

UNITED STATES PATENT OFFICE.

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FERRIC TANNING PROCESS.

1,048,294.

Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that I, JOSEF BYSTRON, a citizen of the Empire of Austria-Hungary, residing at Teschen, Bohemia, Austria-Hungary, have invented certain new and useful Improvements in Ferric Tanning Processes; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

It is known to prepare iron tanning liquors by oxidizing solutions of ferrous salts by means of chromic acid or chromates permanganate of potassium or nitric acid. The iron tans obtained by means of these oxidizing agents show, however, the disadvantage, that considerable deposits are formed in the liquor and on the surface of the hide, furthermore, owing to the necessary presence of large quantities of acid, a very acid and therefore not absolutely insoluble ferric oxid is formed in the hide, and the leather obtained will be brittle and not lasting. When air is employed in likewise known manner for oxidizing ferrous salt solutions, the formation of disturbing deposits is smaller, but the process is so slow, that it is practically of no value.

I have found, that with the aid of oxids of nitrogen, and in particular of dioxid of nitrogen, ferrous oxids can be converted into ferric oxids, without disturbing deposits being formed in the liquor or on the surface of the hide, and that such process will admit of producing highly basic, absolutely insoluble ferric oxid compounds in the hide, which will yield a soft and lasting leather, which may be washed any number of times, without it being again untanned, as would be the case when acid or not quite so highly basic ferric oxid compounds were deposited.

The process can be carried out in various manners: For instance, the hide which has been unlimed and freed of acid, and is to be tanned is placed into a solution of a ferrous salt, say a solution of sulfate of iron at 5-10 Bé., which may also contain large quantities of neutral alkali salts and the oxidation is affected by means of dioxid of nitrogen, by a current of NO_2 gas or of a mixture of NO_2 and NO , produced by the gasification of liquid NO_2 or by the decomposition of nitrites, through the liquor. The dioxid of nitrogen will already while being still cold,

yield oxygen to the ferrous salt, so that a basic ferric salt is produced which is bound *in statu nascendi* by the hide. The NO formed by the reduction of the dioxid of nitrogen will, as long as it is not present in excess and as long as there are present sufficient quantities of surplus ferrous salt, be dissolved by the latter under formation of the known complex, brown compound, without being oxidized, as no heat is applied. The surplus of NO escapes and will on reaching the atmosphere again combine with the oxygen in the latter to dioxid of nitrogen. It is now possible by working in closed tanning vessels and by reintroducing the regenerated dioxid of nitrogen, combine these reactions in such a manner with each other, that a circulation of nitrogen oxids is produced, so that with a given quantity of NO_2 theoretically any amount of ferrous salts can be oxidized or be converted into the tanning salt. Instead of regenerating the nitrogen dioxid with air and oxygen outside of the tanning vessel, this may also be done within the tanning vessel. As the nitrogen dioxid is not consumed in the process, it will then be possible to work in practice also with so small a quantity of nitrogen dioxid, that it acts practically as a catalyser only, by aiding the transfer of the oxygen of the air to the ferrous salts. In such case it is only necessary to introduce into the solution of ferrous salt a small quantity of nitrogen oxid or nitrogen dioxid, which will be thereby reduced to nitrogen oxid; these oxids will combine with the ferrous salt, and through the solution air is then sent. By introducing the air at a higher or lower rate, the oxidation, and therewith also the duration of the tanning process, can be varied at will. Instead of producing the nitrogen oxid or nitrogen dioxid outside of the tanning vessel and introducing it in form of a gas into the latter, it may also be generated within the said vessel, by the ferrous salt solution being treated with a small quantity of alkali nitrite and liberating therefrom by the addition of the calculated quantity of a suitable acid, nitrous acid, which will act as a mixture of NO and NO_2 . Furthermore it is not absolutely necessary to carry out the oxidation of ferrous salt simultaneously with the tanning of the hide; the ferrous salt solution may be first oxidized with nitrogen oxid or nitrogen dioxid and air, whereby a

soluble ferric oxid salt is formed, and the hide may be then tanned with the so formed oxidized tanning liquor, in which case also a highly basic ferric oxid compound is deposited in the hide. Lastly also the non-acidulated hide may be placed into a solution of ferrous oxid salt, whereupon the alkali or earth alkali contained in the hide will precipitate from the solution of ferrous oxid salt an insoluble compound of ferrous oxid which will be converted into a highly basic ferric oxid compound by the aid of the nitrogen oxids or nitrogen oxids and air. In all instances neutral alkali salts may be added to the solution of ferrous oxid salt, and the tanning process is continued with the aid of nitrogen oxids, until the leather is thoroughly tanned, which may be determined by the color of the cut.

I claim:

1. A ferric tanning process consisting in an insoluble ferric compound being deposited in the hide by the oxidation of a ferrous salt with the aid of a nitrogen oxid.
2. A ferric tanning process consisting in an insoluble ferric compound being deposited in the hide by the oxidation of a ferrous salt with the aid of nitrogen dioxid.
3. A ferric tanning process consisting in an insoluble ferric compound being produced in the hide by the oxidation of a ferrous salt with the aid of a nitrogen oxid, and

the nitrogen oxid being continuously regenerated by a fresh supply of air.

4. A ferric tanning process consisting in the hide, after it has been unlimed and freed of acid, being placed in a solution of a ferrous salt and the latter being oxidized by means of a nitrogen oxid, an insoluble ferric oxid compound being formed in the hide.

5. A ferric tanning process consisting in the hide, after it has been unlimed and freed of acid, being placed into a solution of a ferrous salt and the latter being oxidized by means of a nitrogen oxid, an insoluble ferric oxid compound being formed in the hide, and the nitrogen oxid being continuously regenerated over again by a supply of fresh air.

6. A ferric tanning process consisting in the non-acidulated hide being placed into a solution of a ferrous salt and the insoluble ferrous oxid compound deposited in the hide being converted by means of a nitrogen oxid into an insoluble basic ferric oxid compound, the nitrogen oxid being continuously regenerated by a supply of fresh air.

In testimony, that I claim the foregoing as my invention, I have signed my name in presence of two subscribing witnesses.

JOSEF BYSTRON.

Witnesses:

ERNEST L. IVES,
GUSTAV KREUSE.