

UNITED STATES PATENT OFFICE

LINN BRADLEY, OF MONTCLAIR, NEW JERSEY, AND EDWARD P. McKEEFE, OF PLATTSBURG, NEW YORK, ASSIGNORS TO BRADLEY-McKEEFE CORPORATION, OF NEW YORK, N. Y., A CORPORATION OF NEW YORK

BLEACHING

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This invention relates to improvements in the bleaching and oxidation of fibres and fabrics or other materials especially cellulose from wood used in the manufacture of pulp and paper products, of paper pulp, etc., in a simple advantageous manner.

In the common methods of bleaching pulp with chlorine or chlorine compounds such as bleaching powder, the chlorine tends to injure or weaken it. So also, woodpulp bleached with chlorine compounds frequently has a natural wood tint, rendering it inferior for the better qualities of product, and its ash content may be greatly increased by the bleaching operation, particularly when bleaching powder is used.

According to the present invention, we avoid the usual objections to bleaching with chlorine compounds, and we produce a snow-white cellulose product, low in ash, and of good strength, thus making it suitable for many purposes for which cellulose bleached by former methods has been found unsatisfactory.

According to the present invention we carry out the bleaching operation with a manganate or permanganate. When a solution of a manganate or permanganate is added to the material to be bleached or oxidized, not only does the manganate or permanganate exert an oxidizing action on the bleachable or oxidizable constituents of the material, but these constituents exert a reducing action which results in the precipitation of a compound or compounds of manganese, so that the material is given a brown color. This production of compounds of manganese takes place not only when the manganate or permanganate is alkaline, but even when sufficient acid is added to give an acid reaction, provided a sufficiently large excess of acid is not used and the material is not heated to a high temperature or allowed to stand a prolonged time with a small amount of acid. The compounds of manganese which are thus precipitated are to a considerable extent deposited directly on the fibres, and this production of the compounds of manganese appears to take place coincidentally with the action of the manganate or

permanganate upon the materials associated with the fibres; although the formation of compounds of manganese may take place in the solution, where the solution contains oxidizable constituents.

After the treatment of the material to be bleached with the manganate or permanganate (if a sufficiently large excess of acid and high temperatures have not been used or the mix allowed to stand for a long time while slightly acid) the material is, as above stated, of a brown color. It is now treated to dissolve away or remove the manganese compounds, preferably by the addition of a sufficient amount of sulfur dioxide or a solution of sulfur dioxide, or of a bi-sulfite, or a sulfite and an acid, or any other suitable reagent. When sulfur dioxide or other suitable reagent is added to the material to be treated, the brown color disappears almost instantly and the material is left white. The manganese compounds are rendered soluble and thus can be washed free from the bleached material if desired.

We have found that manganates can be successfully used for the bleaching process of the present invention by using an amount larger than when permanganates are used and we include the use of manganates as well as permanganates. However, their bleaching effect is less efficient than that of permanganates; and we regard the use of permanganates as more advantageous. The permanganates can be produced from the manganates by oxidation with suitable agents; and this production of permanganates and their subsequent use according to the present invention can advantageously be combined. For example, sodium manganate, admixed with an excess of alkali, may be treated with chlorine to oxidize the sodium manganate to sodium permanganate and to form sodium hypochlorite with the excess alkali; and the resulting mixture can then be utilized as a composite bleaching or oxidizing agent, as hereinafter more fully described.

The permanganates which we consider as particularly advantageous are sodium permanganate and alkaline earth metal per-

manganates; e. g. calcium permanganate. Potassium permanganate has a limited solubility, as compared with sodium or calcium permanganate, and we have found that its solution is more stable, so that in many instances it is less advantageous for use as a bleaching agent. With sodium permanganate, to explain, stronger solutions can readily be prepared and only a relatively small amount of the solution need be added to the material to be bleached to obtain the desired bleaching effect. Strong solutions can similarly be prepared in the case of calcium permanganate or barium permanganate.

While the permanganates can be used in an alkaline solution, we have found that it is more advantageous to use them in conjunction with acid, while avoiding any large excess of the acid. We have found it advantageous to use a sufficient amount of acid to combine with any alkaline compound produced during the action of the permanganates, as we have found that permanganates are more efficient and render a quicker bleaching action when acid is used than where the solution remains alkaline, although with some materials we have found it desirable to use a neutral or an alkaline liquor.

Instead of adding the manganate or permanganate and the acid together to the material to be bleached, we find it better to add these agents separately and to bring about thorough dissemination of one in the material to be bleached by suitable agitation before the other agent is added; for example, to add the manganate or permanganate to the material and thoroughly mix it therewith before adding the acid and distributing it in the mixture. In this way, a more uniform bleaching action is assured.

When manganates or permanganates are used in conjunction with acid, the bleaching operation takes place readily at ordinary temperatures, i. e., from 5° to 40° C. For example, we have obtained good results at a temperature of about 30°C. by permitting a solution of sodium permanganate to act upon unbleached wood cellulose in the form of a pulp, for a period of about 20 minutes and using an amount of sodium permanganate equivalent to about 3% of the stock (figured on air-dry basis, i. e. containing about 10% moisture).

We have found that the bleaching action of manganates or permanganates upon the material can be accelerated by increasing the temperature of the material within a limited degree, by more intense agitation, or by reducing the pressure by vacuum or other means within a limited degree, and this is desirable for the purpose of control in bleaching certain materials, particularly where acid is not added. When a small quantity of acid is added, the operation can similarly be ac-

celerated by heating, for example, 30° C., up to boiling, but it is one advantage of the process, when acid is employed, that the process can be carried out quickly even at ordinary temperatures as stated and without heating, or with but moderate heating, thus reducing the liability of injuring the materials so treated, which prevails in other processes. The use of a suitable amount of acid in our process accordingly produces economy in the heat, and reduces the time required for bleaching the materials, and the materials bleached in this manner are otherwise benefited by utilizing acid in the operation.

By adding to the pulp or other fibrous material, etc., a manganate or permanganate of an alkaline earth metal forming an insoluble sulfate, and then adding sulfuric acid or a bisulfate, the sulfate radical will react with the alkaline earth metal to precipitate the alkaline earth metal sulfate. For example, by adding a solution of calcium manganate or permanganate and distributing it throughout the pulp or other material, and then adding sulfuric acid or a solution of a bisulfate, and agitating or circulating the mixture to bring about uniformity of distribution and action, calcium sulfate will be formed and precipitated, at the same time that the bleaching action of the manganate or permanganate, or of the manganic or permanganic acid produced therefrom, takes place. The calcium sulfate (or other alkaline earth metal sulfate, such as barium or strontium sulfate, in case barium or strontium manganate or permanganate is employed) will thus be formed in most intimate admixture with the pulp or other materials and it can advantageously be left, in part or in whole, with the pulp or other material as a filling material. Owing to its intimacy of admixture, due to its method of formation, it is retained by the pulp better than when separately produced calcium sulfate or other filling material is separately added. By proceeding in the manner described, the incorporation of the filling material can advantageously be combined with the bleaching operation, and the combined operations carried out as a part of the same process.

The bleaching of the materials can be carried out in common forms of bleaching equipment, which are usually equipped with means for agitation or circulation as required. The manganate or permanganate can advantageously be prepared in the form of a strong stock solution and added in predetermined amounts to the material to be bleached, either before or after a suitable addition of an acid such as hydrochloric or sulfuric acid. When adding a strong solution of manganate or permanganate to the material to be bleached, we find it ad-

vantageous to sprinkle or spray the solution into the stock while the latter is being circulated or agitated, thus avoiding the presence of a large excess of the bleach liquor in contact with any one portion of the material to be bleached and minimizing the possibility of the local production of oxycellulose.

After the manganate or permanganate has acted upon the material the material can then be directly treated with sulfur dioxide or solution of sulphurous acid, a bi-sulfite, or a sulfite and acid, or it can be separated from its accompanying liquor to a greater or less extent before the sulfurous treatment, for example, by washing the material in the bleacher so that a fair portion of the original liquor is replaced by water, and by adding sulfurous material after such washing operation.

Instead of adding the manganate or permanganate all at one time in sufficient amount for the extent of bleaching that may be desired, an economy in the amount of manganate or permanganate required can be effected by carrying out the bleaching in stages, that is, by adding part of the manganate or permanganate and permitting it to act upon the material preferably in the presence of a small amount of acid, then removing soluble oxidizable compounds resulting from this partial bleaching operation, by dewatering or otherwise, then adding a further amount of manganate or permanganate, etc. followed by additional similar treatments if desired for obtaining the desired bleaching result. When only a small amount of manganate or permanganate is used in this way, there appear to be produced compounds which are water-soluble and colorless and some of which are not fully oxidized, and these compounds can be removed from the material by the washing or dewatering operation or otherwise so that they will not be present to consume further amounts of manganate or permanganate.

The amount of sulfur dioxide or other sulphurous material required for converting the brown material produced by the action of the manganates or permanganates may vary somewhat with the amount of manganates or permanganates used. Ordinarily only a small amount is required to form soluble manganese compounds and bring the material to a white color, but sufficient should be used to insure dissolving all the manganese compounds.

We have found that sodium manganate or permanganate and certain of the alkaline earth metal permanganates (calcium and barium permanganates) are less stable than potassium manganate and permanganate respectively, and when used for bleaching or oxidizing give up oxygen more readily, and

we have found that these manganates and permanganates nevertheless, will readily bleach without unduly injuring the materials.

Instead of a permanganate and acid, permanganic acid may be used. It can be obtained for example, by treating a solution of calcium or barium or strontium permanganate with a solution of sulfuric acid, then separating the precipitated calcium, barium or strontium sulfate from the solution; and the resulting solution can then be added to the material to be bleached. In this case little or no salts will be added to the material and no additional acid is required to be added therewith.

When bleaching pulp which is to remain in the wet form until used in the manufacture of paper, any colorless or white manganese salts that may be left in the wet pulp will be unobjectionable as they will combine with the alkaline size and be useful in the sizing operation. If the pulp is to be dried care should be taken to remove any objectionable compounds by washing carefully after the bleaching operation.

It is one advantage of the present invention that the bleaching agents employed when alkali metal manganates or permanganates or permanganic acid are used, are completely soluble and leave no insoluble constituents, so that the bleached and washed material is low in ash as well as of good white color and excellent texture. The bleaching process, moreover, is one which can be carried out quickly at a relatively low temperature, with economy in heat and time required as compared with usual bleaching processes and with less losses.

Instead of bleaching the material such as paper pulp, while in admixture with a large amount of water, sheets or rolls or pads formed from it can be similarly bleached, for example, by impregnating them with a solution of manganate or permanganate and with an acid solution, and subsequently passing a solution of sulfur dioxide or an acid sulphite into the sheets, pads or rolls after the manganate or permanganate has had an adequate opportunity of acting thereon. Using a vacuum tank aids the impregnation with these solutions and greatly facilitates the operation.

As above stated, the permanganate used in the present invention may advantageously be produced from manganates. Alkali metal manganates are commonly made by fusion methods which leave an excess of alkali with the manganate, when economic yields are desired. Instead of neutralizing this excess of alkali with an acid, or otherwise removing it, we have found that it is advantageous to leave it with the manganate, and then treat the mixture of manganate and excess alkali in solution, or in suspen-

sion in part, with chlorine, either after or before adding the mixture to the material to be bleached. Chlorine will act upon the manganate to form permanganate and it will also act upon the excess alkali to form hypochlorite, so that if enough chlorine be added there will be produced a composite solution containing both permanganate and hypochlorite.

When the composite bleaching solution is added to the pulp or other material to be bleached, or when the composite bleaching solution is produced in admixture with the pulp or other material (as hereinafter described), the hypochlorite, especially in alkaline solution, appears to act through the permanganate, by reoxidizing any manganate formed by reduction of permanganate in presence of organic matter and reconvert- ing it to permanganate, although we do not desire to limit ourselves by any theoretical explanation if other chemical action takes place when such a composite bleach liquor is used. The hypochlorite, in such composite bleach liquor, appears to act in a different and more advantageous manner than when used alone, while the action of the permanganate is supplemented by the action of the hypochlorite, so that a lesser amount of permanganate need be used. It may be, as above stated, that the chlorine of the hypochlorite acts through the permanganate and supplements the action of the permanganate in this way.

Insofar as we have been able to ascertain such a composite bleaching agent, containing permanganate and hypochlorite, for example, sodium permanganate and sodium hypochlorite, and its use is new in the art; and we claim such composite bleaching agent as our invention or discovery, as well as the method of bleaching in which such composite agent is employed, and also the method of preparing such composite liquors. Owing to its characteristic composition and properties, this composite liquor can also be advantageously used for other purposes than bleaching, e. g., as a disinfectant, deodorant, germicide, for water purification, sewage treatment, cleaning purposes, etc.

The composite bleaching liquor may be directly made in solution at the time and place of use. For example, if sodium manganate is made by a fusion method and contains an excess of alkali, this can be shipped in a solid state to a laundry, textile factory, paper mill, etc., dissolved in water, and the solution treated with gaseous chlorine sufficient to oxidize the manganate and produce hypochlorite and this solution can then be added directly to the pulp or other material to be bleached. If the manganate or permanganate contains an insufficient amount of excess alkali, alkali or alkaline compounds can be added before the treatment

with chlorine, and the composite solution will be obtained.

Instead of producing the composite solution containing permanganate and hypochlorite and adding this solution to the pulp or other materials to be bleached, the manganate or permanganate and excess alkali or other suitable compounds can be added to and mixed with the pulp or other material to be bleached and the chlorine then introduced, for example, in the form of a chlorine solution or preferably in a gaseous form, care being taken to secure good distribution and absorption of the chlorine.

The proportions of permanganate and hypochlorite in the composite bleach solution can be varied and regulated, for example, by varying and regulating the amount of free alkali in admixture with the manganate which is treated with chlorine. So also, a composite bleach solution of regulated permanganate and hypochlorite content can be made by admixing separately produced permanganate and hypochlorite solutions of known permanganate and hypochlorite content. Such solutions can be produced and admixed prior to the addition of the composite bleaching solution to the pulp or other material to be bleached, or the admixture may take place, for example, in the pulp by separately adding the solutions thereto, with appropriate agitation of the pulp to bring about uniformity of distribution of the reacting materials. The regulation of the proportions of permanganate and hypochlorite makes possible the regulation of the bleaching operation in a simple and advantageous manner, as will be readily appreciated.

When the pulp or other material to be bleached has been treated with the composite bleaching agent, it can be subsequently treated with sulfur dioxide or other suitable reagent in the manner above described. By washing the pulp or other material to be bleached, after the manganate or permanganate and hypochlorite treatment, the pulp etc. can be freed from the greater part of the compounds in solution, prior to the sulfur dioxide or other treatment for dissolving the manganese compounds. Instead of using sulfur dioxide for converting the oxides or other compounds of manganese into a soluble form, other agents which convert the oxides into colorless and soluble compounds can be similarly used. Acids alone can be used for this purpose, such as hydrochloric or sulfuric acids, but a considerable amount of such acids will be required unless the action is carried out or finished at an elevated temperature, or allowed to stand for considerable time. The treatment with sulfur dioxide or sulphurous acid has the advantage that it takes place readily and quickly at ordinary tempera-

tures and without any considerable excess of sulfur dioxide or sulfurous acid.

While we have described the invention more particularly in connection with the bleaching of paper pulp and wood cellulose, for which it is particularly advantageous, yet it will be understood that the invention is also applicable to the bleaching of other fibrous materials, such as cotton, silk, linen, wool, etc., in a similar manner, as well as paper stocks recovered through de-inking processes, etc., and we include the bleaching of such materials within the more comprehensive claims appended hereto. Among the advantages of the process of the present invention is the uniformity of the bleaching action and the desirable condition in which the fibres are left. The fibres, for example, of cotton, silk, paper, etc., are thus left in a form well adapted for subsequent treatment, e. g., for uniform dyeing, etc.

We have found that pulps obtained, for example, by the soda and sulfite processes, so-called, are not only given a white color, but retain their white color much better and longer, when bleached according to the present invention with a manganate or a permanganate, either alone or assisted by chlorine or a hypochlorite, than when bleached by chlorine or a hypochlorite, according to the common methods of bleaching, i. e., without the use of a manganate or permanganate. This advantage of increased permanence of the whiteness of the bleached pulp, is a characteristic advantage of the present invention.

It is a further advantage of the present invention that it makes possible the satisfactory bleaching of wood pulp cellulose produced by what is commonly known as the short-time or quick-cook method, that is, by carrying out the cooking with liquors of various degrees of strength or of concentration, pressure, temperature and time, and stopping the cook before it has been carried to completion. Such pulp, produced by the short-time or quick-cook method, so-called, cannot be readily bleached by ordinary bleaching methods, or gives a bleached product of inferior quality. We have found, however, that such pulp, which heretofore would be considered under-cooked and difficult to bleach by common bleaching methods, can advantageously be bleached by the process of the present invention and brought to a good white color with materially less injury to the stock than with methods of bleaching heretofore commonly used. The present invention makes possible therefore the production of a satisfactory bleached pulp from under-cooked stock, thus avoiding the necessity in many cases of continuing the cooking operation for the normal period of time, etc. The cutting down of

the time of the cooking operation makes possible a material increase in the number of digestions which can be carried out in a given apparatus, and correspondingly increases the capacity of the digesters over the usual practice in the art. We accordingly include and claim as a part of our invention the production and bleaching of such under-cooked pulp by treating such pulp in the manner hereinbefore described.

In addition to the bleaching of under-cooked pulps, the process of the present invention is also of particular value for the bleaching of pulps which are difficult to bleach by common bleaching methods, and enables a superior bleached pulp to be obtained therefrom, of good white color.

There are large supplies of forest products, etc., which, due to their inherent composition and properties, have been unsuited to the production of high grade cellulose material by the processes heretofore commonly practiced. We have found that such materials can advantageously be treated for the production of pulp or cellulose materials by the use of a composite cooking liquor containing both free alkali metal and an alkali metal sulfite, as more fully described in a companion application. The bleaching process of the present invention is of special value in conjunction with such cooking process, and gives a high grade white pulp from cellulose material. In this way, forest materials, bagasse, reeds, grasses, bamboo, corn stalks, straws, etc., which are not commonly considered suitable for the production of high grade pulp or cellulose material can be converted into high grade white products. We, therefore, increase the available supply of raw materials available for the production of high grade pulp or cellulose products. Even when such products are subjected to the usual methods of cooking, the pulp obtained can be advantageously subjected to the bleaching process of the present invention to give a bleached pulp of higher grade and whiter in color than is obtained with the usual bleaching processes.

The process of the present invention, as above stated, is of more or less general application to the bleaching of fibrous material and fabrics, etc., of a bleachable character and will give whiter bleached materials and with less injury than with any of the usual bleaching methods of which we are aware.

While we have described the bleaching process of the present invention as carried out with a manganate or permanganate, or with a composite bleach liquor containing both permanganate and hypochlorite, we do not exclude the use of other bleaching agents, which may be used either simultaneously with the manganate or permanganate, or when separately used. For ex-

ample, chlorine or hypochlorites may be used to bring about a partial bleaching of the material, and the bleaching operation can then be completed with the manganate or permanganate, and, to the extent that residual chlorine or active chlorine compounds remain when the manganate or permanganate is added, the further bleaching operation may partake of the same character as when a composite bleach liquor containing permanganate and hypochlorite is used. So also, other bleaching agents may be used simultaneously with the manganate or permanganate, to modify the bleaching operation. Perborates, for example, may thus be used.

When the material to be bleached contains silica, a small quantity of a solution of a fluoride may advantageously be added thereto. When an acid is added, during the bleaching operation, hydrofluosilicic acid will be formed and the silica will thus be removed. The bleaching operation will also be facilitated by the removal of encrusting compounds.

While we have described the invention more particularly in connection with the use of alkali and alkaline earth metal manganates and permanganates, the invention is not limited thereto, but other suitable manganates and permanganates can be used which are capable of exerting a bleaching or oxidizing action, and such manganates or permanganates can be used either alone, as hereinbefore described, or in conjunction with other agents, e. g., hypochlorites, etc.

When alkali metal manganates or permanganates are employed, they can be produced by any suitable method of production, such as by fusion, electrolytically, etc. One advantageous method of production is by electrolyzing a solution of caustic alkali or alkali metal carbonate, using anodes of ferro-manganese or other suitable manganese-bearing material. In preparing the manganate or permanganate solutions in this way, it is advantageous to discontinue the electrolysis before all of the caustic alkali or alkali metal carbonate is converted into manganate or permanganate, and to treat the resulting still alkaline solution with chlorine to form a composite bleaching liquor containing permanganate and hypochlorite in solution.

The alkali metal manganate can also be prepared by the electrolysis of fused alkali in the presence of a suitable manganese compound or material, for example, by adding an oxidized compound of manganese to the fused alkali, or by supplying ferro-manganese in such a manner that the manganese will be oxidized during the electrolysis, for example, by using the ferro-manganese as an anode. The addition of an oxidized compound of manganese to the

fused alkali has the advantage of economy in the electrolyzing operation. By producing the manganate in this way it is directly produced in a solid form without the necessity of evaporating a solution. In producing alkali metal manganates, for example, sodium manganate, by the use of a fused bath, sodium nitrate may advantageously be used to bring about or promote the oxidation of the manganese, if supplied in such a form that it requires oxidation.

We claim:

1. The method of bleaching fibrous material, which comprises preparing a strong stock solution including an oxidized compound of manganese, adding such strong solution in regulated amounts to such material and subjecting such material to the action thereof in the presence of an acid, and subsequently treating such material to dissolve an insoluble compound or compounds of manganese.

2. The method of bleaching fibrous material, which comprises adding thereto such an amount of bleaching liquor including an oxidized compound of manganese, capable of exercising a bleaching action, as is required for the desired bleaching result, in a series of additions, and removing, between such additions, soluble compounds from the fibrous material after a part of such bleaching liquor has exerted its action and before an additional portion of such bleaching liquor is added, and subsequently treating such material to dissolve an insoluble compound or compounds of manganese.

3. The method of bleaching fibrous material, which comprises subjecting the same to the action of a composite bleaching solution containing permanganate and an alkali metal hypochlorite and subsequently treating such material to dissolve an insoluble compound or compounds of manganese.

4. The method of treating fibrous material, which comprises subjecting such material to the action of a composite bleaching solution containing permanganate and an alkali metal hypochlorite, such solution being produced by the action of chlorine upon a solution including an oxidized compound of manganese containing a base.

5. The method of bleaching fibrous material, which comprises subjecting the same to the action of a composite bleaching solution containing sodium permanganate and sodium hypochlorite, such solution being produced by the action of chlorine upon a solution of an oxidized compound of manganese containing sodium, and an excess of alkaline sodium compound, and subsequently treating such material to dissolve an insoluble compound or compounds of manganese.

6. The method of bleaching fibrous material, which comprises adding a strong solution of an oxidized compound including

manganese containing a base, to such material by distributing such solution with such material while the same is being circulated or agitated, allowing the added agent to act upon such material, and subsequently treating the material to dissolve an insoluble compound or compounds of manganese.

7. The method of preparing fibrous material for use in the manufacture of paper, which comprises bleaching such material by means of a liquor containing a manganese compound capable of exerting a bleaching action, treating such material to dissolve an insoluble compound or compounds of manganese and subsequently treating such material to a sizing operation without drying the material between the bleaching and sizing operations.

8. The method of bleaching fibrous woody material, which comprises preparing a strong stock solution of an oxidized compound of manganese, adding such strong solution in regulated amounts to such material and subjecting such material to the action thereof in the presence of an acid, and subsequently treating such material to dissolve an insoluble compound or compounds of manganese.

9. The method of bleaching fibrous woody material, which comprises adding thereto such an amount of bleaching liquor including an oxidized compound of manganese, capable of exercising a bleaching action, as is required for the desired bleaching result, in a series of two or more additions, and removing, between such additions, soluble compounds from the fibrous material after a part of such bleaching liquor has exerted its action and before an additional portion of such bleaching liquor is added, and subsequently treating such material to dissolve an insoluble compound or compounds of manganese.

10. The method of bleaching undercooked wood pulp, which comprises preparing a strong stock solution including an oxidized compound of manganese, adding such strong solution in regulated amounts to such pulp and subjecting such pulp to the action thereof in the presence of an acid, and subsequently treating such pulp to dissolve an insoluble compound or compounds of manganese.

11. The method of bleaching undercooked wood pulp, which comprises adding thereto such an amount of bleaching liquor including an oxidized compound of manganese, capable of exercising a bleaching action, as is required for the desired bleaching result, in a series of two or more additions, and removing, between such additions, soluble compounds from the pulp after a part of such bleaching liquor has exerted its action and before an additional portion of such bleaching liquor is added, and subsequently

treating such pulp to dissolve an insoluble compound or compounds of manganese.

12. The method of bleaching fibrous materials which comprises subjecting the same to the action of a composite bleaching solution containing a relatively large amount of sodium permanganate and a relatively small proportion of sodium hypochlorite, such solution being produced by the action of chlorine upon a solution of an oxidized compound of manganese containing sodium, and an excess of alkali sodium compound, and subsequently treating such material to dissolve an insoluble compound or compounds of manganese.

13. The method of bleaching fibrous materials which comprises subjecting the same to the action of a composite bleaching solution containing an alkali metal permanganate and an alkali metal hypochlorite, such solution being produced by the action of chlorine upon a solution of an oxidized compound of manganese containing an alkali, and another alkali compound, and subsequently treating such material to dissolve an insoluble compound or compounds of manganese.

In testimony whereof we affix our signatures.

LINN BRADLEY.
EDWARD P. McKEEFE.

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CERTIFICATE OF CORRECTION.

Patent No. 1,768,819.

Granted July 1, 1930, to

LINN BRADLEY ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, line 43, for the words "cooking with liquors" read cook with cooking liquors; same page, line 92, strike out the word "metal"; page 6, line 130, claim 6, for "of an oxidized compound including" read including an oxidized compound of; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 21st day of October, A. D. 1930.

(Seal)

M. J. Moore,
Acting Commissioner of Patents.