

# The Use of Inert Polymer Spheres in Retannage and Fatliquoring Floats.

## Reduced chemical use and environmental advantage

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### Abstract

Inert polymer spheres, when used within processing floats, enhance the uptake of chemicals and products used in leather manufacture. The same float volume can be maintained, but with less water, hence increased chemical concentrations.

This is useful in neutralising, retanning, dyeing and fatliquoring processes, especially where the chemical costs are high, and the materials complex. These applications enable production of the same types of leathers, but from lower chemical offers. It provides significant reductions in unused products, normally discharged for effluent treatment.

## 1 INTRODUCTION

An established technique when washing fabrics on commercial scale is to add inert polymer spheres to the washing cycle. This produces savings in both water and energy consumed, and also in detergent use and conditioning products.

The same loadings and volumes are employed, but the part-replacement of water means higher concentrations of washing aids, hence greater efficiency. At the same time, a gentle massaging or kneading action within the washing cycle develops, that stretches out creases and folds.

Similarly, spheres can be used to introduce chemicals into the leather structure. The float volume (water and spheres) can be the same as the established process, but with less water. This provides a fast distribution of specialised products throughout the processing vessel, being essential for the uniform offer of these materials to the leather. Good separation of the leather in process with full access to chemicals in solution is ensured too. The increase in concentration offers improved efficiency of process. However, upon rotation, the spheres held within the leather folds also aid penetration within the fibre structure. These 'micro-actions' help to avoid over fixation on grain and flesh parts that could otherwise occur due to rapid and efficient chemical uptake.

## 2 DISCUSSION

Cost savings can be made by reducing the quantities of chemicals used in the areas of neutralising, retanning, dyeing and fatliquoring. These can be considerable, but for success – that is the 'same' leather at the end of the process – three quite different events must take place at the same time:

- The conditions within the established process must change to get a better uptake of products. If this is done as a single event (without chemical reductions), the chemical uptake will be greater, but the leather will have too much filling and will be over lubricated.

- There must be a reduction in chemical offer, so that the total uptake matches the original process. This is where the cost savings from lower chemical use becomes clear.

- The products must be distributed throughout the leather structure in the same way as the original process. If this is not achieved, the leather will be 'different'.

This is not an easy matter. Changes within an established process – managing smaller amounts of the same chemicals to create the same products – are limited.

### 2.1 Managing the chemical process

The techniques that control chemical reactions are fixed, and of common knowledge to tanners. They can be summarised as:

- pH control, for manipulation of the charge and the rate of fixation.
- Temperature adjustment, as this directly affects the speed of the chemical reaction.
- Time management, as this optimises the uptake of chemicals in the time available.
- Concentration, as the rate and efficiency of the reaction is dependent upon strength of the chemicals in the float.

Changes to pH, temperature and time in conjunction with a reduced chemical offer, can give the same uptake of products in total, but their locations throughout the leather structure will be different. Typically, there may be an acceptable uptake on the grain and flesh parts, but the inner most sections remain under processed. The leather will be too firm, and probably under filled. Chemical control alone cannot make the same product from a lower chemical offer. However, if a higher concentration is created by using less float, then the process becomes more efficient. This provides the opportunity to reduce the chemical offer so that the leather uptake remains the same in total.

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The greater mechanical action created by the lower float conditions ensures better penetration of those products too, as appropriate, deep into the fibre structure. This is needed to match the original leather characteristics. But increased action can cause an over-stressing of the structure, with a loss in break characteristics, or even tearing. This is especially clear with more sensitive leathers, or of lower substance.

Moreover, lower float conditions do not enable a fast dispersion of products across the processing vessel. This is essential for a uniform uptake of chemicals, and especially important where light surface dyeing, surface lubrication or fixations are needed. If float levels are reduced beyond the level that ensures well-opened pieces in good contact with chemicals in solution, the movement changes to that of a single mass, or bundles of leather. This raises issues of irregular uptake and tangling. Effects include variations in colouration, drawn grain and uneven penetration. These limitations to low float processing depend upon the physical properties of the leather at the time of process, the load weight in relation to the capacity of the processing vessel, speed of rotation, and internal configurations. A high concentration offers a way to improve chemical uptake, but a different type of mechanical action is needed.

## 2.2 Sphere applications in neutralising, retanning, dyeing and fatliquoring systems

Sphere applications were developed by Qualus for six years before the introduction to commercial leather manufacture. In this different approach, inert polymer spheres are added to the process drum together with water.

The volume occupied by spheres and water remains as for normal use to provide good dispersion of products to well separated pieces. However, a reduced amount of water within the float causes an increase in the concentration of products employed. This ensures a better chemical uptake and provides the opportunity for a reduction in chemical offer too. At the same time, the spheres held within the folding and flexing leather pieces during process assist penetration and help avoid overstressing the structure. All other components of chemical control – pH, temperature, time – can remain unchanged.

The technique offers advantages within all aspects of chemical uptake, mainly the high expense areas of retanning, dyeing and fatliquoring. It is an established technology, and typically, overall reductions on full industrial scale are found to range between 10% and 15%.

The technology includes the retention of spheres throughout float exchange and washing sequences. This is regardless of size, services and the internal constructions of the processing vessel. The collection and cleaning of spheres after process, their storage and delivery to subsequent processes are all part of the bespoke packages available to the tanner.

Sphere applications can be used by tanneries of any size, are easily evaluated, and can be moved into production as required. Management of the spheres can be performed within individual tanneries, but also within clusters. Here, a single location can provide washing and cleaning of the spheres, before delivery back to the tanneries for reuse. There are few limitations to implement this technology. It is a safe and

### PANEL I Minimising water use

Reduced water use has long been an objective in leather manufacture. Significant reductions have been made possible by the gradual improvements in the design of processing vessels, fittings and auxiliary equipment. Engineers working with tanners have provided a base for more efficient processing, with less waste of chemicals, energy and water.

However, other approaches to reduce the quantities of water in floats – or even eliminate water – were the subject of speculation and investigation in the 1990s.

Two areas of physical/mechanical innovation were considered by scientific institutions pre-2000 to reduce water use and chemical waste. One involved the direct pressure injection of concentrated solutions at a series of points across the flesh part of hides. This was for both beamhouse operations, and chrome tanning. Another technique employed a steam-induced vacuum (as used for impregnating timber) to introduce dyes and auxiliaries to customise a basic crust leather. Machines were designed, developed and trialled for these purposes.

More recently, liquid carbon dioxide held under pressure using an autoclave has been proposed. There was also the replacement of water with various organic solvents. The outcome from these investigations is not known.

There is a heavy reliance within each of these approaches to avoid early chemical fixation. For the water based solutions, this involves extremely rapid penetration deep into the matrix, whereas organic solvents introduce products in a non-ionic state. These novel approaches strongly rely on the physical characteristics of the substrate to govern penetration before subsequent fixations.

In conventional leather making, hides' and skins' properties – especially the cross-skin variations – are taken fully into account. Here, the location of agents is managed *via* careful chemical control, precise fixations throughout the structure being the key to a uniform and consistent product.

Where inert polymer spheres are used to part replace float water, chemical control remains central to manufacture. Penetration and fixation is managed as within conventional leather processing.

The leather can be made to specification, but with savings in chemical requirements, and water consumption reduced to 70%.

long awaited means to reduce chemical offers, retain quality and reduce waste.

### 2.3 Chemical savings and reduced environmental demand

Leather is a very sensitive indicator of process success. Judgements are based on aesthetic characteristics, physical performance, the value of the final product, and costed chemical savings. Savings in water in process and energy for heating may be calculated and included too.

It is not possible, however, to determine cost advantage from a lowering of specific components in wastewater treatment. Retanning agents, dyestuffs and fatliquors are complex materials, used in multiple combinations, and beyond the scope of normal analysis. A useful technique is to measure the COD of the float against time throughout the process. These measurements need to include unbound materials introduced from previous processing stages, and subsequent washings from the structure. This shows the uptake of organic content in the process from start to finish, but it does not differentiate between individual components. It provides empirical information, but lacks detail. It is perhaps useful to consider a process that is, say, 70% efficient. Here, the uptake would be 70Kg for every 100Kg of product offered, with 30Kg of unused product discharged from process. If the same result can be provided by a 10% reduction in chemicals, the offer would be 90Kg, and the unused product lowered to 20Kg. The load for subsequent chemical treatment, energy for biological treatment, and management of solids is reduced by 33%. If the process were 60% efficient, a 10% reduction in chemical offer would reduce the load by 25%. On the other hand, at 80% efficiency, the load would be reduced by 50%.

These are hypothetical situations, however, they provide insight into the saving opportunities from more efficient processing. Savings in unused chemicals at source – coupled with the elimination of those pristine products in subsequent wastewater treatment – can be seen as significant.

There may also be components within these products that are environmentally persistent and difficult to address within effluent treatment. Any reductions at source makes end-of-pipe discharge to consent limits more secure. Neutral salts are a consideration too, as these are often contained within commercial products. A lowering of TDS has direct implications within reverse osmosis costings, the water made available for reuse, and management of the residual dry solids.

### 3 CONCLUSIONS

- There are many advantages to adopting to the use of sphere technology for the improvement of chemical uptake in leather processing.
- Designed to purpose, this is a safe and long-awaited means to significantly lower chemical offers in established processes.
- Spheres provide refinement of the mechanical actions applied throughout neutralising, retanning, dyeing and fatliquoring processes.
- Quality is maintained, and scope is offered for better processing as new types of leathers are developed.
- Significant quantities of pristine products presently channelled directly to wastewater treatment can be eliminated.
- It offers better use of resources – a major step towards a more sustainable future.

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# Development and Design of the Software System of the Whole-process Management Platform for Chrome Shavings

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## Abstract

This work introduces the background and the design of the platform for the whole-process management and the control of chrome shavings in the leather industry and the requirement for the software development. The platform contained five functional modules, namely, user management, enterprise information reporting, enterprise information query, early warning of the chrome shaving production, and the transportation management of chrome shavings. Finally, suggestions on the platform development and the design for the whole waste management of chrome shavings were put forward.

**摘要：**介绍了制革含铬革屑全程监管平台开发的背景和整个监管平台的设计，基于此，提出了软件开发需求。进而对监管平台的软件系统进行了开发设计，该软件包含5大功能模块，分别是用户管理模块、企业信息上报模块、企业信息上报查询模块、企业含铬革屑预警模块、含铬革屑运输管理模块；结合实际应用需求，提出了制革含铬革屑全程监管平台软件开发设计的建议。

## 1 INTRODUCTION

With the re-adjustment of the leather industry's structure and the re-orientation of production sites, China has become the center of leather production, processing and trade. Similarly, the leather industry is one of the pillar industries of China's light industry and one which makes great contribution to the national economy and foreign exchange. However, accompanying the processing of leather, some environmental problems have occurred.<sup>1</sup> In the tanning process, about 30%-40% of the raw materials are converted into leather waste, and the vast majority of these wastes are chrome shavings.<sup>2</sup> In addition to a small amount of re-utilisation, most of the chrome shavings are discarded, causing serious pollution in the environment.<sup>3</sup> Hence, considering the requirements of sustainable development, chrome shavings require to be effectively monitored and properly disposed of.

The tanning industry both at home and abroad is lacking any method which can solve the pollution problem posed by chrome shavings, although they can be used as the raw materials of recycled leather and industrial gelatin.<sup>4</sup> Because of low yield, the poor grade and low added value, chrome shavings still pile up, pollute the environment, and cause the waste of resources<sup>5</sup> thereby restricting the sustainable development of the leather industry. Therefore, a real-time monitoring system must be developed to track the disposal status of chrome shavings and improve the safety of chrome shavings.

In this work, a real-time whole-process control

system is developed for the supervision of the processing of chrome shavings from generation to conversion. The supervision system includes a supervision software system, BeiDou/GPS\* data transmission module and a data diagnosis system. This work aims to develop supervision software to monitor the production of hazardous solid waste (HSW). Based on data collection and analysis of electricity consumption, labour wages, taxes paid and the production of chrome shavings, the real production of HSW in leather processing enterprises can be scientifically calculated (\*see Appendix).

## 2 OVERALL DESIGN OF THE SUPERVISORY PLATFORM

The supervisory platform, which includes supervisory software, BeiDou/GPS positioning, and data diagnosis systems, is used to monitor the whole treatment of chrome shavings from generation to conversion, track and regulate chrome shavings inside the tannery. The supervision system based on the BeiDou/GPS positioning system can realise a real-time positioning,<sup>6</sup> tracking and data collection with monitoring of the whole process of the HSW treatment. Based on the data collection and the analysis of water consumption, electricity consumption, labour wages, taxes paid, the production of leather waste, chrome shavings and HSW, this supervision system can indicate whether the data is abnormal or not.<sup>7</sup> If an exception occurs, the supervision department will investigate. The detailed technical routine of the supervisory platform is depicted in Fig. 1.

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