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WHITEPAPER- TANNING WITH TRIOSE (KARL FLOWERS)

TRIOSE TANNING–

A BIOGENIC SOLUTION TO CIRCULAR LEATHER PROCESSING.

WHITEPAPER BY KARL FLOWERS

SUSTAINABLE CHEMISTRY

THE MESSAGE IS CLEAR, MODERN TANNING CHEMISTRY NEEDS TO COME FROM GREEN CHEMISTRY BEGINNINGS AND SHOULD LEAD THE FIELD.

The American Chemical Society[1] outlines those Green Chemistry aims as:

- **Prevent waste**
- **Atom economy**
- **Less hazardous manufacture**
- **Design benign chemicals**
- **Benign solvents and auxiliaries**
- **Design for energy efficiency**
- **Use renewable feedstocks**
- **Reduce derivatives (intermediates)**
- **Catalysis**
- **Design for degradation**
- **Pollution prevention monitoring**
- **Accident prevention chemistry**

Presently, no tanning chemical meets all the green chemistry aims listed above. New generation tanning agents should always strive to meet as many of these aims as they can. One of the most interesting sources of new chemistry is the use of waste streams[2]. Many industries have decided to use these streams as desirable chemistry. Waste products from vegetable oils are used to make a monosaccharide called triose that can then be used to effectively create leather.

SUSTAINABLE TANNAGE

THE FUTURE OF TANNING CHEMISTRY IS DEPENDENT ON NEW TANNAGES THAT MAKE LEATHER THE MATERIAL OF CHOICE

Carbohydrates have been used in leather tanning before with limited success.[3,4,5,6,7]

Simple Short chained carbohydrates have been used as fillers or as anti-swelling agents[8] and have been identified aspossible new chemistries[9]. Making non-edible carbohydrates from waste streams, which also fulfil many of the green chemistry goals mentioned above is one of the impressive features of this technology. Another impressive feature is that the product is another impressive feature is that the product is essentially a monosaccharide - in later life these compounds are biodegradable, and so is the tanned leather made from them.

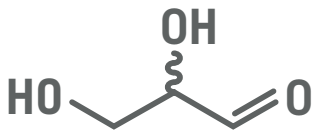
THE OUTCOME OF THIS WHITE PAPER IS TO HELP SET THE SCENE FOR THE NEXT GENERATION OF TANNING AGENTS THAT ARE EMERGING IN LEATHER. NEW TANNING AGENTS CANNOT BE JUST MORE OF THE SAME - AND THEY CANNOT WORK AGAINST THE ENVIRONMENTAL AND SAFETY PRINCIPLES WHICH ARE NOW EMBEDDED BY THE TANNING INDUSTRY.

The 10 goals of green chemistry are widely acknowledged[1]. To meet these aims triose chemistry has been developed for use in modern tannages. The list below lists the characteristics of triose chemistry that meet those:

- **Must come from renewable raw material sources** (#7 Renewable feedstocks)
- **Reduces the need for derivatives in chemical manufacture** (#8 Intermediates)
- **Manufacture of tanning agent has low risk** (#3 Less hazardous manufacture)
- **Manufacture of tanning agent and the tanning process uses very little energy input** (#6 Energy efficiency)
- **Easy to penetrate through lime split, or unsplit pelt** (#2 Atom economy)
- **Must provide the same, or higher tanned leather performance, as compared to current tannages** (#1 Prevent waste)
- **Ideally must give no colour to the tanned material** (#1 Prevent waste)
- **Uses no solvents or auxiliaries** (#5 Benign solvents and auxiliaries)
- **Must not be harmful to the end user of the product or to the environment** (#4 Benign chemicals)
- **Tanned leather should be completely biodegradable** (#10 Degradation design)

MAKING TRIOSE TANNING AGENTS

A highly renewable vegetable oil waste is converted into a triose, see image on the right. The making process generates heat allowing the process to have low energy requirements. Final calculations suggest it has a much lower carbon footprint when compared to other tanning agents.



The chemical structure of triose.

TRIOSE IS MADE FROM VEGETABLE OIL WASTE

Simplicity is key in the tanning business. Tanning agents with complicated application systems (that are difficult to follow) or that require complicated equipment will never last long in the leather business. The same principle can apply to the manufacture of chemicals. The manufacture of triose means that multiple ingredients that need to be transported from global locations would not meet the modern green chemistry aims.

Triose comes from one ingredient and is efficiently converted into the final product and is manufactured close to where the waste stream is located - shrinking those carbon miles. The nature of the triose-making process means that waste streams from the manufacture are virtually zero - a highly efficient atom economy. The making also uses no fancy solvents or auxiliaries and does not use any intermediate steps that would add to the footprint of the process.

The making of the triose does not use poisonous chemistry that would be harmful to chemical workers- no global manufacturer or product restricted substance lists contain triose as a listed chemical.

Triose is designed to be as benign as possible, as described by the American Chemical Society Green Chemistry principles Triose is designed to react with the leather protein which enhances its tanning performance and makes it easy to use by tanning workers.

TANNING WITH TRIOSE

Tanning agents that are replacements to chromium are currently in high demand as tanners want the versatility to make high quality leathers on a range of starting materials (e.g., unsplit hides, pickled sheepskins, or lime-split cattle hides). Catering to the processing requirements of the factory, triose tanning agents can be used for all start points.

In the past, unmodified carbohydrates materials (that were generally large) were used with limited success. Dialdehyde starch is still used in some applications, but the large size of these chemicals meant that they couldn't be easily used on dense, compact, or thick material- the tanning agents would get caught on the outside, leaving the inside layers untanned.

Triose is so small and can be described as unreactive unless certain conditions are met- this means that even on thick material the chemical can penetrate completely. After a complete penetration the tanner can then create the conditions for fixation when the tanner needs it to react.

THE TANNING AGENT IS SMALL ... REACTS WHEN THE TANNER NEEDS IT TO REACT

In making triose, wet-white knowledge of complicated tanning processes, is not required. Strict control of process parameters, particularly in tanneries that do not have state-of-the-art facilities is greatly reduced.

Catching up with technology leaders is simplified using triose tanning agents as deep chemical understanding is not required

AFTER LIFE

LEATHER ENVIRONMENTAL FATE

Independent testing results (ISO 20136, ISO 20200) show that leathers made using triose are fully tanned when compared to untanned collagen and that they degrade significantly in the 28 days of the biodegradability test and have disintegrated within 20 days of composting.

Figure showing biodegradeability OXITOP- measurement

Figure showing plant response test (ecotoxicity)

BIODEGRADABLE AND COMPOST-FRIENDLY

The triose reacts with the leather fibre and stabilizes the structure to ensure that the leather product will be durable and resistant to microbial attack during its working life. When the leather product is placed into its afterlife the fibre structure is designed to fill with water, allowing bacteria and fungi in. The natural collagen fibres are available to breakdown allowing the leather to collapse in on itself disintegrating and being changed into biomass. Independent analysis of plants grown in triose leather compost/ soil mixes showed no difference to plants grown in compost soil mixes with no leather in them- making them ecologically benign, containing no substances of concern.

In the afterlife, the consumer can return the triose leather into soils which will recycle the rich carbon and nitrogen elements of the leather back to the beginning of the natural cycle again- closing the loop.

PREVENTING WASTE

WHAT IS BETTER THAN TANNERIES WHO PRODUCE BY-PRODUCTS THAT CAN ALSO BE SOLD TO INCREASE THEIR SUSTAINABILITY?

As a major part of the environmental sustainability efforts of tanneries and leather product manufacturers, the solid waste that comes from splitting, shaving, buffing, trimming, and cutting can change from a problematic disposal problem to a situation where the waste can be a valuable generator of income (helping to cut costs and environmental impact).

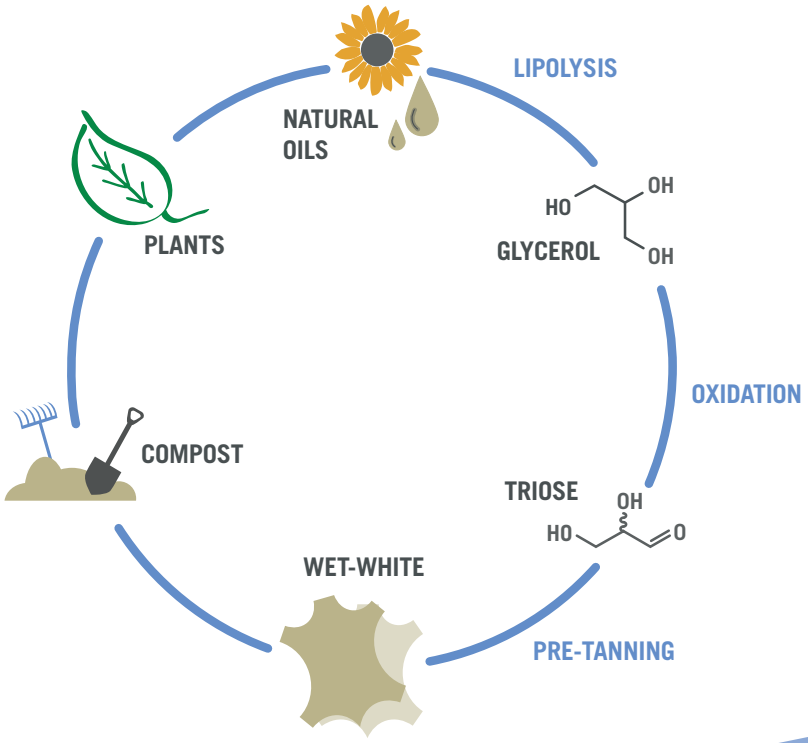
As the number one item on the 12 principles of Green Chemistry, the use of renewable waste vegetable oil as an ingredient in triose and the fact that triose tanned leather going into waste streams can be prevented, makes triose tanning a leader in Green Chemistry waste prevention.

Brands and retailers consistently ask their supply chain how wastes can be prevented so they can tell their consumers how well the chain is performing. Cutting waste forms one of the largest concerns - especially for large panels of aniline leather (which produces some of the lowest cutting yields). Tanning with triose doesn't mean that the cutting waste needs to have no value.

TANNERY WASTES THAT CAN BE USED IN THE FOOD OR AGRICULTURAL INDUSTRIES

Tanned solid by-products (e.g., splits and shavings) produced in a tannery, that makes leather using triose, are very simple to handle, recycle, or transform into other useful materials that other industries can use.

The whole supply chain can lower the cost of manufacture through effective use of all material inputs.



NEW GENERATION LEATHER PRODUCTS

Deep shades have typically been a difficult ask for most wet white systems. The sites on the leather fibre where the tanning material binds are also the binding sites for the dyestuffs. Other wet white tanning systems struggle to give deep dye shades and the fastness levels that most customers are expecting.

The dye shades that result from the triose results from the ability of the triose to have additional bonds with the dye. One of the advantages of chromium tanned leathers is that chromium offers extra binding sites for the dye. Triose doesn't use the same binding mechanism as chromium, but the tanning agent does allow the dye to find a binding place.

The triose tanning agent is so effective at holding dyes that it could even be used as a dye binding agent in other wet white tanning systems. The dye intensity and fixation are a key advantage of this tanning agent. The dye and fatliquor exhaustion allow low chemical waste in the post tanning stages- resulting in a tannery that is not responsible for feeding an effluent plant but is responsible for making high performance leathers.

Tight-grained automotive, shoe-upper, and smooth bag leathers can be easily realised. These tanning agents can also make loose leathers for floating grains and mill-types as well. The fullness, tightness, and softness can also be tailored using the triose tanning system.

A WIDE RANGE OF LEATHERS CAN BE MADE

Wet white tanned materials have been around for 30 years, but there have always been one or two leather types that sit outside their capability range. Triose tanned leathers have enormous versatility. All high-quality leathers are well within the ability of the triose tanning system.

A process that makes a tanning agent (triose) out of a renewable waste material is presented. The process to make triose is done where the waste is created and using an efficient process. The making process is at a low temperature to keep energy and carbon footprints low.

Trioses are small and penetrate thick (or thin) material with ease. The tanning liquors contain the triose and have a gentle tanning mechanism that minimises risk for the operator.

The uptake of the chemistry means low temperature processing, efficiency, profitability, and leather by-products that won't be part of the solid waste headache.

The final leathers are what a modern tanner expects – excellent disintegration in composting allowing products to be part of the circular bioeconomy.

THE FUTURE OF TANNING CHEMISTRY IS DEPENDENT ON NEW TANNAGES. THAT MAKE LEATHER THE MATERIAL OF CHOICE

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