

April 2, 1946.

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2,397,650

MANUFACTURE OF GLUE

Filed Jan. 15, 1942

2 Sheets-Sheet 1

Fig. 1.

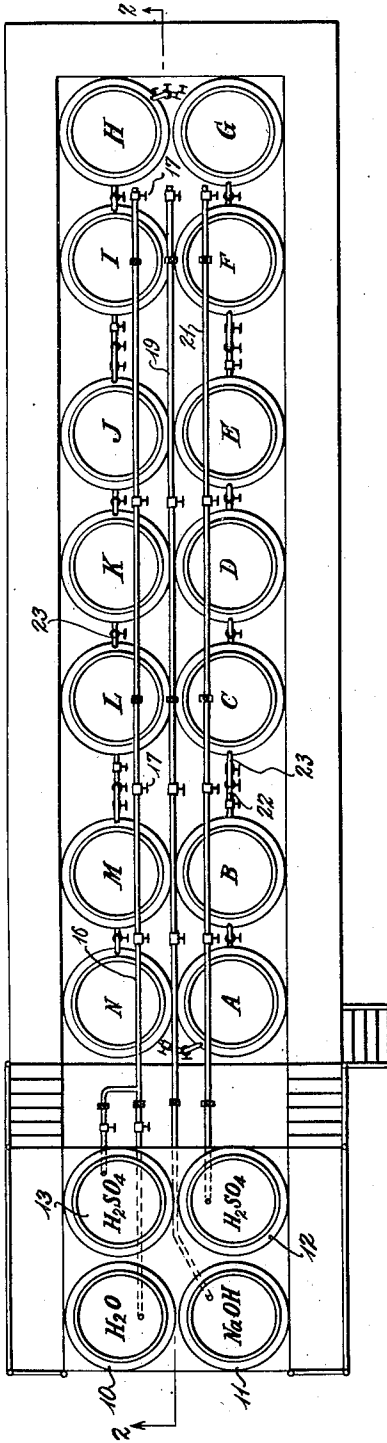
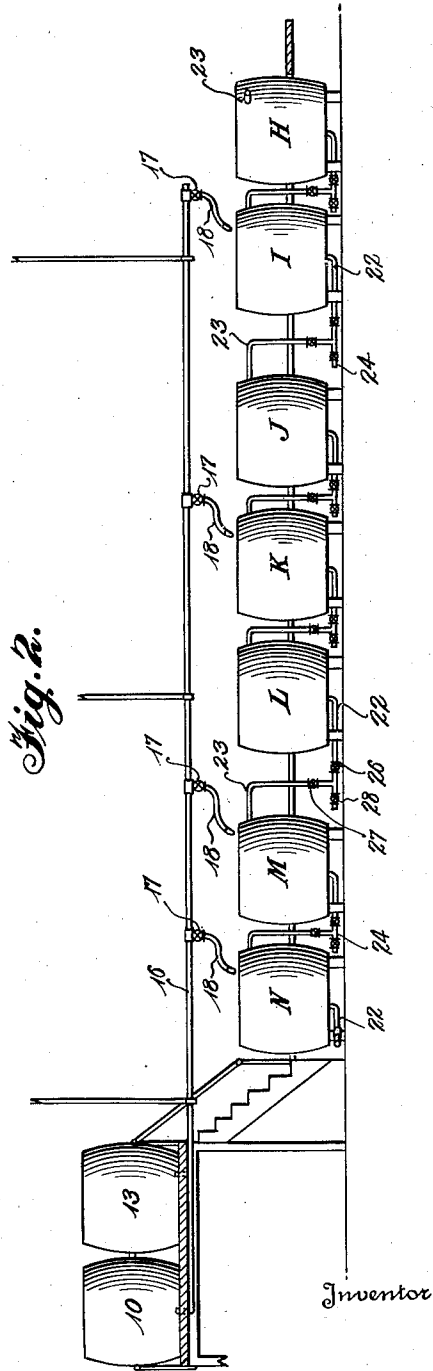


Fig. 2.



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2 Sheets-Sheet 2

Fig. 3.

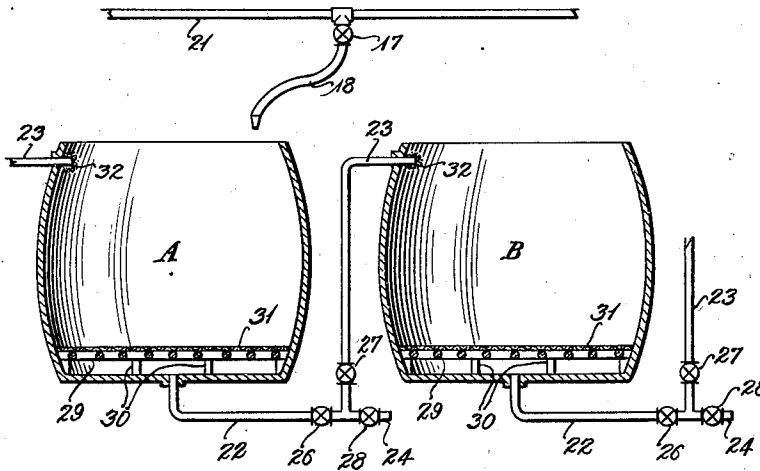


Fig. 4.

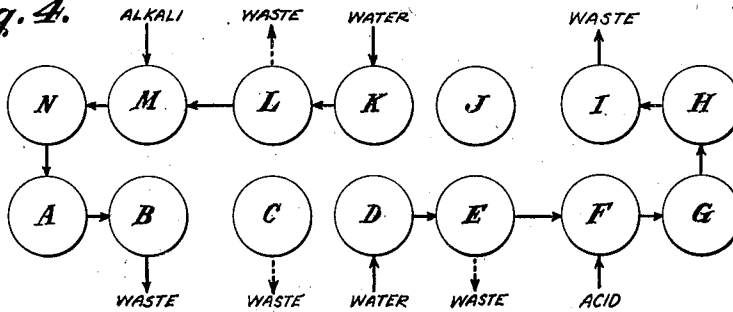
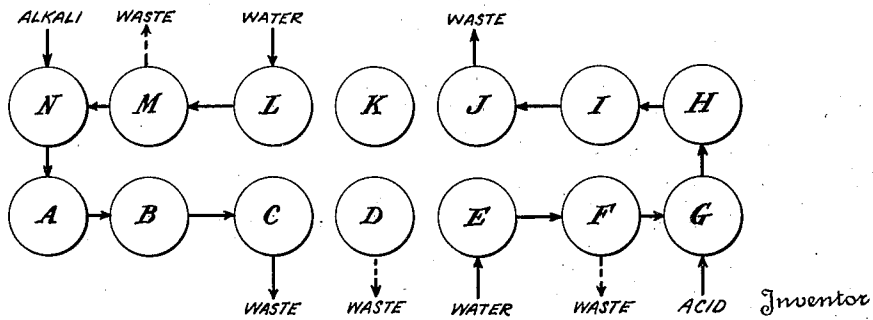


Fig. 5.



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UNITED STATES PATENT OFFICE

2,397,650

MANUFACTURE OF GLUE

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Application January 15, 1942, Serial No. 426,839

4 Claims. (Cl. 260-118)

This invention relates to the manufacture of glue and more particularly to the detanning of leather scrap to condition it for the extraction of glue.

Large quantities of leather scrap are available from the manufacture of leather products and constitute a source of material for the production of hide glue. Before the glue can be extracted from such leather scrap the tanning agents must be removed therefrom. Chrome leather waste is particularly suitable as in the manufacture of chrome leather the hides are subjected to treatments which render the skin practically ready for the extraction of glue just prior to the tanning operation. If the tanning operation is reversed on the leather waste by the removal of the tanning agent this operation regenerates a substance ideally suitable as a material from which hide glue may be extracted.

Numerous obstacles are encountered, however, in removing the tanning agent from the waste. Leather scrap available for glue manufacture exists in two forms, pieces and shavings. The shavings consist of many different size particles, a large portion thereof being substantially in the form of dust and when subjected to treatment with liquids for removing the tanning agent it becomes flocculent and tends to plug nearly any type of filter. Attempts to agitate shavings with solutions of detanning agents and then allowing time for settling is so time consuming that it is not practical. The pieces offer no obstacle to separation of the detanning solutions but constitute a small part of the total leather waste available and also respond more slowly to treatment as they provide a relatively small surface in comparison with their volume. In accordance with the present invention the shavings can be readily and economically treated with detanning solutions and may even be more readily treated than the scrap in the form of pieces. It is therefore within the scope of the present invention to comminute the pieces into shavings prior to detanning.

Although any leather waste may be treated by using the principles of the present invention, chrome leather from which the chromium must be removed is most advantageously treated and the invention will be described specifically with reference thereto.

There are several types of treatments by which chrome leather waste may be dechromed. Perhaps the most common and most widely used has been that of a prolonged lime cure followed by washing and then cooking in the presence of

magnesium oxide. The function of the magnesium oxide is to fix and retain the chromium while permitting the protein to be extracted as glue or gelatin liquor. A second procedure involves the use of peroxides or oxidizing agents capable of converting the chrome from green chromite salts to the yellow or orange chromate which may be leached out with water. A third procedure involves alternate alkali and acid treatment upon the stock whereby the chrome is solubilized by alkali and then leached in an acid medium. In all three of these procedures as previously practiced there are serious drawbacks.

The use of the prolonged lime cure requires excessive vat capacity for the lime treatment in order to maintain a practical volume of production. The use of oxidizing agents such as hydrogen peroxide, perborates, persulfates, etc., is excessively expensive as the amount of oxidizing agent is large for a given amount of glue obtained. The use of alternate alkali and acid reagents has been expensive because of the excessive time required, the quantities of reagents used in prior processes, the cost of filtration and the loss of fine particles of the leather scrap.

In accordance with the present invention it is possible to treat the leather waste alternately with alkali and acid solutions with any necessary or desirable intermediate or final water washing operations without expensive filtering or time consuming settling or decanting operations. It has been found that the various aqueous agents employed may be flowed slowly through a vat or other container filled with the leather scrap without causing the finer particles of the scrap to be carried along by the flowing solution so that plugging of the outlet of the vat is eliminated. By employing a number of vats in series with spaced inlets and outlets, the inlet preferably being at the top and the outlet preferably being at the bottom of each vat a relatively large amount of leather waste may be treated at the same time and the strongest reagent may, when desired, be employed upon the material having the least amount of material to be removed. In the same manner fresh water may be employed to wash material which has the least amount of material to be removed.

It is preferred to arrange the vats at the same levels and make use of gravity feed and flow in order to provide the desired slow movement of the liquids although other arrangements may be employed which do not depart from the essentials of the present invention. The outlets of the various vats are covered with screens or cloths

or both, and the inlets may likewise be provided with screen or cloth or both. An important feature of the invention is to control the flow of the various solutions so that they flow in only one direction through the vats and this direction is preferably downwardly through the vats. By this method of operation all agitation is eliminated and the larger particles prevent the movement of the very fine particles with the liquid. This prevents the fine particles from blocking the outlets of the vats and also the tendency of the liquid to form channels through the stock.

It is therefore an object of the present invention to provide an improved method of detanning leather waste in which expensive and time consuming filtering and decanting operations are eliminated.

Another object of the invention is to provide an improved method of conditioning leather waste for glue manufacture in which the waste is treated in substantially quiescent masses by extremely slow flow of treating solutions.

Another object of the invention is to treat leather waste with detanning solutions in relatively large quiescent masses by maintaining the flow of treating solution through such masses at a rate sufficiently slow to eliminate the tendency of finer materials to be carried along by the solution.

A further object of the invention is to provide a method of dechroming leather waste in which a plurality of quiescent masses of leather waste are treated in series with solutions so that the freshest solution is brought into contact with the waste having the least amount of material to be removed.

A still further object of the invention is to provide an apparatus for detanning leather waste in which substantially quiescent masses of comminuted waste may be treated with the necessary solutions without expensive and time consuming decanting operations and in which the masses may be treated in series with the solutions.

Other objects and advantages of the invention will appear in the following description of a preferred embodiment thereof shown in the accompanying drawings, of which

Fig. 1 is a diagrammatic plan view of a suitable apparatus for carrying out the present invention;

Fig. 2 is a diagrammatic vertical sectional view of the apparatus of Fig. 1;

Fig. 3 is a fragmentary elevation of two of the vats of Figs. 1 and 2 showing connections between the vats;

Fig. 4 is a diagrammatic plan view illustrating the flow of liquids under one condition of operation; and

Fig. 5 is a view similar to Fig. 4 showing a flow of liquids under another condition.

Referring more particularly to the drawings, the apparatus illustrated may include supply tanks 10, 11, 12 and 13 for water, alkali solution, acid solution of low concentration, and acid solution of higher concentration, respectively. The supply tanks are desirably positioned upon an elevated platform 14 so that they are somewhat above a plurality of treating vats A to N, inclusive. A feed pipe 16 connected to the bottom of the water tank 10 may extend adjacent the top of the treating tanks as shown in Figs. 1 and 2 and be provided with a plurality of discharge valves 17 spaced along its length. For convenience in directing the water into any desired treating vat the valve 17 may be provided with

an outlet flexible tubing 18 and by the arrangement shown in Figs. 1 and 2 water may be directed from any valve 17 into any one of four tanks, for example, water from the valve 17 at the extreme left of Figs. 1 and 2 may be directed into any of the vats A, B, M and N.

The supply tank 11 for alkali may likewise be connected to a feed pipe 19 similar to the pipe 16 and provided with appropriate valves and flexible tubing as described with reference to pipe 16. Similarly the supply tank 12 for dilute acid may be connected to a feed pipe 21 likewise provided with valves and flexible tubing. The pipe 16 first described may also have a connection to the supply tank 13 for stronger acid so that this pipe can be used intermittently for supplying stronger acid to any desired treating vat or water may be mixed with the acid in the pipe 16 to supply any concentration. It is apparent that a separate feed pipe may be provided for the acid supply tank 13 and that as many supply tanks and feed pipes may be employed as are necessary for a desired detanning operation. It is also apparent that the supply tanks 10 to 13, inclusive, may be of large size and used to mix the solutions. Preferably they are employed as constant level supply tanks, being furnished with solution from solution preparing tanks not shown and provided with any suitable constant level devices also not shown. Such constant level devices are well known and insure that the gravity head upon the various valves in the pipes 16, 19 and 21 is maintained constant.

The vats A to N, inclusive, may all be interconnected as shown for example in Fig. 3. Thus the vat A may be provided with an outlet pipe 22 connected with a pipe 23 forming an inlet for the vat B and with a pipe 24 connected to waste. Suitable valves 26, 27 and 28 may be positioned in the pipes 22, 23 and 24 respectively. By closing the valve 28 and opening valves 26 and 27 the outlet from vat A is connected to the inlet of the vat B. By closing valve 27 and opening valves 26 and 28 the outlet of the vat A is connected to waste. It will be understood that the vat B may be provided with similar pipes 22, 23 and 24 and valves 26, 27 and 28 for connection to the vat C, etc., so that all of the vats may be connected in series, the vat N being connected to the vat A through similar pipe connections including an inlet pipe 23. It will be further understood that water, alkali or acid may be introduced into any vat A to N, inclusive, by a flexible tube 18 from a valve 17 connected with any of the pipes 16, 19 or 21, the pipe 21 being shown in Fig. 3.

The various vats may be provided with means for preventing the solid material being treated from clogging the outlets. One manner of accomplishing this is to provide a screen supporting grill 29 covering the entire bottom of each vat and spaced a short distance therefrom by projections 30 and covered by a cloth or screen 31. By thus making the screens of large area the current through any portion thereof may be made extremely small so as to minimize any tendency for fine material to be carried to the screen and built up in the form of deposits thereon. As the vats are of relatively large diameter an adequate movement of treating or washing solution there-through may be maintained without causing the current in any portion thereof to be sufficiently great to agitate the leather waste and cause fine material to be carried to the outlet screens. The outlet screen structure shown not only provides

for screens of large area but also enables the screen to be readily removed for cleaning or replacement although it is to be understood that other types of outlet screen structures including structures with screens of smaller area may be successfully employed. The inlet pipes 23 are also preferably provided with screens 32 to prevent loss of leather to waste by any inadvertent reverse flow caused by incorrect manipulation of the valves 27 and 28.

All of the vats A to N, inclusive, are used interchangeably for alkali treatment, washing treatments and acid treatment. For example, as shown in Fig. 4 which is a diagrammatic flow sheet, alkali solution may be introduced into vat M so as to flow through that vat and then through vats N, A and B in series. Sufficient vats may be employed in this series so that the alkali solution is substantially exhausted upon leaving vat B, which contains the waste having the greatest amount of tanning agent. The spent alkali solution may be exhausted to waste. As one example of carrying out the invention, it is assumed that the material in vats L and K has already been treated with alkaline solution and is being washed with water. Such an intermediate washing step is preferred but may be omitted as hereafter explained. The water may be introduced into the vat K so as to flow through the vats K and L in series. Since alkali solution is left in the vats K and L after the alkali treatment, the wash water from vat L may be also introduced into vat M as long as it contains a substantial amount of alkali after which it may be delivered to waste from the vat L.

The vat J in the preferred embodiment of the invention may, under the conditions of operation shown in Fig. 4, be employed for an acid soaking operation. The wash water which was previously in vat J, if an intermediate washing step is employed, may be completely or partially drained to waste and a relatively strong solution of acid initially added to the vat J. This acid solution is then allowed to stand in the vat J in contact with the alkaline treated leather waste for a substantial length of time, for example two or three hours, before the inlet of vat J is connected to the outlet of vat I as shown in Fig. 5. Instead of draining the wash water from vat J sufficient relatively concentrated acid may be added to provide the desired solution strength. If no washing operation is employed after alkali treatment, the alkali solution in vat J from the previous alkali treatment may be at least partly drained and enough acid solution of proper concentration to neutralize any alkali remaining in the vat and provide an acid solution of the desired strength may be added to vat J for the acid soaking operation. It has been found that sudden initial addition of relatively strong acid to the alkali treated leather waste produces improved results over first treating the material with weak acid solution.

In Fig. 4, acid solution may be continuously introduced into the vat F so as to flow in series through the vats F, G, H and I, the material in these vats having been previously treated with alkali and in the preferred operation having been washed and given an acid soaking treatment. Sufficient vats may be employed in this series so that after the solution from the previous acid soaking step has been discharged from the vat the acid solution is substantially exhausted after passing through vat I which is the vat in the acid series which contains the leather waste having

the greatest amount of alkali solubilized chromium. The spent acid solution from tank I may be likewise discharged to waste. It is assumed that the vats D and E contain material which has been acid treated. Wash water may be introduced into vat D so as to flow through vat D and vat E. As long as this water contains a substantial amount of acid it may be also introduced into tank F and thereafter discharged to waste.

The material in vat C is assumed to have been treated with both alkali and acid with or without an intermediate washing step and with a final washing step so that this material may be removed from vat C and constitute the material employed for glue extraction. After the treated leather waste has been removed from vat C this vat may be charged with a fresh mass of untreated leather waste and the weak or nearly spent alkali solution from vat B delivered to vat C. This arrangement is shown in Fig. 5 in which weak alkali solution from vat B is being delivered to vat C and then to waste. As soon as the material in vat M (Fig. 4) has been substantially completely treated with the alkali, the alkali inlet to the system may be shifted to vat N as shown in Fig. 5 and wash water from vat M, if an intermediate washing step is employed, is delivered to vat N as also shown in Fig. 5. Similarly as soon as the alkali treated material being washed in vat K (Fig. 4) has been substantially completely denuded of alkali the water inlet may be shifted to vat L as shown in Fig. 5 and acid solution introduced into vat K for the acid soaking step as previously explained relative to vat J of Fig. 4.

As soon as substantially all of the chromium has been removed by the acid in vat F (Fig. 4) the acid feed may be shifted to vat G as shown in Fig. 5 and the acid containing water from vat F also supplied to vat G. As soon as the acid treated material being washed in vat D (Fig. 4) has been substantially completely denuded of acid the water supply may be shifted from vat D to vat E as shown in Fig. 5. The water remaining in vat D may, if desired, be drained to waste as shown in Fig. 5 and then this vat emptied of the treated material and recharged with fresh material as previously described.

It will then be seen that the process progresses counter-clockwise around the series of vats shown in Figs. 4 and 5, that in a series flow step the strongest reagent or freshest water is always supplied to the leather scrap having the least amount of material desired to be reacted or removed and that the various reagents with the exception of the waste and liquors may be substantially completely used before discharge to waste. Even in the case of acid from the acid soaking step, this acid may be at least partly drained to a separate storage after the acid soaking operation and supplied to one of the vats in the acid treating series to more completely use up excess acid. The acid soaking step can be omitted and a satisfactory operation carried on by merely connecting the vat in which alkali treatment has been completed, for example the vat J in Fig. 4 to receive weak acid solution from vat H. Best results are accomplished, however, by initially and rapidly contacting the alkali treated leather waste with acid of sufficient strength to produce a pH of less than 2 as the chromium is thereby more completely and rapidly leached from the leather waste. Initial contact with relatively strong acid prevents any substantial refixing of chromium in the leather.

By discontinuing the supply of wash water

from a subsequent washing operation to the alkali treating vats, for example by delivering the water from vat L in Fig. 4 to waste instead of to vat M near the end of the treatment with alkali in vat M, the material in this vat may be treated with relatively strong alkali to solubilize the last remaining traces of chromium therein. If no washing step after alkali treatment is employed, the material in vat M, or any vat into which the alkali solution is being introduced, receives treatment with full strength alkali, the material in such vats being that containing the least amount of insoluble chromium. Similarly the material under acid treatment, for example in the vat F of Fig. 4, may be treated with strong acid just prior to completion of acid treatment in the vat F by delivering the wash water from vat E to waste instead of to vat F. Depending upon the strength of the solutions employed, the rate of flow thereof through the various vats and the amount of tanning agents present in the leather waste, any desired number of the vats may be employed for alkali treatment or acid treatment or for washing treatments. Also the total number of vats employed in the process as well as the size of the vats may be varied depending upon the desired output. In all of the vats the velocity of the current therethrough is maintained sufficiently low that substantially no agitation occurs and the coarser particles prevent the finer particles from being carried to the outlet screens.

In the treatment of chromium leather waste the concentration of the alkali delivered to the alkali treating step may vary widely, for example from $\frac{1}{2}$ to 10%, but the most economical and practical operations employ alkali equivalent to a caustic soda concentration of $\frac{1}{4}$ to 1%. Various alkaline agents may be employed but it is preferred to use soluble alkali metal compounds having an alkaline reaction, the most effective agent being caustic soda. The length of alkali treatment will vary with the temperature, concentration and flow of alkali solution as well as the acid and chromium content of the leather scrap, but will usually fall within a range from 10 to 18 hours. The completion of alkali treatment can be determined by the operator by the characteristic chromite green color developed in the vat. Water washing after the alkali treatment will also vary with the rate of flow and the degree of washing desired and will usually range from 1 to 5 hours. The washing step after alkali treatment can be completely omitted in which case acid is used up in neutralizing alkali left in the leather waste causing a loss of both alkali and acid. The expense of the additional reagents is, however, at least partly compensated by the less time and equipment necessary for the process.

Acid treatment will likewise vary with temperature, concentration and rate of flow of acid solution as well as the chromium and alkali content of the alkali treated stock and is carried on until the stock is chrome free as indicated by the absence of coloration due to chromium. The acid treatment will usually range from 12 to 24 hours. The range of concentrations of the acid solution is somewhat more limited than that permissible with alkali solution but may vary over any range in which the chrome is not re-fixed upon the hide substance. In general the pH of the acid solution should not exceed 2 in any vat in which the material is being treated with acid. Below this pH the chromium leaches

out of the acid solution but tends to be re-fixed if the pH is substantially greater than 2. The preferred acid is dilute sulfuric but other inorganic acids such as hydrochloric or phosphoric can be employed. Any acid which forms a soluble chromium salt may be employed, even organic acids such as citric, tartaric, oxalic, acetic, etc.

It has also been found advantageous to add to the acid solution, soluble salts, either salts of the acid employed or salts which do not form insoluble compounds with the acid employed or with chromium. In general salts of the alkali metals such as sodium chloride, sodium phosphate, sodium sulfate, or equivalent potassium salts are suitable. The acid or neutral salts are preferred in order to eliminate use of part of the acid reagent for neutralizing alkaline salts. The presence of such salts prevents excessive plumping of the stock in the acid medium and thereby facilitates the diffusion of the chromium from the stock undergoing treatment. The amount of soluble salts will depend upon the degree to which it is desired to prevent plumping and will range from an amount producing a 1% solution up to a saturated solution.

It is apparent that the detanned leather from the process above described may be treated with peroxides or other oxidizing agents to remove the last traces of chromium, if desired, and that the waste liquids or wash water from the acid treatment containing chromium may be treated to recover the chromium. It is also apparent that other types of leather waste having other tanning agents therein may be treated with appropriate solutions by the same general method and apparatus herein disclosed. For example, other mineral tanning agents such as iron and aluminum may be removed in a similar manner. While I have shown a preferred arrangement of vats it is further apparent that other arrangements can be employed, for example, the connections between the vats shown can be varied so that the process proceeds around the circuit in the opposite direction from that shown or in any other sequence and that the vats can be placed at different levels from that shown if suitable pumps and control valves are provided. Also the direction of flow of treating liquids through the vats may be from bottom to top or from side to side although flow from top to bottom of the vats has been found most advantageous.

It will thus be seen that I have provided an improved process and apparatus for detanning leather waste which is applicable to various types of waste and which provides for economical removal of tanning agents from leather waste while obviating the difficulties heretofore encountered in such processes.

While I have disclosed the preferred embodiments of my invention, it is understood that the details thereof may be varied within the scope of the following claims.

I claim:

1. The process of dechroming comminuted leather waste which comprises, providing a first series of separate masses of said leather waste, flowing a dilute solution of alkali through the end mass at one end of said series and from said end mass consecutively through the other masses of said series so as to substantially exhaust the alkali from said solution, providing a second series of separate masses of said leather waste which has been previously treated in said first

series, flowing a dilute solution of acid through the end mass at one end of said second series and from said last mentioned end mass consecutively through the other masses of said second series so as to effectively use up excess acid from said acid solution, periodically removing the end mass from said first series and adding a fresh mass at the other end of said first series, periodically removing the end mass of said second series and adding to the second series at the other end thereof the end mass which has been previously removed from the first series, the pH of the acid solution during the entire acid treatment being not substantially greater than 2.

2. The process of dechroming comminuted leather waste which comprises, providing a first series of separate masses of said leather waste, flowing a dilute solution of alkali through the end mass at one end of said series and from said end mass consecutively through the other masses of said series so as to substantially exhaust the alkali from said solution, providing a second series of separate masses of said leather waste which has been previously treated in said first series, flowing a dilute solution of acid through the end mass at one end of said second series and from said last mentioned end mass consecutively through the other masses of said second series so as to effectively use up excess acid from said acid solution, periodically removing the end mass from said first series and adding a fresh mass at the other end of said first series, washing said end mass removed from said first series, adding said washed end mass of said first series to the second series as the beginning mass thereof, periodically removing the end mass from said second series, washing said end mass of said second series after removal from said second series, and removing said washed end mass of said second series from said process, the pH of the acid solution during said treatment being not substantially greater than 2.

3. The process of dechroming comminuted leather waste which comprises, providing a first series of separate masses of said leather waste, flowing a dilute solution of alkali through the end mass at one end of said series and from said end mass consecutively through the other masses of said series so as to substantially exhaust the alkali from said solution, providing a second series of separate masses of said leather waste which has been previously treated in said first series, flowing a dilute solution of acid through the end mass at one end of said second series and from said

last mentioned end mass consecutively through the other masses of said second series so as to effectively use up excess acid from said acid solution, periodically removing the end mass from said first series and adding a fresh mass at the other end of said first series, draining the alkali solution remaining in said end mass from the previous alkali treatment after removal thereof from the first series, rapidly adding an amount of a relatively strong acid solution to said drained mass sufficient to lower the pH of the resulting solution to not substantially greater than 2, soaking said drained mass from said first series in the resulting acid solution for a substantial length of time, adding said soaked mass of said first series to the second series at the other end thereof, periodically removing the end mass from said second series, and washing said end mass of said second series after removal from said second series, the pH of the acid solution during the entire acid treatment being not substantially greater than 2.

4. The process of dechroming comminuted leather waste which comprises, providing a first series of separate masses of said leather waste, flowing a dilute solution of alkali through the end mass at one end of said series and from said end mass consecutively through the other masses of said series so as to substantially exhaust the alkali from said solution, providing a second series of separate masses of said leather waste which has been previously treated in said first series, flowing a dilute solution of acid through the end mass at one end of said second series and from said last-mentioned end mass consecutively through the other masses of said second series so as to effectively use up excess acid from said acid solution, periodically removing the end mass from said first series and adding a fresh mass at the other end of said first series, washing said end mass from said first series, rapidly adding to said washed end mass removed from said first series an amount of an acid solution sufficient to lower the pH of the resulting solution to not substantially greater than 2, soaking said end mass from said first series in the acid solution for a substantial length of time, adding said soaked mass of said first series to the second series at the other end thereof, periodically removing the end mass from said second series, and washing said end mass of said second series after removal from said second series, the pH of the acid solution during the entire acid treatment being not substantially greater than 2.

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