A modern view on vegetable extract products

Vegetable tannins are compounds of vegetable origin from various parts of trees and plants.

They are used and known from the tanners for quite two thousand years (1) by different civilization (Mesopotamian, precolombian…) and till the XIX century mainly into the form of raw, untreated material like bark. Than chemical companies start to increase he yield of tan content by proceeding into extraction with autoclave and spraydrying leading to extract such as Chestnut or Mimosa having more than 70% tan concentration.

But still the main use of this vegetable extracts was the process of vegetable tanning or heavy vegetable retans. Famous East Indian tanning (I.E tanning) is one of this article where myrobolam (terminalia chebula), avaram (assia auriculata), Konnam (Cassia fistula) extracts or myrobolam + mimosa (acacia mearnsii) extracts where mainly selected based on high tan content. (2)

With the boosting of automotive leather article and the trend to use and promote natural products, more and more application of vegetable derivatives found its way into modern process of leather.

As we will see, today vegetable tan could be used to reduce or prevent the formation of Cr VI , promote antioxydation propertie, enhance burnishability and glazing, fix cationic dye and nitrogen resin, gives fullness to wet-blue leather and much more.

Nowadays, the important thing to select is more the specifics functions of the vegetable product than only the tanning content. We will also see how **STAHL** with its specific line of vegetable range select, purify and blend the different raw material to propose the right natural chemical in line with the article specifications.

RAW MATERIAL

In the below table, the main part of plant used to source tannins

barks	woods	Fruits & pods	leaves	roots	Plant galls
Wattle (Acacia sp)	Quebracho (Shinopsis sp)	Myrobolam (Terminalia chebula)	Sumac (Rhus sp)	Canaigre (Rumex hymenosephalus)	Oak (Quercus sp)
Oak (Quercus sp)	Chestnut (Castanea sp)	Valonea (Quercus aegilop)	Gambier (uncaria gambier)	Rhubarb (Rheum rhabarbarum)	Allepo (Quercus infectoria)
Eucaplyptus (Eucalyptus sp)	Oak (Quercus sp)	Divi-divi (Ceasalpinia coraria)	Dhawa (Anogeissus latifolia)		Tamarix (Tamarix articulia)
Avaram (Cassia auriculata)	Cutch (Acacia catechu)	Algarobilla (Ceasalpinia brevifolia)			Pistacia (Pistacia sp)
Babul (Acacia Arabica)	Wandoo (Eucalyptus wandoo)	Tara (caesalpinia spinosa)			Chinese (Rhus semialata)
Willow (Salix caprea)		Teripod (Caesalpinia digyna)			
Mangrove (Rhizophora sp)		Cashew husk (anacordium occidentale)			

The main raw materials selected by Stahl are:Anacardium occidentale is an evergreen tree that growth to an average height of twenty meter and mainly cultivated for the collection of cashew nut (food industry) and the cashew nut shell liquid present in the fruit (used in varnish and paint industry)

Husk (residue after peeling the kernel) contains a fair percentage of tannin and the main advantages are the high percentage of antioxidant epicatechin and tocopherol which both act as free radical scavenger.

Husks are washed, dried, finely grinded, sieved and blended into a proprietary recipe with other useful ingredients to adjust pH and astringency.

Stahl is marketing this product under **Synektan VW** trade name. It is highly recommended for strong lightfast dye, white leather with a vegetable character and to enhance heat fastness on chrome free leather.

Caesalpina spinosa is a shrub or small tree up to 5 m high. It is called “tara” and grows in the forests and semi desert areas of the Interandine region.

For tanning purpose the pods are the part of the tree which is selected. It contains high percentage of tannin (above 50%) from the hydrolysable family as well as gallic acid.

These components make the product ideal for chrome free tanning with a good lightfastness.

The most important parameter is the de-ironing process and the final particle size. STAHL is managing this difficulties with integrated magnetic grinder and accurate, controlled sieving process. It is marketed under **Synektan TP trade name**

Rhus coriaria, is commonly known as “sumac”, are shrubs and small trees that can reach a height of ten meters. This specific species is cultivated in Mediterranean area.

The leaves contain high percentage of gallotannin and natural free radical scavenger like ascorbic and gallic acid.

For tanning purpose,leaves are collected, dried, grinded finely than sieved.

Beeing prone to iron and having high content of chlorophyle, STAHL is marketing a proprietary blend who has been bleach chemicaly, adjusted to right pH and made less sensitive to iron.

The final product is marketed under **Synaktan SU** trade name. It is an ideal product for chrome VI scavenger, nubuck and print retention article.

Uncaria Gambier is a wild shrub which grows in Malaysia and Indonesia.

Leaves contain high percentage of tannin, waxes and useful mineral. The leaves cannot be grinded as it is and extraction has to take place before. The extract is then dried into cube and crushed into fine powder. The main tanning extract is low molecular weight polyphenol of catechin structure.

Stahl gambier is bleached (to remove red ton), but not de-waxed to allow strong reactivity while burnishing or glazing process. This is an ideal compact product for shoe upper article. STAHL market gambier extract based product under **Synektan GA** trade name

Chestnut belong to castanea species and in tannery industry more specifically castanea sativa which growth in middle and south Europe, mainly France and Italy.

From the wood, the tan is extracted ,sweetened and spaydried. It contains mainly vescalagin and castalagin derivative. The yield on tan content is rather high.

STAHL has developed two important products based on Castanea sativa. In the first one **Synektan R-982** , the polyphenol is copolymerized with acrylic monomer leading to an unique resin like vegetable polymere giving full, round leather with fairly tanning properties and good resistance to oxidation. In the second one **Synektan CC**, the chestnut is double bleached and made less astringent than crude extract. This allow fast and homogeneous penetration specially on wet-blue leather, making it ideal for vegetable like article and giving the specific spring of chestnut.

CONSTITUTION

Vegetable tannins could be defined as polyphenol of various molecular weights.

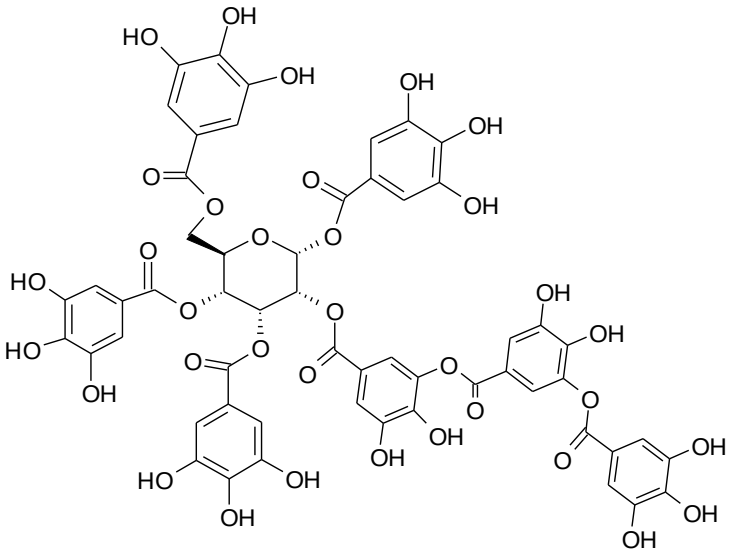
As for the syntan, an optimized size is required for the tanning purpose which is linked to the molecular weight and the number of free OH groups. Optimum tanning effect is founded with molecular weight from 600 to 3000.

Below 600, virtually no tanning action takes place and above 3000 the formation of insoluble polymer leads to poor diffusion of the polyphenol (this insoluble substances are called phlobaphene for the catechic tan and bloom for the hydolysable one)

Vegetable tannin could be classified in two main groups:

1. Hydrolysable tannin
2. Condensated tannin

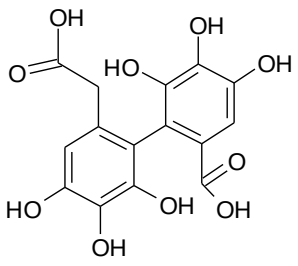
The first group, hydrolysable tannins, are ester of gallic acid with carbohydrate (sugar) with various ratio of gallic acid linked to the glucose central molecule. Tara is mainly one glucose linked with 3 gallic residus and one or two digallic, so get an average molecular weight of 1000-1100:



Tara gallotannin

Sumach, Divi-divi, belong also to this group.

Among hydrolysable tannin we have also ellagitannin with a very complicated structure based on ester of hexahydroxydiphenic acid and are of higher molecular weight than the gallic derivatives. Practically this kind of tannin gives firmer leather due to high binding capacity with the fiber. The product is acidic in nature and so gets self fixing properties, this was the main use in older time of Oak extract in vegetable pit.

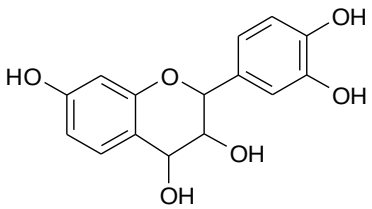


Hexahydroxydiphenic acid

Chestnut, oak, myrobolam, valonea belong to this group.

The second group, condensated tannin does not hydrolyze but are prone to oxidation and polymerization .So they will be not lightfast but will bring high fullness to the leather (higher molecular weight).

The structure is based on combined flavonoid derivative such the flavanne-3-ol or flavanne 3,4 diol with various degree of condensation.



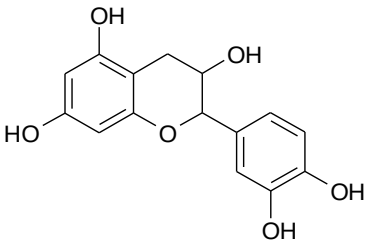
Flavanne 3,4 diol

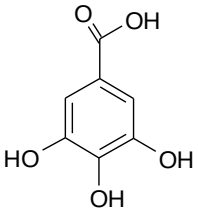
Catechic tannin are polymer of the above structures. Quebracho has more than 50% of it component being above the pentamere from molecular weight 1000 to 15000. Gambier extract has lower polymerization components and less tan. This is compensated by the presence of natural gum and thickener which gives to this particular product its properties of tightness, fullness and glazing ability.

Chemicals present in the vegetable tan having less than 600 Molecular weight are sugar, organic acid like gallic acid, pectin,lignin, antioxidant and gum. They are very important actually in the modern taning/retaning recipe as they give some specifics performance to the product.

Antioxydant are very usefull as they prevent the leather from heat yellowing and in case of chrome tanning from the formation of Cr VI. All polyphenol has antioxidant properties but it has been shown (3) that the activity is higher with low molecular weight polyphenol. So it is not a surprise that product having high percentage of gallic acid and epicatechin as such, like cashew husk (one of the main component of **Synektan VW**) gives excellent whitening effect to the leather. This is particularly true with **Synektan VW** because the other components of this vegetable extract are organic acid derivative and gum which can combine easily with the chrome and gives full, white and light fast leather. Leather retan with **Synektan VW** are much whiter than Tara retanned. The dye color is not affected and is very bright because of the mordant properties of the organic acid.

Exemple of structure in **Synektan VW**





Epicatechin Gallic acid

Sugar are polysaccaride. They give some moisture balance to the final leather bringing a better control of the softness. Somehow they act also as organic filler when the polymerization rate is higher.

So despite a low tanning power of **Synekatan VW**, (10%) this kind of vegetable bring excellent properties to leather superior to classic commodity tanning extract

Dimer and pentamere of Gallic acid is one of the best scavenger of CrVI and this is why tannin like Tara (**Synektan TP**) or Sumach (**Synektan SU**) are highly recommended for this purpose has they contains naturally a fair percentage of this component.

PRACTICAL USE AND COMPARISON

We have seen that components of vegetable extract have all an influence to the leather characteristic and, if the nature of tan (hydrolysable or condensate) is important, the non tan (antioxidant, acid,polysaccarariide filler, gum…) also.

STAHL contribution to the vegetable range is to select and valorize some of the main chemical present into the vegetable raw material to gives solutions and opening new doors to the tanner.

STAHL vegetable	Main bases	Color on leather	Leather softness	Antioxidant activity	Grain retention	Tan content	Filling action	Grain tightness
Synektan SU	Tannic acid gallic acid	Light green	+++	++	+++	++	+	+++
Synektan TP	Galloyl ester Gallic acid	Off white	++	+	+	+++	+	++
Synektan VW	Epicatechin Tocopherol	White	+	+++	++	+	+++	++
Synektan GA	Epicatechin Wax, gum	Light brown	++	+	+	+++	++	+
Synektan CC	Ellagic acid vascalagin	Light brown	+	-	++	+++	+	+++
Synektan R-982	Acrylic acid Ellagic acid	Light beige	++	-	+++	+	+++	+
			- hard + not soft ++ soft +++ very soft	- nil + fair ++ good +++ strong	- nil + fair ++ good +++ strong	+ 10-20 % ++ 20-30% +++ >30%	+ fair ++ good +++ strong	+ fair ++ good +++ strong

Characteristic table

Knowing the effect and value of the main chemicals present into the vegetable, tanners could combine the products to achieve its target. As an example, **Synektan VW** with its high content of antioxidant could be used alone with **Synektan TP** for chrome-free automotive article. **Synektan TP** will bring the tan content fairly lightfast to tan the leather and **Synektan VW** will improve the heat and lightfastness to a higher degree.

In the same kind of article, tanner could stay in the vegetable side during retanning, using **Synektan R-982** giving roundness and print retention as a retanning compact system which can positively replace syntan+ acrylic + vegetable.

Some of the vegetable combinaison are also very usefull during dyeing process. **Synektan SU** and **Synektan VW** are excellent mordant for basic dyes, meaning they combine easily with the cationic dyestuff, improving its fixation and avoiding bronziness, two common drawbacks of basic dyes.

Synektan VW enhances also the deepness of acid dyes as it doesn't contain any sulfite and as we have seen some strong antioxidants which stabilize the dyestuff strength.

A last example is shoe upper article where limited stretch some inner softness, tight grain and good reactivity to heat are the basics parameter. It is well approuved that gambier extract such as **Synektan GA** are the best for that purpose. Here also a combination of **Synektan GA** with **Synektan CC** could be the right solution to combine the advantages of gambier with the high tightness characteristic of chestnut family.

At last it is always advisable to combine more “synthetic” material when using vegetable derivative products in order to optimize the effect. Here below a list of product this has proved its efficiency with vegetable extracts:

- **BEMANOL SW**: enhance penetration speed of vegetable extract. Prevent iron patches
- **SYNEKTAN NBN,LE**: High dispersing effect of polyphenol
- **SYNEKTAN GTA:** Pretanning syntan based on masked glutaraldehyde. Allow chrome-free article with optimium percentage of vegetable extracts
- **SYNEKTAN PN:** Dihydroxyphenyl sulfon syntan. Combine with **SYNEKTAN VW** gives white and lightfast leather
- **CORILENE SIT, CORILENE LN:** Highly efficient, stable fatliquor on chrome-free leather containing high amount of vegetable extract.