text{ClO}) + \text{X} \\ \text{X} - 6\text{H} &= (\text{NaCl} + \text{NaO}, \text{ClO} + 11\text{HO} + 3\text{HCl}) + \text{X} \\ \text{X} - 12\text{H} &= (2\text{NaCl} + 13\text{HO} + 3\text{HCl}) + \text{X} - 14\text{H}. \end{aligned}$$

The stirrer in vat F should be at once set in motion, as the contact of air and the movement of the materials greatly assist the bleaching. After this bleaching has been effected, the residues of the bleaching-vat may be advantageously employed for preparing the lye, or may be recovered and saturated afresh with hypochlorous acid.

The vessels C D may, by the suction of the pump, be charged through the same pipes *k l* as were used for emptying them, the cocks on the respective communicating-pipes *g g f* being suitably regulated for the purpose. Thus if the materials to be bleached require to be acted on repeatedly each time for a short period, rather than by the more energetic action of a single passage through the bath of chlorozone, this may be readily done by this system of successive decantation and saturation of the bleaching-liquid.

In some cases it would even be advantageous to saturate the alkaline liquor in presence of the material to be bleached, for which purpose the vat C would be arranged to receive the material. In this case the agitation of the air replaces the action of the stirrer. The vat D would in all cases receive the gas escaping from the vat C.

It is obvious that after the action of the chlorozone the bleached materials should be carefully washed. The bleaching action of ozone is accompanied also by a peculiar phenomenon, which is, that it strengthens the ligneous matter—*i. e.*, the resistance of its fibers—as is the case in bleaching on meadows.

The cost of chlorozone per one hundred kilograms of material to be bleached does not exceed that of chloride of lime now used for bleaching an equal quantity of material, and the advantages of the former over the latter are as follows:

First. The long and objectionable preparation of the chloride-of-lime bleaching-bath is avoided.

Second. The acids added to strengthen the reaction of the bath, to the detriment of the fiber and the loss of hypochlorous acid, are dispensed with.

Third. The direct contact of the material to be bleached with the lime (which is deposited in the fibers in the form of insoluble salts, cannot be removed by washing, and in time destroys the fiber) is avoided.

Fourth. The bleaching action is most rapid and never destructive, and is accompanied by the saponifying action due to the soluble al-

kaline base, and thus both time and raw material are saved, as well as expense.

Fifth. All intermittent washings with water and acids between the several successive immersions in the bleaching-bath are dispensed with, one single bath of chlorozone of suitable strength being capable of bleaching any vegetable matter without a repetition of the treatment, whereby an economy in labor, acids, water, machinery, apparatus, and fuel is effected.

Sixth. The residue of the bleaching-bath is utilized, whereas that of a chloride-of-lime bath is useless.

I claim—

1. The manufacture of a new product called "chlorozone," which may be used in acid or alkaline form—*i. e.*, an oxygenated and chlorous decolorizing agent having for a base a soluble alkali or alkaline earth—substantially as herein shown and set forth.

2. The process hereinbefore described of obtaining the product called "chlorozone," which consists in saturating an alkaline solution by a more or less considerable current of hypochlorous-acid gas, produced by the decomposition in the cold of hypochlorites or of chlorates by an acid, and a current of air, essentially as described.

3. The process of bleaching herein set forth, which consists in the employment of chlorozone in acid or alkaline solution, as set forth.

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