UNITED STATES PATENT OFFICE.

CHARLES W. TUCKER, OF NORTH ANDOVER, MASSACHUSETTS, ASSIGNOR OF ONE-HALF TO THOMAS A. KELLEY, OF LYNN, MASSACHUSETTS.

PROCESS FOR THE RECLAMATION OF BICHROMATES.

1,201,392. Specification of Letters Patent. Patented Oct. 17, 1916.

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To all whom it may concern:

Be it known that I, CHARLES W. TUCKER, a citizen of the United States, residing at North Andover, in the county of Essex and State of Massachuetts, have invented a certain new and useful Improvement in Processes for the Reclamation of Bichromates, of which the following is a specification.

This invention pertains to an improved process for the reclamation and saving of the unused excess of sodium or potassium bichromate from waste liquor baths resulting from the practice of various processes, and more particularly the reclamation and saving of said substances from baths employed in the process of chrome tanning of skins or hides. This bichromate in solution forms an important ingredient in the bath in which the skins are soaked as one of the steps of the tanning process. It is necessary that an excess of bichromate should be supplied in the bath in order that enough of the substance required for tanning may be absorbed by the skins and a large amount is left in the liquor when the skins are removed. This excess cannot be used in such condition and the result has been that prior to the development of my invention it has been looked upon generally as a waste product, and thrown away. In fact, only about one-half of the sodium or potassium bichromate used in the two-bath tanning process of chrome leather can be effectively used, and the remainder has been wasted. The larger the tannery, the greater, of course, the waste, and as both sodium bichromate and potassium bichromate are comparatively expensive, the loss of so much of the substances during a day is a very serious item.

I am aware that attempts have been made to utilize the refuse liquor from the bath, and also to convert the chromates in the waste into lead chromate for use in other arts, but none of such attempts have, so far as I have been able to ascertain, been satisfactory.

My invention involves a new and improved mode or process of treatment of the refuse liquor by virtue of which the bichromate constituent of the bath may be reclaimed as a pure potassium or sodium bichromate, either crystalline or in concentrated solution ready for reuse, or for sale.

Briefly, and in general, the process forming the basis of the present invention may be said, preferably, to involve the following steps: First, neutralization of the waste bath with an alkaline agent, though this is not absolutely essential under certain circumstances; second, clarifying the bath by mechanically removing the suspended foreign matters, this being effected by introducing into the bath a clarifying agent which acts to carry or throw down the finely-suspended dirt, or by filtering the liquid; third, the addition of a suitable material, as a soluble carbonate, to precipitate any alkaline earth which may be present, but this step is not essential; fourth, evaporation to a suitable point or degree of concentration for the removal of those salts which are less soluble than the chromates or bichromates; fifth, acidification, if necessary for transformation of the normal chromates to bichromates in those instances where the bath is or has been made alkaline.

The first step is not absolutely essential, though preferable, this primarily for the reason that if the waste liquor has been rendered alkaline the second step may be more readily carried out, and the fourth step, that of evaporation, may then be carried out in a metal evaporator. So, too, if the liquor be acid when evaporated, it is not necessary to add acid as the fifth step to reform the bichromates. In performing the first step of the process, I introduce potassium carbonate or sodium carbonate or ammonia, or other suitable alkaline agent, or it may be the same material which is used to form the clarifying substance of the second step. Usually this neutralization is necessary, as with the materials preferably employed in the next step the bath must be in an alkaline state. Moreover, it is desirable that the bath should be in an alkaline condition at the time of evaporation as it would be objectionable to evaporate an acid bath in a metal evaporator, which is commonly used.

In performing or carrying out the second step, that of clarification, I prefer to place or produce in the liquor a suitable clarifying agent which is preferably, though not necessarily, aluminum hydrate. The bath, after the skins have been taken from it, contain salts left from the other steps of the tanning process, dirt from the skins, lime salts and various other impurities, and I find that by the introduction of aluminum hydrate the

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bath is efficiently clarified. It removes, by mechanical action, all of the insoluble matter (however fine) in the liquor, and carries it to the bottom of the tank. It does not remove the lime or other salts, but this is accomplished later.

The aluminum hydrate may be prepared outside the clarifying tank and added during stirring of the neutralized liquor, or an aluminum salt may be added to the liquor and then an alkaline agent introduced to produce the aluminum hydrate in the liquor.

In some tanning processes and in connection with one in which my process has been successfully employed, aluminum sulfate has already been brought into the bath by a treatment of the skins with such material previous to their introduction into the chrome bath, and the aluminum hydrate may be precipitated by a suitable alkaline agent, such as caustic soda, carbonate of soda, etc. If the aluminum sulfate be not present, as just indicated, it may be introduced and followed up by the substances above mentioned to bring about the formation of aluminum hydrate. While I prefer aluminum hydrate as the clarifying agent, other materials may be employed, such as calcium phosphate, chromium hydrate, silica or silicic acid. The material employed must be flocculent and as it settles in the bath it acts to carry down with it the finely-suspended dirt and foreign matter. Silica or silicic acid may be used without first neutralizing the bath and evaporation could take place without the necessity of adding acid to reform the bichromate. Any of the materials might be added directly to the bath or formed therein as above indicated in connection with the aluminum hydrate.

The second step, or that of clarification of the liquor, which as above noted may take place at the outset without preliminary neutralization, may likewise be effected by filtering the liquor instead of employing a flocculent agent to entrain the materials held in suspension as above set forth. In other words the act of filtering, or of entraining the matter held in suspension are in effect the same, producing a mechanical separation or gathering of the undissolved and suspended foreign matters from the liquor.

After clarification is effected by either of the foregoing methods, and the cleared liquor is drawn off, the removal of the alkaline earths, as lime and magnesia, is effected, when necessary or desirable. This is done by precipitation brought about through the addition of a suitable carbonate, such as sodium or potassium carbonate. The precipitate thus formed is allowed to settle and the liquor drained off.

The next step, or that of evaporation of the cleared and softened liquor, is then carried out to effect a separation of the salts which are less soluble than the alkali chromates or bichromates. This is best carried out in a vacuum evaporator, although any other method of evaporation may be used. When evaporation has been carried to a suitable point of concentration, the crystallized salts are removed, preferably by drawing off the liquor through a suitable filter. The evaporation is preferably carried on to such a point that when the liquor is cooled the alkali bichromates will crystallize.

The next step, the fifth, is that of acidification. The liquor is tested for alkalinity and the requisite amount of acid is added to reform the bichromates, if during the process of treatment which the liquor has undergone, its state of acidity has been changed so that it is more alkaline than the bichromates. This is preferably accomplished by the addition of sulfuric acid, though other acids may be used.

Crystallization takes place when the sufficiently concentrated solution containing either of the bichromates is cooled to the ordinary temperature. The resultant crystals may then be further purified by resolution in boiling water and recooling, when very pure crystals are obtained. The residual liquor in each case is then added to the next body of liquor to be evaporated, and so continued, so that there is no loss of the bichromates.

It will, of course, be appreciated that the concentrated and filtered liquor, properly acidified to bring about the reformation of the bichromates, may be directly employed in the tanning baths without going through the step of crystallization, as just specified, and the subsequent step of redissolving the bichromate crystals.

Having thus described my invention, what I claim is:

1. The method of recovering sodium or potassium bichromate from spent liquors containing said materials, which consists in removing suspended impurities therefrom; removing alkaline earths from such clarified liquor by the introduction of an alkaline carbonate and thereby causing a precipitation of the alkaline earths; and evaporating the liquor thus cleared and softened to separate less soluble salts than the bichromates.

2. The method of recovering sodium or potassium bichromate from spent liquors containing such substances, which consists in removing suspended impurities therein by the action of aluminum hydrate; thereafter effecting a precipitation of the alkaline earths contained in the liquor; evaporating the liquor thus treated to remove by crystallization the less soluble materials contained in the liquor; and finally adding such quantity of acid as is necessary to reform the bichromates.

3. A method of producing sodium or potassium bichromate, which consists in taking a waste tanning liquor; removing solid suspended impurities by a mechanical clearing action; removing alkaline earth salts by chemical action; removing salts of less solubility than the bichromate by concentration and oversaturation; and regaining the bichromate in crystalline form or concentrated solution.

4. The method of recovering sodium or potassium bichromate from spent tanning liquors, which consists in rendering the liquor neutral by the addition of a suitable alkali; thereafter effecting a mechanical or physical separation of the suspended impurities; then causing a precipitation from the solution of the alkaline earths therein; evaporating the resulting solution to effect a crystallization of the less-soluble materials contained therein; and finally adding acid to effect a reformation of the bichromates.

5. The method of producing sodium or potassium bichromate from spent liquors containing such substances, which consists in mechanically gathering and thereby removing foreign matters held in suspension therein, and thereafter evaporating the liquor to remove the less soluble salts therefrom.

In testimony whereof I have signed my name to this specification.

CHARLES W. TUCKER.