

# The New Vision on Chrome Tannage

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**Abstract:** The effect of chrome in leather making is discussed in this paper. Based on the relationship between chrome and human health, the authors expounds the health function of chrome and calls for people to have a new understanding of the influence of chrome on the environment. It will be a scientifically fundamental argument for continued application of chrome in leather making. The new methods of recycling of the offal and the waste water from chrome tanning are also introduced in this paper.

**Key Words:** chrome tanning; leather manufacture; clean production

## 1 The role of chrome tanning

The tanning is a process of qualitative change which makes raw leather into leather with some tanning materials, which is the crucial process in the leather production. The advantage of leather rather than raw leather is non-leather expansion of water, non-perishable, better hot-wet stability, and able to break down micro-organisms. On the other hands, Leather has a certain shape, and porosity, and full deflection and so on. Not only the fiber structure of the skin is retained, but also the leather has excellent physical and chemical properties.

In order to gain characteristics more than skin, the tanning, arrangement and some other processes is a must. For access to some characteristics (such as hand and full degrees, back flexibility, etc.) the processes of preparation, tanning, refueling, filling and finishing are needed to gone through. However, it is tanning hides the key steps in making the qualitative change. No wonder the tanning industry say there is: ready to lay the groundwork, tanning is the key, finishing efforts. It shows the importance of tanning.

Practical application in the middle of the tanning agents, chrome tanning agent is the best. Since 1858 German F. Knapp raised the basic theory of chrome tanning, the application of more than one hundred years of history has proved that chrome tanning method has a number of superior performances which other inorganic or organic tannages can't be replaced. Thus, the chrome tanning method has become the most important tannage since then. The effect of a variety of commonly used tanning agents on the shrinkage temperature is shown in Tab.1 [1]:

**Tab.1 Effects of some Tanning Agents on the Shinkage Temperatures of Leathers**

Tanning agent	the Shrinkage Temperatures (°C)
Basic Chromium Sulphate	above 30~35
Vegetable tannin extracts	-2~24
Formaldehyde	15~20
Zirconium sulfates	20~25
Basic aluminum sulfates	10~20

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Synthetic tanning agents	0~22
Resin tanning agents	0~30

In addition to shrinkage temperature, the leather in water caused by changes in steam resistance degrees can also be said, which are showed in the Tab. 2 [1].

**Tab. 2 Effects of Some Tanning Agents on the Steam Resistance of Leathers**

Sample	The steam resistance (%, indiscrptible cortex see the 10 hours )
Bare skin (pH 5-8)	0~10
Plant tanning-skin	60~92
formaldehyde tanned leather	80~85
wet blue leather	98~99
oil tanned leather	80

In addition to give the chrome-tanned leather a better performance, the chrome-tanning makes the entire tanning process relatively simpler. It makes the post-tanning leather blanks positive charge, which makes a number of anions retanning agent, fat liquor more easily penetrate the skin and in combination with the leather fibers is more easily anionic dye staining

Trivalent chromium can make a firmly combination of strong collagen fibers and chrome tanning processed products Will not wash or sweat free from chromium which to ensure that the chromium tanning will not harm or to stimulate the skin, coupling with a lesser proportion of chromium tanning. This is why the chrome tanning has become so popular.

## **2 Chrome tanning impact on the environment**

However, because of the limitation of the mechanism of chemical reactions, the absorption rate of chromium salt be absorbed by raw hides is only 60-70%, and the remaining part of the waste water are released into the environment along with tanning. In addition, the chrome tanning production progress will generate large amounts of chromium-containing solid waste. At present, people have not yet found an effective solution yet. Therefore, chrome-tanned progress is considered one of the main sources of pollution by the public.

There are several major reasons are responsible for what the waste water of chrome tanning regarded as the most heavily polluted industrial ones. In the first place, a large mount of waste water containing chromium ions were leased into the environment. And the long-term accumulation will increase a serious crisis to the local water system and soil, which will pose a threat to human health. Second, so many emitted neutral salt that has increased the salinity in soil year by year. Third, this acidic waste water is harmful for soil. Therefore, it becomes one kind of industrial waste water under strictly supervision by environmental protection departments.

At present, the methods of handling solid wastes containing chromium in general can be summed up in two categories. One is known as the industrialized approach, that is, the wastes are used to produce gelatin, reproduced leather, adhesives, and surfactants. The other way is reusing the wastes as feed additives for the feed industry, however, which may have a negative impact on the safety of animal husbandry and food industry because of they are not completely dechromed.

As mentioned above, the absorption rate of chromium salt be absorbed by raw hides is only 60-70%, and the remaining parts are released into the environment along with tanning waste water. In general, a tannery with a annual productivity of 1 million pieces of cow leathers will release  $\text{Cr}_2\text{O}_3$  from 200 to 300 thousand kilograms every year. Year by year, in the same area, the emission is so large that must exert a negative effect on the local ecology for its excessive emissions in the region. In addition, chrome tanning generates large amounts of chromium-containing solid waste as well, and its weight (including the second floor of leather) will be more than 50% of the weight of raw skin. The solid waste will cause hazardous to humans, if it has been used out of control.

### **3 The methods of improving the chrome tanning**

For a long time, leather and the related chemists have researched a great deal methods to reduce emissions of chromium tanning, including: high-exhaustion chrome tanning method, non-chrome tanning method, combined with tanning, etc. A variety of representative new methods are discussed as follows.

#### ***3.1 Chromium used combining with other tanning agent in order to reduce the amount of chromium***

Under the circumstance that other tanning methods can not completely replace the chrome tanning, studying tanning combine chrome with other agents for reducing the amount of chromium which also can be regarded as a good measure to reduce chromate pollution. The combination of chrome tanning can be divided into inorganic and organic tanning.

The combination tanning of chromium with organic tanning agents are: the combination tanning of chromium with pant agents, chromium glutaraldehyde, etc. In the tanning of combination chrome with glutaraldehyde, the green leather's shrinkage temperature is higher than 95 with only 0.5% of the amount of  $\text{Cr}_2\text{O}_3$ . However, all the properties of leather have been able to meet the requirements of chromium and the waste water volume is less than 20 mg / L. To a large extent, it reduces wastewater pollution containing chromium. While the combination of Chrome tanning agent with the resin, they will form complexes, thereby enhancing the utilization of chrome, reducing the chromium content in waste water. In the use of chrome tanning agents combined with other tanning method, in varying degrees, the cost of production of leather tanning process raise, at the same time, it become more intricate. Hence, this may largely lower its cost.

#### ***3.2 Craft with wit-white leather***

The wit-white leather consists of three processes. Firstly, the leathers should be tanned in other approaches; then they are shaved evenly; finally, they are tanned with chrome agents. These two-story leathers and leather shavings have not been tanned with chrome, which not only decrease the use of chromium, but also make the recovery of them easier. At present, it is dominant method is first pre-tan with Mongolian glutaraldehyde, such as the Derugan200 produced by the United States Schili & Seilacher's company, then followed by chrome tanning again. In this way, the content of formaldehyde in the liquid is very low, just only 6 ~ 15mg / L, when the liquid ratio is 0.5-0.7. The result is lower than the concentration of microbial growth inhibition 25mg / L in the sewage treatment plants companies. In

chrome tanning, it can save substantial and reduce its content in waste, in the meanwhile, it can increase the size of the yield of gram.

The size has increased by 8%-14% comparing with blue chip leather and increased by 1%-2% comparing with the film gray skin. But the amount of glutaraldehyde should be strictly controlled, if being used too much or too little it will affect the performance of leather. At the same time, the process is relatively more complicated comparing with a single-tanning chrome tanning process.

### ***3.3 Wet-white leather process without chrome***

In the tanning process completely without chrome, research and application of a maximum of one organic or combination of inorganic and organic tanning were performed. Al-sik and sik tanning, as well as a combination of aldehyde tanning agent were used to produce synthetic leather for better performance. Besides, the use of organic phosphorus is in place of chrome tanning agents. Study at home and abroad is more tanning methods. Non-chrome tanning method is fundamental solution to the tanning process chromium pollution. However, due to a variety of tanning agent has its own shortcomings, not a tanning agent performance as excellent as chrome tanning agents, it is still not widely used.

### ***3.4 recycling utilization of chrome tanning waste water***

It is a relatively perfect less chrome tanning solution, which reuse the chrome after recovering and disposing waste water containing chrome. This method not only saves the chrome tanning agents, but also greatly reduces the emission of waste water. It is better applied in the production of dark-colored leather rather than in light-colored production for its adverse effects on the color. In addition, the production progress will become relatively more complex because of it need a certain number of humane and mechanical operations during the recovery and adjust progresses.

## **4 The new thinking of Chrome tanning**

Under the experiences of the author long been engaged in the research of chrome tanning, he ascribe the major reason why chrome tanning is regarded as a resource of Serious pollution to the uncontrolled emission of a huge quantities of waste water containing chromium and neutral salt. Regarding the toxicity of trivalent chromium, it is unnecessary to fear when referring to chrome. On the contrary, people should make a scientific analysis, not only Catching on to the awareness of its harm, but recognize the beneficial aspects. It is entirely impossible to achieve a harmless and clean chrome tanning technology, only if it is understood rationally, controlled efficiently and utilized scientifically.

### ***4.1 Chromium and Human Health***

Cr (chromium) is firstly discovered by a French chemist, Lvauquelin, in 1797. With the increasing depth of the research, micro-distribution Chromium has been found in both various environmental and biological factors (including people), but unevenly. In 1955, the glucose tolerance factor (GTF) is found by Mertz and Schwarz in a experiment, and is firstly reported that it has biological activities and its important structural component Cr (III) in 1959. And then, the biological function of chrome captured more extensive attentions. Subsequently, the chrome is proved to be one of essential micro-elements for animal, and is identified to be a necessary micro-element for humane, and then be included as one of the four necessary elements for humane health (the others are iron, zinc and copper). In recent decades, it is generally accepted that the mechanism of chromium is that it can enhance the binding of insulin and receptors, increase the number of insulin receptors and assist the Phosphorylation of insulin receptors and so on. What's more, the chrome assist insulin pays a role when the body takes up glucose, and glucose transform into carbon dioxide or fat. Even in the metabolism of insulin-dependent sugar, insulin-

dependent protein and insulin-dependent fat.

Apart of synergy with insulin as the active ingredient of GTF, the chrome plays an important role in the metabolism of sugar, fat, protein and nucleic acid. The function of preventing and curing diabetes is certificated universally, that is, chrome exerts a certain effect on reducing blood sugar and diabetes, at the same, organic chromium is evidently superior to inorganic chromium. Chromium supplement has become a nutritional intervention for diabetes. Chrome can be used as supplementary drugs, even be used alone also demonstrated some efficacy.

In addition, the lack of chromium may also cause by other diseases, such as Arteriosclerosis, Coryza, schizophrenia, Chizophrenia, Esophageal Cancer, Chronic Keshan Disease, and Womb Cancer etc. Like the lack of chromium can cause a vicious circle, excessive chrome will bring some diseases, such as bronchitis, liver, renal cell carcinoma breast cancer etc <sup>[4]</sup>. The chrome poisoning can result in protein denaturation, nucleic acid and nucleic protein precipitation and interference enzyme system. What's worse, the toxicity of hexavalent chrome is far higher than trivalent chrome. The former can be red blood cell infiltration and inhibit the activity of glutathione reductase while the hexavalent chromes are reducing to trivalent, which can lead Hemoglobin into methemoglobin and then give rise to hypoxia phenomenon. So, it is crucial to control the emission of chrome.

#### ***4.2 Chromium the state line and transformation in nature***

There are two main channels for chromium entering the human body. For one channel, it can enter directly the human body by drinking. For another important channel, the chrome in the soil can be transported to humane body and played a corresponding role after the chrome in soil absorbed by plant. The form of chromium in soil is divided into water soluble, exchangeable, precipitated state (including the Mn-bound), organic bound and residual, while the major states in natural soil are residue and sediment. In reducing conditions, the chrome has a trend to transform organic bound, hence, organic-bound chromium increased with time. At the same time, the concentrations of soluble and exchangeable bound increased slightly as well. When the PH of the soil decreases; the content of water soluble and exchangeable chromium increases while precipitation state and the residual chromium reduce <sup>[4]</sup>.

Redox makes Cr (III) and Cr (VI) transforms each other. The process is mainly related to the concentration of pH and need the existence of an appropriate amount of reducing agents, lygands and a catalyst. Movable Cr (VI) can be reduced by organic reducing agents, when reactants contain an appropriate amount of hydroxides or oxides, Cr (III) could be translated into the oxidation state. This circular oxidation-reduction reaction can be regarded as a progress of organic compounds being oxidized by oxygen in the air with the effect of Cr (VI) / Cr (III) act as a catalyst. When organic be produced directly or indirectly through photosynthesis, the chrome circulation proceed in the opposite direction, therefore which can be seen as the progress of consumption energy while accumulate energy in the photosynthesis. In this ongoing transformation process, the activity of chromium compounds can be absorbed and transferred through the food chain by organism <sup>[4]</sup>.

Whether chromium is essential element for plant growth or not, we haven't caught on to the idea, but it is undisputed truth that plants are able to absorb chrome. It is inevitable to make adverse effect on environment for a huge amount of waste water containing chrome produced by tanning companies day by day.

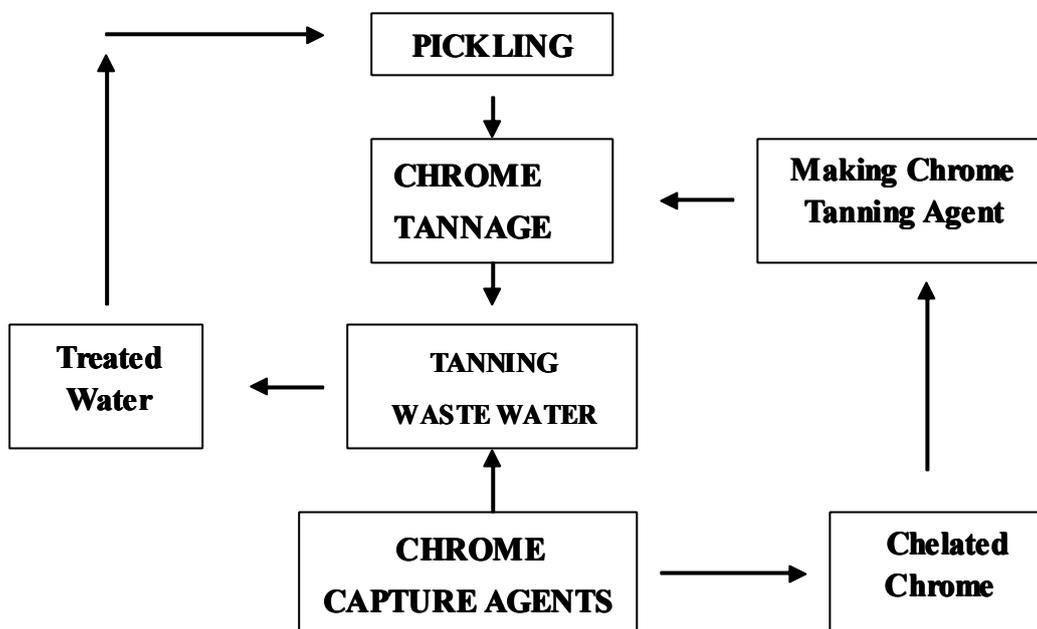
### **5 The resolution to solve the environment pollution caused by chromium tanning**

It is an unquestionable truth that conventional chromium technology lead to serious hazards to environment, however, what does not mean it is unpreventable and uncontrollable. The major sources of

chromium pollution in leather industry are waste water and solid waste which containing chrome. So, they can be taken by different treatments.

**5.1 The treatment recycling of chrome tanning waste water**

Recently, author invented a new patent technology about how to deal with chromium waste water. The main points of the method is how to extract chromium from the liquid with specialized chromium capture agents, then reuse the remaining water (including a large number of neutral salt) to the progresses of pickling, chrome tanning, which can make the into a closed system. In this approach, not only the pollution of chromium and neutral salt is eliminated, but a large number of water is saved. Because of the leather water no longer contains chrome, it facilitates to deal with other waste water as well as reduce the costs of treatment of the sewage. A new system of recycling tanning waste water is showed in Fig. 1.



**Fig. 1 chrome tanning waste water treatment and recycling process**

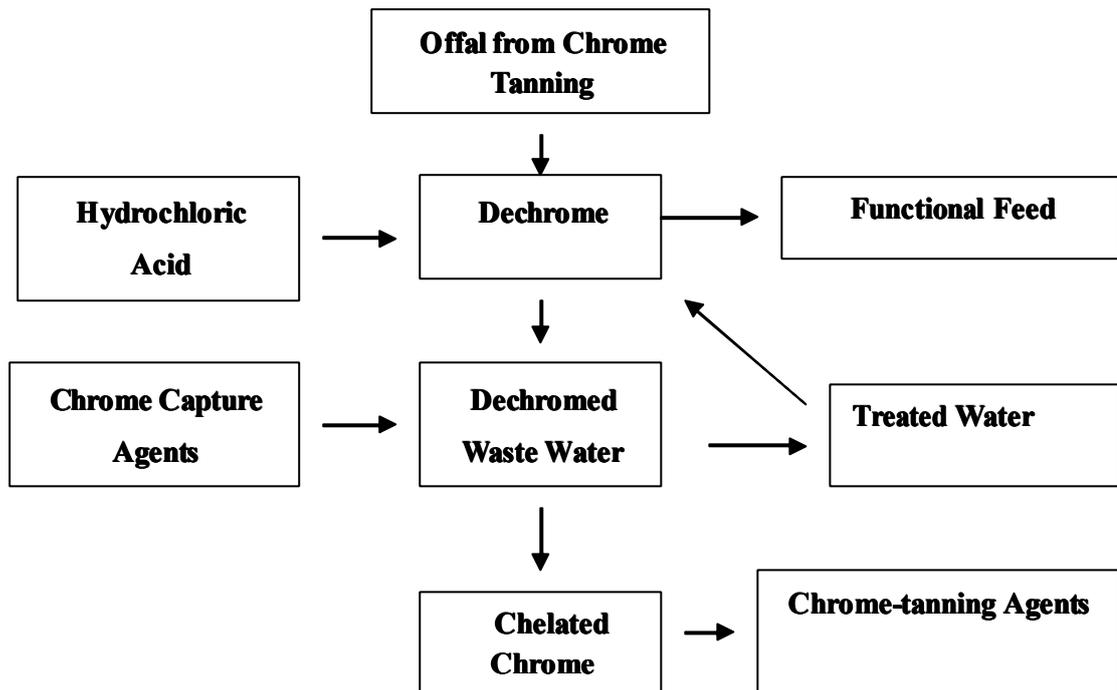
This approach can be used not only the beginning of tanning, can also be used in retanning section, as well as other sections that generate chromium-containing wastewater .

**5.2 The treatment of chrome tanning solid waste and resource utilization**

We have a certain scientific understanding on the biological effect of chrome from the research results about the effects on humane body have been researched by the medical profession, which will provide us a scientific basic about how to deal with and reuse these chrome tanning solid waste effectively.

Now, we can firstly carry out dechromed treatment, followed by reusing this solid waste to make functional feed in order to produce eggs or poultry meat products containing trace elements of chromium which supply in diabetic patients to help them back to health. If this ideal become into practice, it is not just a resolution to the problem of pollution caused by chromium solid, but a good new to diabetic patients. Because, after all, diet therapy is always superior to treatment, prevention is always better than cure.

Fig.2 briefly indicates the disposal and reuse process of chrome tanning solid waste.



**Fig. 2 The disposal and reuse process of chrome tanning solid waste**

It is worth noting that, for the handling of chrome-tanned solid waste, it needs strictly dechromed control standards to ensure the safety of feed.

## 6 Conclusions

According to research results of the medical profession, we can think that the chromium has an irreplaceable role in human health as a trace element. At the same time, chromium salt is the best tanning material, until now people have not found a tanning agent which can completely replace chromium salt, and its a good tanning effect and relatively low production costs make it will be chrome salt as the main tanning materials in a short period. However, the emission of large amount of neutral salt containing a high concentration of chrome tanning wastewater, will seriously affect the ecological environment. Dealing with scientifically and reusing effectively the chrome tanning wastewater and solid waste will reduce or even eliminate the negative impacts on the environment, which is the correct choice currently to treat chrome tanning process and technology.

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