UNITED STATES PATENT OFFICE.

GEORG ORNSTEIN, OF NEW YORK, N. Y., ASSIGNOR TO ELECTRO BLEACHING GAS COMPANY, A CORPORATION OF NEW YORK.

PROCESS OF BLEACHING.

1,298,554. Specification of Letters Patent. Patented Mar. 25, 1919.

No Drawing. Application filed December 4, 1916, Serial No. 134,829. Renewed February 15, 1919. Serial No. 277,304.

To all whom it may concern:

Be it known that I, GEORG ORNSTEIN, a citizen of the German Empire, residing at New York city, in the county of New York and State of New York, have invented certain new and useful Improvements in Processes of Bleaching, fully described and represented in the following specification.

This invention relates to processes of bleaching; and it comprises a method of bleaching organic materials, such as animal and vegetable fibrous materials and materials derived therefrom such as paper, cloth, pyroxylin, etc., wherein the materials are exposed to the action of a bleaching liquor containing free HOCl and neutral chlorids; such liquor being produced by mingling chlorin, which may be in a gaseous state or in a state of aqueous solution, with water and a base, the operation being advantageously continuous with a continuous addition of chlorin to a flowing current of water, base being added to such current either at the point of addition of the chlorin or at another point, and the amount of such base added being proportionate to the amount of chlorin used, as hereinafter explained; as in feeding regulated amounts of chlorin, or chlorin solution, into a flowing current of water passing through a tower or the like while simultaneously supplying to such flow a small amount of a solution of a base, such as caustic soda, carbonate of soda, etc., in the amount sufficient only to neutralize the acidity of the HCl developed from the chlorin, and passing the bleaching liquor so formed into contact with the goods to be bleached as it is formed, that is, allowing such current to flow into the bleaching vessel; or in some cases forming the solution and allowing it to accumulate and then supplying it to the bleaching vessel from time to time—in the latter case, however, no substantial period of storage being allowed so that the bleaching liquor shall be used substantially at the time of its formation; the base so used being most advantageously an alkali carbonate such as normal sodium carbonate, and the amount used being such as to be equivalent to the chlorin employed, that is, the equivalent of one molecule of normal sodium carbonate for the equivalent of one molecule of chlorin, Cl_2, whereby the HCl produced in the hydrolysis of the chlorin converts the alkali carbonate into alkali bicarbonate which is not materially affected by HOCl, the bleaching solution thereby produced being in substance a mixture of equivalent quantities of bicarbonate, HOCl and a neutral chlorid, such a liquor being one in which the bicarbonate will exactly neutralize the secondary HCl formed by the consumption of HOCl in bleaching the fibrous material, with the ultimate production of a waste liquor which is a solution of a soluble neutral chlorid; all as more fully hereinafter described and as claimed.

In bleaching vegetable fibrous and other materials, it is the usual custom to employ neutral hypochlorites, of which bleaching powder is the one ordinarily used. Chlorin, while it has been used in the bleaching art for a very long time, is practically never used to-day in direct solution for bleaching fibrous materials for the reason that chlorin as such has a tendering or destructive action on most fibrous materials. Its direct use is practically restricted to cases where some measure of destructive action is desired, as in bleaching incrusted fibers where the incrusting material is to be removed. Instead of using chlorin directly, recourse is made to the neutral hypochlorites such as bleaching powder.

On contacting chlorin with water, a reversible reaction takes place in the sense of the following equation:

$$Cl_2+H_2O=HCl+HOCl$$

If the amount of water is sufficiently great, chlorin is practically entirely converted into its hydrolytic products HOCl and HCl, while on the other hand HCl and HOCl react upon each other in the absence of relatively large amounts of water to form chlorin. The reaction is one which is reversible; that is, it will go either to the right or to the left according to circumstances.

As I have discovered, and have disclosed and claimed in certain other co-pending applications, the stated reversible reaction may be very usefully employed in bleaching goods with chlorin in what is practically a direct bleaching. I have found, for example, that if chlorin be passed into water so as to produce a solution of very high dilution, substantially all the chlorin as such disappears and the resulting liquid which

contains its hydrolytic products, HCl and HOCl, is a very effective bleaching liquor and, because of the absence of free chlorin, is not harmful. Such a bleaching liquor may safely be directly applied to all manner of fibrous material for the purpose of bleaching the same. This way of employing the untreated hydrolytic products of chlorin in bleaching is disclosed and claimed specifically in my application Serial No. 134,749, filed December 2, 1916. Instead of relying merely upon the action of water to dilute the HCl of this reaction to a point where chlorin cannot exist in substantial amount, I have also found that I may use bases in various ways to remove the free HCl from the solution, thereby causing substantially complete conversion of the chlorin to take place with a relatively less amount of water than is required in the absence of basic material. Most of the bases will not combine with HOCl, while they will combine with HCl; and there are in addition other substances, or basic materials, (such as sulfate of soda), which, although not strictly bases, also have the property of taking up hydrochloric acid while they will not react with HOCl. With bases and bodies of this character, useful bleaching liquors may be readily produced which contain HOCl in a free state but do not contain any amount of HCl. In another application, Serial No. 134,748, filed December 2, 1916, I have described and claimed a method of bleaching wherein such bleaching liquors are employed.

There are, however, a number of basic materials which are cheap and convenient for use, which do not have the stated property of combining only with HCl to the exclusion of HOCl. Among these bases are caustic soda, caustic potash, slaked lime, baryta, strontia and the alkali carbonates, sodium carbonate and potassium carbonate.

These bases which are all more or less soluble, cannot be used with the hydrolytic products of chlorin to make bleaching liquors without formation of hypochlorites and danger of loss of free HOCl unless the precaution be taken of adding them in controlled quantities. A momentary or local excess however may do no great harm since the hypochlorites thereby formed are readily decomposed by HCl with the formation of chlorids and reliberation of HOCl.

In the present invention, I advantageously prepare my bleaching liquor by introducing chlorin, or a solution of chlorin, into a continuously flowing current of water passing through a tower or other suitable mixing or absorption device. This current of water may contain or may have added to it, either before or after the chlorin is added, one of the strong bases of the kind above referred to which is capable of combining with HOCl, either in solution or in suspension, in amount suitably proportioned to the amount of chlorin supplied, that is, in amount sufficient to take up all or substantially all the HCl formed in the conversion of the chlorin, but not enough to react with any or substantially any of the HOCl. I may, for instance, add a solution of caustic soda in water or a suspension of lime in water. This liquid I introduce into the bleaching vessel either continuously as fast as it is formed, or in the event that it is stored, after only a short period of storage. In the present invention it is eminently desirable that the liquid be not allowed to stand for any length of time and that it be used at, or substantially at, the time of its formation. The liquid so introduced into the bleaching vessel may constitute the entire body of liquid in the bleaching vessel if of the desired dilution. Usually, however, I provide a stronger solution to be mingled with a larger amount of water in the bleaching vessel, the increased strength being that necessary to compensate for the amount of such water. Strong solutions containing free HOCl are unstable. The bleaching liquor made as described is substantially a solution of neutral chlorids and free hypochlorous acid; there being substantially no free HCl and no combined HOCl. Ordinarily I use in the bleaching operation a liquid having about 0.01 to 0.1 per cent. HOCl. For some classes of materials, solutions somewhat stronger may be used and for other classes, solutions which are somewhat weaker, but in any case of great dilution.

Any convenient source of chlorin may be employed such as an electrolytic cell producing chlorin. I find it more convenient, however, to use the commercial liquid chlorin. By weighing a cylinder of chlorin, and allowing the chlorin to escape in a slow stream, the amount of chlorin used may be readily controlled by observing this diminution in weight of the cylinder, or the flow of chlorin gas may be readily metered by suitable means. Either affords a very convenient way of securing the desired measured and controlled supply of chlorin and the desired accurate proportioning between the amount of alkali and the amount of chlorin.

The bleaching liquor made as just described, if produced with an amount of one of the stronger base, such as caustic soda or lime, equivalent to one HCl for each Cl_2 introduced is initially neutral (as regards HCl); but in use in bleaching it develops what may be termed secondary HCl; that is, HOCl loses O in bleaching the goods and HCl remains. This secondary HCl may be neutralized in the same manner as the primary HCl produced in making the bleaching liquor; that is by regulated additions of one of these strong bases to the

bleaching liquor; the addition of such base being continuous and as near as possible at the rate at which the secondary HCl tends to develop. This neutralization of the secondary HCl in the bleaching vessel is not always necessary but in many cases it is highly advantageous. In some cases, however, it is better not to neutralize the secondary HCl.

In neutralizing the secondary HCl in the bleaching vessel, it is sometimes more convenient to employ bases or bodies which do not react with HOCl, such as sodium bicarbonate, calcium carbonate (chalk), zinc carbonate, zinc oxid, alumina, barium carbonate, magnesium carbonate, strontium carbonate, etc. Such bases are convenient to use because they may be used in excess, and the presence of an excess of such bases is not harmful in some cases and may even be desirable.

In the method of operation just described, where the secondary HCl is neutralized, it will be noted that addition of base is in two stages, the primary HCl being first neutralized by one addition and then the secondary by another. A more convenient method of operation, at least in many cases, and one involving but one addition of a measured amount of base is afforded by using a soluble basic body of such a nature that it will itself automatically, so to speak, perform the neutralization in the desired two stages; by using a basic body which will first neutralize the primary HCl without also combining with the HOCl and will then neutralize the secondary HCl as it develops. The alkali carbonates are soluble basic bodies which may be so used.

When an alkali carbonate in solution in water is treated with chlorin in suitable proportion free HOCl, a bicarbonate and a neutral chlorid are formed, the primary HCl formed in the hydrolysis of the chlorin taking away half the alkali of the carbonate and converting it into a bicarbonate. The bicarbonates do not neutralize HOCl although they are decomposed by HCl. As the bleaching with such a liquor progresses, the secondary HCl formed from the HOCl is taken care of by the bicarbonate.

In employing sodium carbonate or potassium carbonate, I use the carbonate in the proportion of one molecule for each molecule of chlorin (Cl_2). This is for the reason that one Cl_2 produces one HCl and one HOCl, and the reaction of one HCl with one molecule of normal alkali carbonate converts the latter into alkali bicarbonate; a substance which is not affected by HOCl.

For example, to the chlorin and water in the reaction chamber or tower previously described, there may be added a solution of sodium carbonate in the stated ratio of molecule for molecule. The sodium carbonate neutralizes the primary hydrochloric acid with the formation of sodium bicarbonate and NaCl. The bleaching liquor at this stage is an aqueous solution of the equivalent amounts of HOCl, NaCl and sodium bicarbonate, and this amount of sodium bicarbonate is the amount necessary to take care of the secondary HCl developed in the bleaching vessel. In operating with this bleaching liquor the ultimate product is a harmless solution of common salt, NaCl.

Any amount of the alkali carbonate not less than half the molecular equivalent of the chlorin will serve to neutralize the HCl produced from the chlorin, that is, the primary HCl, and an amount greater than this but less than the molecular equivalent of the chlorin will result in all the primary HCl and a part of the secondary HCl being neutralized. With such a base, therefore, removal of all the HCl resulting from the hydrolysis of the chlorin, and the complete conversion of all the chlorin and disappearance of chlorin as such, without any of the HOCl being neutralized, may be secured without the necessity of exact proportioning of the amount of base to the amount of chlorin. In such case, any unneutralized HCl may be neutralized, if desired, by supplying to the bleaching solution a suitable base which will not combine with HOCl.

Basic material which is capable of reacting with HOCl, and which requires to be supplied in amounts only sufficient to neutralize the HCl in the solution, need not necessarily be supplied to a flowing current of water into which the chlorin is introduced. The full amount of such a base required may, for example, be supplied all at once to a body of water into which the full amount of chlorin has already been introduced, or it may be supplied gradually concurrently with gradually introduced chlorin to a body of water which may or may not contain at the time the material to be bleached.

What is claimed is:

1. The process of bleaching, which comprises mingling chlorin and water in the presence of a basic material capable of reacting with both HCl and HOCl, the amount of such basic body being merely that reacting with the HCl produced in the hydrolysis of such chlorin and the amount of water being sufficient to give a solution of great dilution, and submitting the material to be bleached to the action of the bleaching liquor so produced at the time, or substantially at the time, of the production thereof.

2. The process of bleaching, which comprises mingling chlorin and water in the presence of such an amount of a normal alkali carbonate as will merely suffice to

react with the HCl produced in the hydrolysis of such chlorin and to form a neutral chlorid and alkali bicarbonate without also acting upon the HOCl also produced in such hydrolysis, the amount of water being sufficient to give a solution of great dilution, and submitting the material to be bleached to the action of the bleaching liquor so produced at the time, or substantially at the time, of the production thereof.

3. The process of bleaching, which comprises mingling chlorin and water in the presence of such an amount of normal sodium carbonate as will merely suffice to react with the HCl produced in the hydrolysis of such chlorin and to form a neutral chlorid and sodium bicarbonate without also acting upon the HOCl also produced in such hydrolysis the amount of water being sufficient to give a solution of great dilution, and submitting the material to be bleached to the action of the bleaching liquor so produced at the time, or substantially at the time, of the production thereof.

4. The process of bleaching, which comprises producing a flowing current of water, mingling with such current proportioned amounts of chlorin and of a soluble basic body, the relative amount of such basic body being merely that which will suffice to react with the HCl produced in the hydrolysis of the chlorin without its reacting with the HOCl, and contacting the bleaching liquor produced with the material to be bleached.

5. The process of bleaching, which comprises mingling chlorin and water in the presence of an alkali carbonate, the equivalent of one molecule of such alkali carbonate being used for each molecule of chlorin, Cl_2, employed, and submitting the material to be bleached to the action of the bleaching liquor so produced at the time, or substantially at the time, of the production thereof.

6. The process of bleaching, which comprises mingling chlorin and water in the presence of sodium carbonate, the equivalent of one molecule of such sodium carbonate being used for each molecule of chlorin, Cl_2, employed, and submitting the material to be bleached to the action of the bleaching liquor so produced at the time, or substantially at the time, of the production thereof.

7. The process of bleaching, which comprises supplying a measured flow of chlorin to a flowing current of water, and continuously supplying the solution so produced to a body of water containing the material to be bleached, the conditions of formation of such solutions being such as to cause a substantially complete disappearance of the chlorin as such in the solution.

8. The process of bleaching, which comprises producing a solution of HOCl by introducing a measured flow of chlorin into a flowing current of water and causing substantially complete conversion of the chlorin by supplying sufficient basic material to take up substantially all the HCl formed in the solution without combining with substantially any of the HOCl, and continuously supplying the solution so produced to a body of water containing the material to be bleached.

9. The process of bleaching, which comprises mingling chlorin and water in the presence of an alkali carbonate, the amount of such alkali carbonate employed being not more than the equivalent of one molecule of the alkali carbonate for each molecule of chlorin, Cl_2, and submitting the material to be bleached to the action of the bleaching liquor so produced at the time, or substantially at the time, of the production thereof.

10. The process of bleaching, which comprises mingling chlorin and water in the presence of an alkali carbonate, the chlorin and the alkali carbonate being supplied continuingly and in proportionate amounts and the amount of the alkali carbonate supplied being not more than the equivalent of one molecule of the alkali carbonate for each molecule of chlorin, Cl_2, and submitting the material to be bleached to the action of the bleaching liquor so produced at the time or substantially at the time of the production thereof.

11. The process of bleaching, which comprises supplying measured and proportionate amounts of chlorin and of alkali carbonate continuingly to a stream of water, and passing said stream into contact with the goods to be bleached.

12. The process of bleaching, which comprises supplying a measured amount of chlorin continuingly to a stream of water, and passing said stream into contact with the goods to be bleached.

13. The process of bleaching, which comprises supplying a measured flow of gaseous chlorin continuingly to a stream of water, supplying base to take up HCl, and passing the stream of HOCl solution thus produced into contact with the goods to be bleached.

14. The process of bleaching, which comprises bringing together continuingly quantitatively regulated amounts of chlorin and quantitatively regulated amounts of absorbing liquor, maintaining the proportionate amount of the latter such that all the chlorin as such disappears and substantially all of the HOCl formed remains in the free state, and subjecting the material to be bleached to the action of the liquor so produced.

15. The process of bleaching, which comprises bringing together continuingly quantitatively regulated amounts of chlorin and quantitatively regulated amounts of absorbing liquor, maintaining the proportionate

amount of the latter such that all the chlorin as such disappears and substantially all of the HOCl formed remains in the free state, and supplying the liquor so produced to a body of water containing the material to be bleached.

16. The process of bleaching, which comprises bringing together continuingly quantitatively regulated amounts of chlorin and quantitatively regulated amounts of absorbing liquor containing a base which will combine with HOCl, maintaining the proportionate amount of the absorbing liquor such that all the chlorin as such disappears and substantially all the HCl formed is neutralized and substantially all of the HOCl formed remains in the free state, and subjecting the material to be bleached to the action of the liquor so produced.

17. The process of bleaching, which comprises supplying quantitatively regulated amounts of chlorin continuingly to absorbing liquor containing base, and withdrawing the solution so produced and subjecting the material to be bleached to the action thereof at the time, or substantially at the time, of the production thereof.

18. The process of bleaching, which comprises producing a bleaching liquor containing free HOCl and neutral chlorid by introducing into water continuingly proportionate amounts of chlorin and of a base capable of reacting with both HCl and HOCl, and subjecting the material to be bleached to the action of the bleaching liquor so produced.

19. The process of bleaching, which comprises producing a bleaching liquor containing free HOCl and neutral chlorid by introducing into water continuingly proportionate amounts of chlorin and of a base capable of reacting with both HCl and HOCl, withdrawing continuingly the liquor so produced and supplying it to a bleaching bath containing the material to be bleached.

20. The process of bleaching, which comprises continuingly bringing together quantitatively regulated amounts of chlorin and quantitatively regulated amounts of absorbing liquor proportioned to result in the substantially immediate disappearance of the chlorin as such with formation of HOCl and the production of a liquor containing in the free state all the HOCl so formed, maintaining the dilution of the liquor so produced so great that under the existing conditions of alkalinity, plus or minus, it shall be substantially stable, and subjecting the material to be bleached to the action of the liquor so produced.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

GEORG ORNSTEIN.

Witnesses:
G. W. M. Rhodes,
A. L. Kent.