

Lignosulphonates in Tanning

The use of lignosulphonates in tanning was already common knowledge in the last century. Originally only raw lignosulphonates compounded with calcium salts were used with varying results.

Later, however, it was realized that lignosulphonates or the so-called cellulose extracts, have to be free from calcium and iron, if these comparatively cheap tanning agents were to enjoy extensive industrial application.

Our lignosulphonate LIGTAN was the first practically calcium-free lignosulphonate that was also practically ash-free. For this reason it can be said that LIGTAN played a major role in promoting the intensive application of lignosulphonates in the tanning industry.

The excellent suitability of LIGTAN as a tanning agent lies in the irreversible bonding property of lignosulphonates with the skin substances. However, the bonding properties of vegetable tannins and those of lignosulphonate differ in some aspects. Today it is generally agreed that vegetable tannins bind with the skin proteins in at least the following two ways:

- 1) Co-ordination - based on the hydrogen bonding of the phenolic structures of the vegetable tannin on the peptide groups of the skin proteins and
- 2) Saline bonding - between the vegetable tannins and the amino groups of skin proteins.

The lignosulphon acids in LIGTAN bond almost exclusively with the skin proteins, which is why LIGTAN cannot completely replace vegetable tannins in the tanning process.

On the other hand the vegetable tannins provide a comparatively limited bonding with the amino group of skin acids. For this reason one can safely say that the vegetable tanning agents and the lignosulphon acids complement each other in the tanning process. This explains the excellent absorption of the tanning liquids by the skin substance when LIGTAN is added to the tan liquor.

By adding LIGTAN, up to 25% of vegetable tanning agents can be saved irrespective of the type of leather being processed.

The advantage of using LIGTAN can be summarised as follows:

- better leather colour is achieved
- quicker impregnation of the hide
- more efficient absorption of tannins by the skin
- less ground sludge
- cost effective

Tanning with lignosulphonates

Our lignosulphonate can be applied in all tanning processes in which vegetable tannins are used, including pure vegetable or combination tanning.

Except in pretanning, LIGTAN should always be used in conjunction with vegetable tannins. LIGTAN can be used with all vegetable tannins, but the best results are achieved with the catechu tannins e.g. Mimosa, Quebracho etc.

Because of its effect of dissolving the phlobaphenes (bark tanning substances) LIGTAN results in an almost sludge free tanning liquid.

- CLEANER TANNING LIQUID RESIDUE

LIGTAN accelerates the diffusion of the vegetable tannins into the skin substance while simultaneously increasing the absorption capacity thereby shortening the tanning process.

— SHORTER PRODUCTION TIME

The use of LIGTAN permits tanning at a lower pH-count without the risk of grain hardening, thus giving the leather a brighter colour.

— BETTER OPTICAL RESULTS

Furthermore because LIGTAN binds irreversibly with the skin substances, it cannot be displaced by the vegetable tannins, which results in a higher processed leather yield per quantity of tanning liquid used.

— MORE ECONOMICAL

LIGTAN is almost lime and iron free. The ash content is negligible.

— MINIMISES NEGATIVE EFFECTS ON LEATHER QUALITY

LIGTAN is an excellent iron sequestering agent as the iron complex is bound by the lignosulphon acids. This prevents the discoloration caused by iron.

— REDUCTION OF IRON DAMAGE

LIGTAN is used by tanneries in the following ways:

- as admixture in vegetable tan liquor
- as pretanning agent
- as charger agent
- for the retanning of chrome leather

- 1) LIGTAN mixed with vegetable tanning extracts (Soles, quick tanned sole leather, upper, etc.)

LIGTAN is applied in combination with vegetable tannins in all the stages of the various tanning process systems and replaces a significant proportion of those vegetable tannins. The most efficient proportion of LIGTAN tannins depends on the quality of the tanning agent being used; however, in the case of the astringent tannin types, like Quebracho and Mimosa, up to 25% ALF can be added. In the case of less astringent agents a smaller percentage of between 15 and 20% is recommended.

Starting with a proportion of 5 - 10%, we recommend that the amount is gradually increased in the course of the process. To achieve the most efficient absorption of LIGTAN by the skin substance it is important that the pH-count is kept low; 3.3 - 4.3 pH is recommended for the colouring process while approximately 3.5 is recommended for the submersion. These values can vary in specific productions and must be adapted accordingly. Working with lower pH-counts brings correspondingly better results.

It is best to mix LIGTAN with the vegetable tanning mixture during the extraction process. Because of the excellent effectiveness of LIGTAN on the tannins in the bark layer, the amount of sodium bisulphite normally used can be significantly reduced and eventually left out altogether.

The remarkable property of LIGTAN to absorb iron reduces the danger of colour quality loss which can be caused by the iron content in the tanning liquids.

The following experiment was carried out by the Technological Institute of Copenhagen and demonstrates that LIGTAN beneficially influences the absorption of the tanning agents by the skin substances.

Three equal sized and similar pieces of skin were tanned in the following three tanning solutions under exactly the same conditions:

- 1) 100% Mimosa
- 2) 85% Mimosa and 15% LIGTAN
- 3) 75% Mimosa and 25% LIGTAN

In order to obtain reliable comparable data, the pH-value was kept at exactly 3.3 during the experiment and the concentration of the different solutions constant at 7.0 bé. After 30 days the leather pieces were taken out of the solution, washed, drained and analysed. The following interesting observations were made:

Analysis of the tanned pieces of leather

| Tannin liquids | 100% pure Mimosa | 85% Mimosa with 15% LIGTAN | 75% Mimosa with 25% LIGTAN |
|-----------------------------------|---------------------|----------------------------------|----------------------------------|
| Water soluble | 20,9% | 17,9% | 15,5% |
| Ash content | 0,1% | 0,2% | 0,2% |
| Fat content | 0,6% | 0,8% | 1,0% |
| Skin substances | 42,6% | 41,8% | 41,4% |
| Irreversibly bound tannins | 17,9% | 21,5% | 24,0% |
| Yieldl | 235 | 239 | 242 |
| Degree of tannage | 42,0% | 51,5% | 58,0% |
| pH-count of water soluble content | 3,29 | 3,40 | 3,50 |

This shows that the degree of tannage, as well as the percentage of water soluble content corresponds to the quantity of LIGTAN used in the tanning solution. Our table shows that the greater the percentage LIGTAN used in the solution, the bigger the degree of tannage and the lower the content of water soluble.

2) Lignosulphonates in the pretanning process

With all leathers including sole leathers, inner soles, sheepskins, etc. pretanning with LIGTAN depends on the preparation of the skins before the actual tanning process with vegetable tannins is started.

Pretanning with LIGTAN offers the following advantages:

- significant saving of vegetable tanning agents
- acceleration of the vegetable tanning procedure with a simultaneous increase in leather weight yield and/or effectively shorter tanning process

The affectivity of our lignosulphonates in pretanning lies in the bonding properties of the lignosulphon acids with the basic protein groups in the skin substances; to achieve the best absorption of LIGTAN into the skin substances a low pH-count and a high acidity is required. In this way our lignosulphonate can be applied directly before the tanning process.

The amount of lignosulphon acids absorbed by the hide in the course of the process can vary significantly depending on the amount of LIGTAN used to substitute vegetable tannins. Experience is the best judge of how much this should be and it must be adapted accordingly to the type of leather being processed.

Here are a few guidelines for the use of lignosulphonates in the pretanning procedure. Pretanning can be carried out in various ways depending on factors such as the type of leather being produced and the production equipment and organisation (drum or pits).

The general rule is that a dose of 25 kg of LIGTAN per 100 kg Pelt weight results in a tannage of 25%.

Case A

Pretanning in tanning drum

The skins are delimed and bated according to the method used for chrome leather. After that the skins are submerged in a drum containing liquor made up as follows:

100% water

10% salt

1% - 2% formic or sulphuric acid

(% is related to pelt weight) and processed.

After this pickle lasting 4 - 6 hours the pH-count of the solution should be between 2.8 and 3.0

At this stage 20 - 25% LIGTAN (again the % based on the pelt weight) should be dissolved in 50% water and added to the drum solution. The drum must be turned very slowly and the pH-count of the liquor must be checked regularly, and if necessary either sulphuric or formic acid must be added to ensure that the pH-count remains at 3.5.

The skin should be thoroughly processed within 24 hours.

Leather that has been pretanned in a solution containing LIGTAN can now be tanned with vegetable tannins according to any of the usual methods. In order to shorten the tanning time you can start with a tan liquor of 10 bé in the drum. The leather should then be processed within about 48 hours.

Case B

Pretanning in Pits

The advantage of this method is that large costs for barrels and part of the hanging installations are saved. Furthermore the problem of large quantities of used tan liquor takes care of itself.

Renewing used tanning liquor

The used lignosulphonate liquid can be renewed by adding a 12% solution to reach an amount of up to 4.0 Bé. It must be mentioned that 120 kg lignosulphonate powder per cubic meter float results in an increased concentration of 7.0 Bé. 100 kg pelt weight requires an average 110 - 130l lignosulphonate solution.

Temperatures

High temperatures promote the impregnation of the skin substances with LIGTAN by increasing the absorption capacity. Correspondingly a very low temperature of 55°C substantially reduces the absorption of LIGTAN by the skin substances. Based on our experience we can recommend temperatures between 18 - 20°C.

Duration of pretanning

The longer the pretanning, the greater the absorption of LIGTAN. On average thorough pretanning requires 4 days.

The skins

The pelts can be suspended in the pretanning liquid without being delimed; however deliming increases the skins' capacity to absorb LIGTAN and improves the grain elasticity.

Tanning process

The tanning process proceeds according to the production requirements and conditions. At this stage, you can either proceed to the dye process, or in order to shorten production time the pretanned hides can be put straight into drums.

The efficiency of our lignosulphonates in promoting the absorption of tanning agents by the skin substances and in

increasing the yield of tanned leather is depicted in the following table. This was the result of an analysis carried out by a big European manufacturer of sole leather, whose production includes pretanning in pits.

The skins were pretanned in a lignosulphonate liquor for a duration of 1, 2, 4 and 7 days and then tanned in liquor consisting of the same tanning agents under normal conditions. The finished leather was analysed with the following results:

| Duration of pretanning | 1 | 2 | 4 | 7 days |
|--|-------|-------|-------|--------|
| Water soluble content | 22,6% | 21,6% | 21,4% | 21,7% |
| Lime content | 1,8% | 1,3% | 1,5% | 1,7% |
| Fat content | 2,6% | 1,7% | 1,7% | 2,0% |
| Bound tannin | 21,2% | 23,2% | 24,2% | 25,9% |
| Skin substance | 33,5% | 33,5% | 34,7% | 32,4% |
| Yield | 281 | 282 | 288 | 309 |
| Degree of tannage | 59,5 | 65,4 | 69,8 | 80,0 |
| pH-count of water soluble substances | 3,56 | 3,62 | 3,61 | 3,63 |
| % Lignosulphonate content of the total bound tanning content | 0% | 15,6% | 22,5% | 24,5% |

This analysis clearly demonstrates that the degree of tannage as well as the yield of tanned leather increased as a result of the pretanning. Further it is clear that there is a correspondence between these results and the duration of the pretanning.

Closer analysis of leathers pretanned with or without LIGTAN on the basis of their physical properties shows no great deviation when compared.

The leather pretanned with LIGTAN does have a lighter colour.

Cost effectiveness

Under the conditions mentioned above in case B (liquor up to 4 bé; pH-count 4.0, temperature of 18 - 20°C, pretanning duration of about 4 days) the skins will have absorbed enough LIGTAN so that a tanning degree of 15 to 17 can be achieved. If we take for example a tanning degree of 70 for the finished leather, we can expect the percentage of irreversible bound tannins of our LIGTAN to amount to 21 - 25%; with proper pretanning with LIGTAN the yield is increased by 7%.

3) Lignosulphonate as charger and retanning agent (for all weighted leathers tanned with vegetable tanning agents)

Weighting and retanning is carried out on tanned leather. Tumbling works concentrated extracts into the skin to make the leather more firm and to improve its natural resistance to water as well as its durability. In choosing these extracts it is important to pay consideration to their particular properties. For instance Quebracho extract makes leather hard and firm, whereas oak bark extract produces a soft and pliable leather. The remarkable property of our lignosulphonate is that it is absorbed thoroughly and quickly into the leather structure. This gives the leather a good and bright colour. What is more important for tanners is its comparatively small lime content, which means that when LIGTAN is used for charging there is no significant increase in the lime content on the leather.

Apart from the well known vegetable extracts mentioned, sometimes other kinds of agents are built in to weight the leather, which are either salt based or contain sugar. For instance magnesium sulphate or barium chloride is used to

bind the tannins. To prevent shrinkage and drying out during storage, glucose and sometimes syrup and dextrin are used. Whether a higher or lower content of sugar is better depends on the circumstances. Sodium sulphite or oxalic acid can be used to regulate the pH-count. Sodium sulphite is used when the pH-count in acid leather has to be increased. Oxalic acid is used mainly for leather with a high pH-count and bleaches the leather and removes rust stains.

The percentage of filler extracts absorbed can amount up to 30% of the dried leather weight; however, the absorption capacity depends on the preparation of the leather.

The filling process is usually carried out in a drum tumbler according to the two following main methods.

A. Filling with a concentrated tanning liquid

The leather is treated with a 150 - 200% concentrated tanning mixture. The drum should be revolved relatively quickly, so that the friction caused by the tumbling causes the temperature to rise about 45°C. This in turn causes the concentrated tanning liquor to lose viscosity. The absorption capacity of the leather is exhausted after a run of about 12 - 24 hours.

About 60% of LIGTAN is added to the tanning liquor consisting of the tanning extracts normally used. However, when our lignosulphonates are used the same results are achieved without the use of admixtures.

B. Charging the leather with fillers in powder form

After the leather has been tanned in concentrated tanning liquor, rinsed and pressed, it is then processed in a hot air drum with a filling agent in powder form. Acid components, e.g. magnesium sulphate, aluminium sulphate and oxalic acid, which promote the binding of the tanning substances with the skin substances, as well as the tanning extracts are added in powder form.

Our lignosulphonates, which are very well absorbed by the skin substances, result in a good leather colour, and can be used here - either alone or together with other substances. Leather can be oiled during the filling process. The oils can either be added to the filling mixture or straight afterwards.

In practise one tries to heat the contents of the drum to between 45 and 50°C, either by pumping in warm air or increasing the friction caused by the tumbling of the leather in the drum. After 1 - 2 hours the charging process should be completed.

4) Lignosulphonates in the retanning of chrome leather (Boxcalf, ox and goatskin leather)

Chrome tanned leather has a great capacity for absorbing lignosulphonates and our lignosulphonate is broadly used in the retanning process of chrome leathers.

Lignosulphonate is either used alone or together with vegetable tanning agents in accombined tanning process.

Our lignosulphonate LIGTAN results from a so called ammonia disintegration process which occurs in cellulose production. This substance, ammonia-lignosulphonate, has the special quality of spontaneously bonding with chrome complexes, and this has a beneficial effect on the retanning process.

LIGTAN acts as a neutralising agent when used in combination

with chrome tanning. This is because it forms a bond with some of the basic protein groups in the leather while simultaneously reacting with some of the chrome complexes, with the interesting result that the chrome complex is masked and the cationic charge of the leather is diminished. This in turn means a decrease in the normally high rate of reaction between chrome leathers and anionic dyes and vegetable tanning agents. It can be said that LIGTAN promotes evenness in the dye process when acidic dyes are used and in retanning which vegetable tanning agents. Correspondingly the binding capacity of the basic dyes and cationic auxiliary agent is more efficient.

LIGTAN has the important quality of being absorbed particularly well by the softer skin substances, which gives the leather better buffing properties. This is particularly important in the production of Nubuk and Suede leathers. This property of LIGTAN also enhances the grain as it firms the grain structure, which is particularly important in the production of leather uppers.

LIGTAN works as a dispersion agent in oil tanning liquors. This means that the application of LIGTAN promotes the absorption of fatty substances into the leather; in this way the efficiency of greasing agents in the processing of soft and viable leathers is improved by the application of LIGTAN.

Our lignosulphonate can be used alone or in combination with vegetable tanning agents and resin tannins.

It is recommended that LIGTAN is added to exhausted chrome tan liquor before neutralising, in order to save on one process and at the same time gives the leather a good feel. Our experience has been that an amount of between 3 and 5% in relation to the folded weight is about right.

Combination tanned leathers

About 40% LIGTAN is mixed with the vegetable tanning agents. Our lignosulphonate promotes the absorption of these agents by the leather substances and thereby significantly increases the impregnation of the leather.

Because lignosulphonates have a bleaching effect, leather can also be dyed in pastel tones and colours.

Because of its very good binding and impregnation properties, our lignosulphonate is especially good in combination tanning of sole leathers. It promotes a greater absorption of tannins by the leather substances and therefore a more efficient yield, without affecting the durability of the leather. Yet another tanning problem – this time in the process of sole leathers – which can be solved by our lignosulphonate LIGTAN.

LIGTAN – Product Data

% based on powder form

| | |
|---------------------------|---------------|
| Description | powder |
| Volume weight g/l 20 deg. | 600 |
| Colour | light brown |
| Total solid content | 95 (+/-2) |
| Solubility | 99 |
| Ash (700°-7h) | 5,5* |
| Calcium (Ca) | 2,5* |
| Nitrogen (N) | 3,5* |
| Amoniacalnitrogen | 3* |
| pH (in 2% solution) | 5,2 (+/- 0,5) |
| Reducing matters | < 15 |
| Sulphur (S) | 7.5* |

* Typical values!

Please note:

The data information contained herein is believed to be true to the best of our knowledge. No warranty or representation for which Otto Dille assumes legal responsibility is implied. The information refers only to the controlled product described herein and does not relate to use of the product with any other materials and processes. Otto Dille encourages customers to consider, investigate and verify information for their uses. Otto Dille assumes no responsibility for damage to property or equipment or third party person as a result of misuse or handling of this quality product. Customers are encouraged to conduct appropriate testing before use of the product. The user must be assure that use of information contained herein is done according to all applicable laws regulations.

REV. 06/2004