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BLEACHING PROCESS.

1,298,553.

Specification of Letters Patent.

Patented Mar. 25, 1919.

No Drawing.

Application filed December 2, 1916, Serial No. 134,748.

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 Bleaching Processes, 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., by the aid of chlorin, wherein bleaching is effected by a bleaching liquor initially composed of a solution of neutral chlorids and free HOCl; as in a method of bleaching wherein chlorin is brought into solution in water in the presence of sufficient base to convert all or substantially all the HCl formed into a neutral chlorid while leaving the HOCl formed unaffected, the amount of water employed being sufficient to insure that the bleaching solution so formed shall be dilute enough to be non-corrosive to the fiber or material to be bleached, such great dilution being usually of the order of magnitude of a tenth per cent. or so of HOCl, and such solution or bleaching liquor being formed in contact with the goods to be bleached or being produced immediately prior to contacting it with such goods, and the base employed being either one which will not combine with HOCl at all, in which event the amount may be relatively large, or being one which will combine with HOCl as well as with HCl, in which event only the amount necessary to neutralize the HCl is employed; and it further comprises a method of bleaching wherein such a bleaching liquor containing initially no free HCl is kept free of HCl formed from the reduction of the HOCl during the progress of the bleaching by the presence or addition of a base adapted to combine with such HCl as fast as formed; all as more fully hereinafter set forth and as claimed.

Chlorin has been used in bleaching for a very long time. The direct introduction of free chlorin into the bleaching solution was, however, quickly abandoned in favor of various bleaching agents made with its aid; i. e. it was converted into something else and the other thing then used, such other

thing being ordinary bleaching powder or something analogous. Chlorin as such is used only when some other action than bleaching is also desired, as in removing incrusting material from fiber. Chlorin exercises an energetic action upon nearly all organic matters, the action being sometimes a combination of the chlorin with the organic matters (chlorination) and sometimes a more or less far going attack. The bleacher wants a destruction of the relatively sensitive organic substances which constitute coloring matters associated with the fiber, but he does not want any attack on the relatively less sensitive organic substances of the fiber itself; the fiber must not be attacked or weakened. This fact and the difficulty of controlling the action of chlorin led to its abandonment in favor of the use of bleaching powder whose action was milder and more certain.

This interposition of a separate manufacturing step, the production of bleaching powder, between the production of chlorin and the bleaching operation, inevitably however adds to the cost of bleaching; and the more so since for certain reasons pointed out hereinafter, there is a marked loss in bleaching efficiency due to the intermediate step.

In the manufacture of bleaching preparations, the chlorin in the presence of moisture and a sufficient amount of caustic alkali such as lime forms a hypochlorite and a chlorid; calcium chlorid, CaCl_2 , and calcium hypochlorite $\text{Ca}(\text{ClO})_2$, for example. Bleaching powder is in substance a mixture of these two compounds with an excess of lime. Some lime in excess is necessary to insure combination of all the hypochlorous acid and stability of the product. Any free hypochlorous acid in contact with a hypochlorite leads to production of chlorates, which have no bleaching power. The formation of more or less chlorates is however inevitable in the making of bleaching powder, since even with an excess of lime present, there may be local over-concentration of chlorin, producing free hypochlorous acid, or the lime may be somewhat carbonated. Hypochlorous acid does not decompose carbonate of lime nor react with it.

In use, the efficacy of bleaching powder depends upon a liberation of hypochlorous acid in some manner, the latter having ma-

terially stronger bleaching action than neutral hypochlorites. Liberation of hypochlorous acid, however, from a hypochlorite involves a new reaction to be effected, and
 5 to develop the hypochlorous acid in this way in a slow, uniform and progressive manner is difficult.

In the present invention I have substituted for the methods of the older art an
 10 operation in which while the bleaching is substantially effected by hypochlorous acid the intermediate formation of neutral hypochlorites and the reliberation of hypochlorous acid are avoided; the operation from a
 15 practical point of view, however, being the use of chlorin itself. In order to do this I produce the bleaching solution by introducing the chlorin into sufficient water and supplying also material capable of combining
 20 with hydrochloric acid, this material, for many purposes, being most desirably one which will not combine or react with hypochlorous acid. The chlorin may be added to the water containing the material to be
 25 bleached so that the HOCl is produced in the actual physical presence of the material, and it may be added as a gas or in the form of a strong water solution, such as may be obtained by contacting chlorin with water
 30 in an ordinary tower device. Addition of chlorin or solution may be continuous or intermittent; and any suitable type of bleaching apparatus may be used. The addition of base may be continuous or intermittent; or
 35 if the base is one which will not combine with HOCl all that may be necessary in the operation may be supplied at one time prior to the beginning of the bleaching.

Chlorin when brought into contact with
 40 water forms, to some extent, a direct solution of the gas ("chlorin water"), and to some extent it reacts with the water to form hydrochloric acid and hypochlorous acid in the sense of the following reversible or equilibrium reaction:



In the presence of sufficient water, the reaction will go entirely to the right, the chlorin
 50 as such disappearing, being wholly hydrolyzed into hydrochloric and hypochlorous acids. With less water, other conditions being the same, the hydrolytic products tend to react on each other and limit the movement of the reaction to the right and more
 55 or less chlorin as such remains in the solution. With complete, or substantially complete, hydrolysis of chlorin resulting from the presence of sufficient water alone, bleaching liquids can be obtained which contain the
 60 two acid hydrolytic products and have high bleaching efficiency with substantially no corrosive action on the fiber. In another application, Serial No. 134,749, filed December 2,
 65 1916, I have described and claimed a process

of bleaching depending upon this fact and involving bleaching with the aid of the acid hydrolytic products of chlorin. In said other application, in the operation as described and
 as claimed broadly more or less of the HCl 70 may be neutralized by the use of bases; but specifically the bleaching is in a solution containing substantially all the HCl.

In the present invention, I modify this procedure to the extent of producing a sub-
 75 stantially complete neutralization of the HCl formed in the hydrolysis with substantially no neutralization of the HOCl. HOCl when neutralized loses much of its rapid bleaching action. With the formation of free HOCl
 80 comes of course the question of its stability, HOCl not being a very stable body and particularly in the presence of neutralized HOCl, that is to say, of hypochlorites. But
 85 where the HOCl, as in the present invention, is used in bleaching substantially as soon as it is formed, the bleaching action commences too quickly to permit the instability of the HOCl in the dilute solutions of
 90 the present invention to be of any importance; and under these conditions the reaction which leads to the formation of chlorates becomes of no practical importance, because it is a relatively slower reaction, and
 95 dependent usually on the formation of hypochlorites which is substantially or wholly avoided in my process.

Also, free chlorin may tend to decompose the hypochlorous acid to chlorate with loss
 of bleaching power. The rapid decomposition 100 of the HOCl is caused by heat, or free chlorin, or hypochlorite salts or by high concentration. When both HCl and HOCl in the free state are produced from Cl_2 and remain in solution, very great dilution is
 105 necessary to completely dissociate the Cl_2 and eliminate the destructive action of the Cl_2 on the HOCl. By neutralizing the HCl the hydrolysis of the Cl_2 is allowed to proceed without such very great dilution. Thus
 110 the upper limit of concentration is raised by this partial neutralization without producing too great instability. Even then, strong solutions are unstable. While, therefore, the
 115 neutralization of the HCl makes it possible to secure greater dissociation of the Cl_2 and therefore substantially stable solutions of much greater concentration than those contemplated in the process claimed specifically
 120 in the co-pending application above referred to, nevertheless, as indicated elsewhere herein, I prefer not to exceed a fraction of 1% of free hypochlorous acid in the bleaching solution.

While the theories as to the exact way in
 125 which HOCl effects bleaching are many and various, the net result of the action is that O disappears by combination with the coloring matters to be removed and HCl, or free
 130 hydrochloric acid, is left. In the ordinary

bleaching operation with bleaching powder a transitory formation of HCl is supposed to occur more or less continuously; as the HOCl is formed and decomposes it furnishes HCl

5 which sets free more HOCl. In operating according to the present invention, I may, and it is sometimes most desirable to, neutralize this HCl formed from the HOCl in the bleaching operation as well as the HCl
10 formed by the hydrolysis of the chlorin.

In one practical embodiment of this invention I charge the bleaching vessel with water, the goods to be bleached and a suitable quantity (which may be an excess) of material
15 capable of combining or reacting with HCl but not with HOCl, and then slowly introduce chlorin, either as gas from a chlorin generator or from the more convenient commercial tanks containing liquid chlorin.

20 Again I may preliminarily convert such chlorin in measured amounts into chlorin water solution and then add such solution. Addition of chlorin gas or solution may be progressive during the bleaching operation.

25 As the material to take up the HCl and which will not combine with HOCl, I may use sodium bicarbonate, potassium bicarbonate, borax, sodium phosphate, sodium sulfate, chalk, or limestone, zinc oxid or carbonate,
30 barium carbonate, strontium carbonate, etc. HOCl as a matter of fact, for practical purposes, does not react with any of the basic bodies save caustic soda, caustic potash, caustic lime, baryta, strontia, potassium carbonate and sodium carbonate.
35

Under the stated circumstances, the chlorin hydrolyzes with the water to form HCl and HOCl in the sense of the equation given ante. But as something is present to remove the
40 HCl as fast as formed, the reaction readily proceeds entirely to the right with the formation of HOCl. This HOCl exercises its bleaching action and gives more HCl which is also taken up by the basic bodies present.
45 The final result is a solution containing neutral chlorids and the excess of the base if soluble. If the basic body is insoluble, as with chalk (calcium carbonate), it remains undissolved and the exhausted bleaching liquid is
50 a neutral solution of chlorids.

Where bases capable of uniting with HOCl are used, as they may be, they should be used quantitatively in order to neutralize substantially all of the HCl without sub-
55 stantially neutralizing the HOCl, and it is best to add them in the required quantity progressively during the production of HCl. A slight temporary excess does no great harm since HCl as soon as formed will
60 break up any hypochlorites and reliberate the HOCl. And no time is afforded in the present operation for any substantial amount of action between the hypochlorous acid and the hypochlorites, that is, for the
65 formation of chlorates.

The use of a base capable of reacting with both HCl and HOCl is claimed specifically in my co-pending application, Serial No. 134,829, filed December 4, 1916.

The various bases and other materials 70 used for preventing the presence of HCl and which will not combine with HOCl may also, if desired, be added progressively during the operation, either intermittently or continuously. Portions of a suspension of cal- 75
cium carbonate in water may be, for example, added to the bleaching vessel from time to time or as a slow stream. A sodium bicarbonate solution may be added in the same way. 80

The rate of introduction of the chlorin depends upon the speed with which bleaching can be effected; but I ordinarily manage it so as not to have at any one time a concentration of over, say, a tenth per cent. or 85
so free HOCl in the bleaching liquor as used.

In the operation which has been particularly described, it will be noted that in substance chlorin is used directly for bleaching, being directly introduced into the bleaching 90
apparatus, though the actual bleaching is due to hypochlorous acid. The bleaching is done in a solution which is substantially neutral; neutral, that is, as regards any acidity due to HCl. Where sodium sulfate 95
or sodium phosphate are used the solution may become somewhat acid due to the formation of sodium bisulfate or monosodium phosphate but the presence of HCl is nevertheless obviated, and the solution is there- 100
fore not acid in that sense. HOCl itself is so weak an acid that its acidity may be disregarded.

In the present invention, where I am bleaching with HOCl produced directly 105
from chlorin, I find that in addition to a great certainty and safety of operation I am enabled to effect notable economy over the ordinary process in which the chlorin is first converted into bleaching powder or other 110
hypochlorites and then this bleaching powder used. In bleaching paper pulp, for example, I achieve important economies which at times have amounted to as much as 30
per cent. less chlorin when using it direct as 115
compared with using chlorin in the round-about way, via bleaching powder, of the usual art.

In addition to the economy over the usual process offered by doing away with decom- 120
position of HOCl to form products without bleaching power, the present operation affords the economy due to exact work. For with the contemplated slow and regular but direct introduction of chlorin the possibility 125
of exact measurement of quantities is given. A commercial cylinder of liquid chlorin may for instance be weighed and a slow stream of gas allowed to escape through a suitable reducing valve, the operation being discon- 130

continued as soon as the cylinder shows the calculated loss in weight; or the flow of gas may be through a suitable meter. When using a solution of chlorin, a flow of water through a tower may govern, through suitable mechanism, a reducing valve on such a cylinder so as to give proportioned amounts of chlorin and water in the absorption tower thereby producing chlorin solutions of known strength which may be conveniently used in the present operation.

While I have hereinbefore described an embodiment of the invention where the HOCl is produced directly in the presence of the goods to be bleached, the chlorin, either as a gas or a solution, being directly introduced in the vessel, the HOCl being developed and the HCl being neutralized therein, yet of course so long as no substantial time is afforded for the decomposition of the HOCl, it may be formed at a point more or less remote from the goods; that is, it is not necessary in my invention, in its broader aspect, to produce the HOCl in the actual physical presence of the goods. It is sufficient if it be brought into contact with the goods substantially as rapidly as it is formed and without delay, most desirably flowing from the point of production to the point of use as fast as it is made without delays for storage, etc. I may make a weak solution of a strength safe for the goods to be treated and deliver this weak solution directly to such goods. I may, for example, develop it in another vessel connected to the bleaching vessel, producing an active circulation of liquid between the two vessels. This method offers a certain amount of convenience. But, since the exhausted bleaching liquor, that is the liquor after the disappearance of HOCl, is not of value, I may do the whole operation in a flowing current of liquid passing into and through the bleaching vessel, bleaching the goods as it goes and using up the HOCl it contains. In so doing it is often convenient to develop the free HOCl outside the bleaching vessel itself. For example, a weighed or measured amount of chlorin may be led into a tower in continuous manner and there contacted with a proportioned flow of water, the mixture so formed flowing over, say, pieces of limestone or chalk and flowing thence directly to the bleaching vessel. In so doing, while the HOCl is not developed in the bleaching vessel, yet the utilization after the formation is so quick that, for the present purposes, it is much the same thing. In so using a flowing current of liquid containing HOCl and introducing it into the bleaching vessel, it may be allowed to accumulate therein until the full amount necessary is obtained.

In using this flowing current method of producing the bleaching liquor it is not

necessary to use an insoluble base in a tower in the way described, for, obviously, the same result, for the present purposes, can be attained by adding any other substance capable of reacting with HCl. For example, the current of water which is brought into contact with the chlorin may contain a sufficient amount of sodium bicarbonate dissolved therein. Or milk of lime, or any other insoluble or soluble base, may be added to the current and allowed to react with the HCl. Here, as before, it is only necessary to use such precautions as to neutralize the HOCl while leaving the HOCl unaffected. In the present invention it is sought to bleach in the presence of free HOCl in solution in the substantial absence of chlorin either as such or as HCl.

When using this flowing current method wherein HOCl is made outside the bleaching vessel proper but immediately introduced therein, there is the question of the disposal of the HCl formed from the HOCl in the bleaching operation. Where an insoluble base or basic material, such as limestone, is used in the tower, it is ordinarily desirable to have further base in the bleaching vessel proper. And the same is true where insoluble basic bodies are added to or contacted with a flowing current in other ways outside the bleaching vessel, unless they be suspended in the liquid. Where the basic body is one which is soluble in water but not capable of reacting with HOCl, the full amount may be added in the flowing current. An excess of sodium bicarbonate passes forward with the HOCl and reacts with the secondary HCl during the bleaching. Where a soluble base capable of reacting with both HCl and HOCl is added in the flowing current method outside the bleaching vessel, obviously only enough must be added to combine with the HCl formed during the formation of the bleaching liquor. In this event, a subsequent addition of base in the bleaching vessel may be made, such base being supplied concomitantly to the development of the secondary HCl therein if it is one which will combine with HOCl.

In this flowing current method of developing HOCl, instead of using gaseous chlorin for contacting with the current of water, I may of course use a solution of chlorin made elsewhere. That is, I may make, for instance, a saturated solution of chlorin in water by passing chlorin gas through a tower in countercurrent to water and then use this saturated solution for mingling with more water to form the HOCl solution.

This flowing current method of forming the bleaching liquor, and, more broadly, the method involving a continuous or continuing supply of regulated amounts of chlorin, which may be carried out in this flowing

current way, is claimed specifically in my co-pending application Serial No. 134,829, filed December 4, 1916.

Where the solution is made before the beginning of the bleaching operation, the bleaching solution is, as regards HCl, initially neutral. This initially neutral liquid from which the primary HCl formed in the hydrolysis of chlorin has been removed, when introduced into the bleaching vessel may become progressively acid, due to the conversion of HOCl into HCl. The secondary acidity may be obviated by addition of basic material, or it may be neglected. Where the amount of water in the bleaching liquor is quite great, and in the case of many materials to be bleached, the presence of HCl is unimportant and may be even advantageous. Both methods of operation, that is, where the secondary acidity is neutralized and where it is not, have their advantages in special relation and both are within the purview of the present invention.

In the case of material containing some alkali, as is frequently the case with alkali treated goods, such as soda rag pulp, the alkali so contained must of course be allowed for in calculating the total amount of base to be used in the present invention. And in the event that the goods are too alkaline to permit development of free HOCl in the manner contemplated in the present invention, it is sometimes advisable to neutralize all or a portion of such alkali with a suitable acid prior to the beginning of the bleaching operation proper.

The term "basic material" as used in the claims is to be understood as including all substances or materials which will react with free HCl to produce a chlorid, and where I have in the claims indicated the introduction of chlorin I mean to imply that it may be introduced either as a gas or as a solution.

What is claimed is:—

1. The process of bleaching, which comprises producing a solution of HOCl by introducing chlorin into water and causing substantially complete conversion of the chlorin by supplying sufficient basic material to take up substantially all the HCl formed by hydrolysis in the solution, the amount of water employed in making such solution being sufficient to give a solution of great dilution, and submitting the material to be bleached to the action of such solution at the time or substantially at the time of the production of the HOCl.

2. The process of bleaching, which comprises producing a solution of HOCl by introducing chlorin into 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, the amount of water employed in making such solution being suffi-

cient to give a solution of great dilution, and submitting the material to be bleached to the action of such solution at the time or substantially at the time of the production of the HOCl, basic material being present during such bleaching action to take up HCl formed by the reduction of HOCl incident to bleaching.

3. The process of bleaching, which comprises producing a solution of HOCl by introducing chlorin into water and causing substantially complete conversion of the chlorin by employing sufficient water to give a solution of great dilution and supplying sufficient basic material to take up all the HCl formed by the conversion of chlorin and in the bleaching operation, such material being one which will combine with HCl but not with HOCl, and submitting the material to be bleached to the action of such solution at the time or substantially at the time of the production of the HOCl.

4. The process of bleaching, which comprises producing a solution of HOCl by introducing chlorin into 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, the amount of water employed in making such solution being sufficient to give a solution of great dilution, and submitting the material to be bleached to the action of such solution at the time or substantially at the time of the production of the HOCl, part or all of the HOCl being formed in the bleaching vessel.

5. The process of bleaching, which comprises forming free HOCl in an aqueous medium with the aid of chlorin and a basic material, and in the presence of sufficient water to give a solution of great dilution, and submitting the material to be bleached to the action of such solution at the time or substantially at the time of the development of the HOCl.

6. The process of bleaching, which comprises introducing chlorin into water in the bleaching vessel in the presence of sufficient basic material to take up substantially all the HCl formed in the hydrolysis of such chlorin and in the bleaching operation without uniting with substantially any of the HOCl formed in such hydrolysis, and maintaining the concentration and rate of introduction of chlorin such that the bleaching solution will be substantially stable.

7. The process of bleaching, which comprises introducing chlorin into water in the bleaching vessel in the presence of sufficient basic material to take up substantially all the HCl formed in the hydrolysis of such chlorin and in the bleaching operation, such material being one which will not re-act with HOCl, and maintaining the concentration and rate of introduction of chlorin

such that the bleaching solution will be substantially stable.

8. The process of bleaching, which comprises introducing chlorin into water in the bleaching vessel, the introduction of the chlorin being a gradual introduction and continuing during at least a part of the bleaching operation, and supplying basic material to the water to take up substantially all the HCl formed in the hydrolysis of the chlorin and in the bleaching operation.

9. The process of bleaching, which comprises introducing chlorin into water in the bleaching vessel, the introduction of the chlorin being a gradual introduction and continuing during at least a part of the bleaching operation, the water containing sufficient basic material which will combine with HCl but not with HOCl to take up all the HCl formed in the hydrolysis of the chlorin and in the bleaching operation.

10. The process of bleaching which comprises supplying a measured flow of chlorin to water under conditions which result in the substantially immediate formation of HOCl and disappearance of chlorin as such, producing a solution containing in the free state all the HOCl so formed, basic material being supplied to the water to take up at least a part of the HCl formed in the solution, and subjecting the material to be bleached to the action of the solution so produced, the introduction of chlorin being a gradual introduction and continuing during at least a part of the bleaching operation.

11. The process of bleaching, which comprises producing HOCl and HCl directly from Cl_2 in the presence of sufficient water to give a solution containing not more than a tenth per cent. or so of HOCl, neutralizing the HCl only, and bleaching fiber with the solution of HOCl formed.

12. The process of bleaching, which comprises producing HOCl and HCl directly

from Cl_2 in the presence of sufficient water to give a solution containing not more than a tenth per cent. or so of HOCl, neutralizing the HCl only, and bleaching fiber with the solution of HOCl formed, HCl formed from the HOCl in bleaching being also neutralized.

13. The process of bleaching, which comprises subjecting the material to be bleached to the action of a dilute and substantially stable bleaching liquor containing free HOCl and sufficient base which will not combine with HOCl to substantially neutralize the HCl produced during the bleaching operation.

14. The process of bleaching, which comprises subjecting the material to be bleached to the action of a dilute and substantially stable bleaching liquor containing free HOCl and a base adapted to neutralize HCl but which will not unite with HOCl.

15. A bleaching solution produced directly from chlorin and containing HOCl and a base adapted to neutralize HCl but which will not unite with HOCl, the solution being initially without unneutralized HCl and containing substantially all the chlorin in the form of free HOCl and neutral chlorid.

16. A bleaching solution produced directly from chlorin which contains HOCl and neutral chlorid and a base adapted to neutralize HCl but which will not unite with HOCl, the solution being initially without unneutralized HCl and containing substantially all the chlorin in the form of free HOCl and neutral chlorid.

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

GEORG ORNSTEIN.

Witnesses:

A. L. KENT,

PAUL H. FRANKE.

Copies of this patent may be obtained for five cents each, by addressing the "Commissioner of Patents, Washington, D. C."