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I hereby recommend that the thesis prepared under my supervision by Al. Lee Cropton entitled Particle Size Study of Influence of a Synthetic Inorganic Material on Aqueous Diffusions.

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PARTICLE SIZE STUDIES  
THE INFLUENCE OF A SYNTHETIC TANNING  
MATERIAL ON QUEBRACHO INFUSIONS

A dissertation submitted to the  
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### ABSTRACT

The effect of tannin concentration and the addition of synthetic tanning material on the particle size of ordinary quebracho tannin - water infusions, was studied. The study was made by ultrafiltration. The results show no apparent change in particle size either with change in tannin concentration or addition of synthetic tanning material, within the limits of concentration studied.

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### Introduction

Two of the most interesting and important phenomena induced by the addition of a synthetic tanning material to a vegetable tannin infusion are the solubilization of phlobaphenes and stabilization of the infusion against electrolytes. As has been previously pointed out (3) the solvent action of a synthetic tanning material may be explained by one, or a combination of two or more, of the following hypotheses:

1. the action of the synthetic tanning material is primarily dispersive, forming smaller particles of tannin which are more easily dissolved in the solvent.

2. the synthetic tanning material unites chemically with the vegetable tannin to form a more lyophilic colloid.

3. the synthetic tanning material is adsorbed on the vegetable tannin particles and the resultant particles are more lyophilic than the original vegetable tannin particles.

The stabilization of vegetable tannin infusions against electrolytes may also be explained by these hypotheses (4).

### Purpose

In this study ultrafiltration is used to investi-

gate the size of the particles in ordinary quebracho infusions at various concentrations and in ordinary quebracho - synthetic tanning material infusions.

### Historical

There has been much discussion as to the mechanism by which synthetic tanning materials solublize vegetable tannins. On the addition of a synthetic tanning material to a vegetable tannin liquor containing phlobaphenes it can be easily seen that the large phlobaphene particles are reduced in size. Pollak (9) states that this is the only influence exerted by the synthetic tanning material - that it has no effect on the solubility of natural tannins. However, Stiasny and Orth (11) state that the synthetic tanning material disperses not only the coarse (slightly soluble, relatively lyophobic, phlobaphene - like) particles, but also disperses the smaller particles which do not settle out of the infusion when it is permitted to stand. They also state that the synthetic tanning material does not combine chemically with the vegetable tannin but merely reduces the particle size. Stiasny and Orth based their conclusions on the experimental study of the influence of Gerbstoff F on tannin fixed by hide powder from vegetable tannin infusions, upon the decrease of insolubles, and the stabilization of the infusion against sodium chloride. Stather and Lochner (10), study-

ing a number of synthetic tanning materials, using the technique employed by Stiasny and Orth (11), drew the same conclusions. Thuau and Hough (12) differ with Stiasny and Orth in that they believe that the synthetic tanning material combines chemically with the tannin of the extract to form a more complex tannin. As support for this conclusion Thuau and Hough cite the color change observed when synthetic tanning material is added to a vegetable tannin. A further indication of a possible reaction between the synthetic tanning material and the vegetable tannin is shown by the marked influence of a synthetic tanning material on the "retained" and "associated" waters in vegetable tanned leather (1).

The best evidence for the dispersive action of a synthetic tanning material is that reported by Stiasny and Orth (11), and confirmed by Stather and Lochner (10). However, their method is based on the assumption that an increase in the stability of a colloidal system toward electrolytes is due to a decrease in the size of the particles of the disperse phase. As has been pointed out previously, this assumption is not necessarily true.

### Procedures

The ultrafiltration procedures, apparatus, and membrane preparation and calibration have been described in a previous publication (2). The membranes used are prepared from an ethyl alcohol-ether-acetone-amyl alcohol solution of Parlodion. The Average Pore Diameter is controlled by the addition of glacial acetic acid or water. These membranes are calibrated by an application of Poiseuille's Law. In the ultrafiltration of tannin infusions successive samples of the ultrafiltrate from the membrane under consideration are analyzed for tannin. The maximum amount of tannin in the filtrate is then recorded. These maxima, plotted against the Average Pore Diameters of the membranes used, leads to the determination of the Limiting Pore Diameters, which is proportional to the average particle diameter.

The liquors were prepared for ultrafiltration by dissolving the desired amount of ordinary quebracho extract in 900 ml. of distilled water at 85° C. The synthetic tanning material was added in the water. The quebracho - synthetic tanning material - water mixture was heated in a water-bath until the extract was completely dissolved. The infusion was permitted to stand at room temperature overnight, made up to one liter, and then filtered with the aid of kaolin. This filtered infusion was

then used in the ultrafilters.

Since the ultrafiltration procedure requires the analysis of small quantities of filtrate, frequently with very low tannin concentrations, a sensitive method of tannin estimation is required. As a means of tannin estimation we used a turbidimetric method based on the nephelometric method developed by Grassmann, Chu, and Schelz (8).

The tannin content of the solutions analyzed by this method should be between 0.5 and 3.5 mg. of tannin per 100 ml. Analyses of solutions containing more than 3.5 mg. of tannin per 100 ml. are subject to considerable error. In extreme cases solutions containing less than 0.5 mg. tannin per 100 ml. can be analyzed with reasonable accuracy. The non-tannin fraction from A.L.C.A. Official Analysis shows some tannin by this method, but this correction is so slight that it could be neglected in this study. In the concentrations used in the study the synthetic tanning material had no apparent effect on the analyses. However, at relatively high concentrations the synthetic tanning material caused an apparent increase in the amount of tannin present in a solution of known concentration.

The following solutions are used in the turbidimetric method of tannin estimation:

1. Cloud Reagent
2. N/2 sodium acetate
3. N/2 acetic acid
4. Standard tannin solutions
5. Unknown tannin solutions

The standard tannin solutions are prepared from a tannin extract of known tannin content, the analysis being made by the Official A.L.C.A. method. This primary standard must be the same kind of tannin as that being studied. The primary standard solution is prepared by dissolving a portion of the extract containing 1.00 g. of tannin in 900 ml. of distilled water at 85° C. The solution is permitted to cool and is held at room temperature overnight. It is then made up to one liter with distilled water. The standard solutions for the determination are prepared from the primary standard solution by making the proper dilutions.

These materials are used in the preparation of the cloud reagent:

- |                         |         |
|-------------------------|---------|
| 1. urea                 | 80 g.   |
| 2. 40% formaldehyde     | 375 ml. |
| 3. distilled water      | 125 ml. |
| 4. N. hydrochloric acid | 5 ml.   |
| 5. N. sodium hydroxide  | --- ml. |

The cloud reagent is prepared as follows:

The water and formaldehyde are added to the urea in a one liter, round bottomed flask, equipped with a stirrer, and a reflux condenser. The flask is heated in an oil bath. After the urea has dissolved in the formaldehyde solution the hydrochloric acid is added with stirring. The solution is stirred 10 minutes in the cold. Heat is then applied so that the temperature of the bath is raised to 120° C. in one hour. When the reaction mixture boils (b.p. 98° C.) the temperature of the bath is permitted to fall to 115° C. and is maintained at this temperature for 2 hours with continuous stirring. The white slurry which appears during the reaction should completely disappear before the end of the heating period. The reaction product is permitted to cool slowly and is stored at room temperature for one week. At the end of this aging period, the pH of the product is adjusted to approximately 10 with N sodium hydroxide. The cloud reagent is then ready for use.

For the estimation of tannin, buffered cloud reagent is freshly prepared (at most this solution should not be more than 30 minutes old). This buffered cloud reagent is prepared by mixing 25 ml. of the cloud reagent, 50 ml. of N/2 acetic acid, and 50 ml. of N/2 sodium acetate in a 250 ml. volumetric flask. The flask is then filled to the mark with distilled water, shaken thoroughly, and the buf-

ferred cloud reagent is ready for use.

A Klett - Summerson Photoelectric Colorimeter equipped with a No. 22E filter is used for the determination. The instrument is standardized against distilled water.

The analyses are carried out as follows:

A twenty ml. aliquot of the tannin solution is placed in a 50 ml. beaker, then a 20 ml. aliquot of the buffered cloud reagent, freshly prepared, is added with stirring. The mixture is then stirred occasionally during a 40 minute aging period. At the end of this period the turbidity is determined by means of the colorimeter. The aging period must be timed fairly accurately, with 0.5 minute.

The colorimeter readings obtained with the various solutions of known tannin content are plotted against the tannin content. The tannin content of the unknown solutions are then read from this calibration curve. A new calibration curve should be determined for each lot of buffered cloud reagent.

Infusions containing 5, 10 and 20 grams of ordinary quebracho extract per liter were used in the study. The synthetic tanning material - quebracho extract ratio varied from 0.1 to 0.4 g. of synthetic tanning material per gram of quebracho extract. The higher synthetic tanning

material - quebracho extract ratio approximates that ratio at which the synthetic tanning material has maximum solvent action on quebracho extract (3).

### Experimental Results

The tannin reported in the experimental results is the tannin contributed by the quebracho extract only, since the turbidimetric analysis used in this study does not respond to the synthetic tanning material.

The "per cent original tannin in filtrate" is calculated from the maximum amount of tannin found in a series of samples taken during the ultrafiltration operation (2).

Tables 1, 2, 3 and 4 and Figure I, show the results obtained on the ultrafiltration of infusions containing 5.0 g. of ordinary quebracho extract and varying amounts of synthetic tanning material per liter.

The results tabulated in the separate divisions of the tables are results obtained with a given infusion, the tannin analysis of which is given above the section.

The Limiting Pore Diameter, as determined from the plot of the data in the table, is given at the bottom of the table.

TABLE I

ULTRAFILTRATION OF ORDINARY QUEBRACHO INFUSION

5.0 g. Quebracho Extract Per Liter.

0.275 g. tannin /100 ml.		0.319 g. tannin /100 ml.		0.300 g. tannin /100 ml.	
<u>Average Pore Diameter</u>	<u>% Original Tannin in Filtrate</u>	<u>Average Pore Diameter</u>	<u>% Original Tannin in Filtrate</u>	<u>Average Pore Diameter</u>	<u>% Original Tannin in Filtrate</u>
14.3	14.1	33.6	70.0	35.0	18.7
11.0	28.0	19.8	40.1	26.8	10.4
10.6	1.1	13.1	4.6	18.2	6.9
8.7	73.0	8.4	48.7	8.6	0.1
0.303 g. tannin /100 ml.		0.304 g. tannin /100 ml.		0.299 g. tannin /100 ml.	
<u>Average Pore Diameter</u>	<u>% Original Tannin in Filtrate</u>	<u>Average Pore Diameter</u>	<u>% Original Tannin in Filtrate</u>	<u>Average Pore Diameter</u>	<u>% Original Tannin in Filtrate</u>
26.8	37.0	26.8	8.9	33.6	14.0
13.3	3.1	18.2	43.0	19.8	14.6
11.2	47.0	13.1	91.0	13.1	75.0
9.3	64.0	10.0	75.0	9.7	17.0

Limiting Pore Diameter 9 - 12 millimicrons

TABLE II  
ULTRAFILTRATION OF ORDINARY QUEBRACHO-SYNTHETIC

TANNING MATERIAL INFUSION

5.0 g. Quebracho Extract Plus 2.0 g. Synthetic  
Tanning Material Per Liter

0.317 g.		tannin /100 ml.		0.532 g.		tannin /100 ml.		0.525 g.	
Average	% Original	Average	% Original	Average	% Original	Average	% Original	Average	% Original
Pore	Tannin in	Pore	Tannin in	Pore	Tannin in	Pore	Tannin in	Pore	Tannin in
Diameter	Filtrate	Diameter	Filtrate	Diameter	Filtrate	Diameter	Filtrate	Diameter	Filtrate
35.0	101.0	26.8	96.4	19.8	92.0	19.8	92.0	19.8	92.0
19.8	9.7	14.7	5.8	15.1	11.5	15.1	11.5	15.1	11.5
13.1	73.5	12.2	5.5	10.0	3.1	10.0	3.1	10.0	3.1
8.6	50.0	8.6	79.0	8.8	31.6	8.8	31.6	8.8	31.6

Limiting Pore Diameter 9 - 12 millimicrons

TABLE III  
ULTRAFILTRATION OF ORDINARY QUEBRACHO-SYNTHETIC

TANNING MATERIAL INFUSION

5.0 g. Quebracho Extract Plus 1.0 g. Synthetic Tanning Material Per Liter

0.313 g. tannin /100 ml.		0.313 g. tannin /100 ml.		0.291 g. tannin /100 ml.	
Average Pore Diameter	% Original Tannin in Filtrate	Average Pore Diameter	% Original Tannin in Filtrate	Average Pore Diameter	% Original Tannin in Filtrate
59.0	54.0	60.5	95.0	23.1	14.4
19.8	100.0	33.6	86.0	14.7	55.0
19.8	11.5	18.2	46.0	12.2	55.0
13.2	3.4	12.0	24.0	9.7	100.0
8.7	13.4	8.7	83.0		

Limiting Pore Diameter 9 - 12 millimicrons

TABLE IV  
ULTRAFILTRATION OF ORDINARY QUEBRACHO-SYNTHETIC

TANNING MATERIAL INFUSION

5.0 g. Quebracho Extract Plus 0.5 g. Synthetic Tanning Material Per Liter

0.303 g. tannin / 100 ml.		0.302 g. tannin / 100 ml.		0.298 g. tannin / 100 ml.	
Average Pore Diameter	% Original Tannin in Filtrate	Average Pore Diameter	% Original Tannin in Filtrate	Average Pore Diameter	% Original Tannin in Filtrate
35.0	68.0	59.0	37.0	23.1	43.0
18.2	100.0	23.1	44.0	14.7	82.0
11.1	62.0	12.0	0.7	12.3	10.0
8.7	0.3	8.8	29.0	10.8	65.0

Limiting Pore Diameter 9 - 12 millimicrons

# ULTRAFILTRATION OF QUEBRACHO INFUSIONS

5.0 GRAMS QUEBRACHO EXTRACT PER LITER

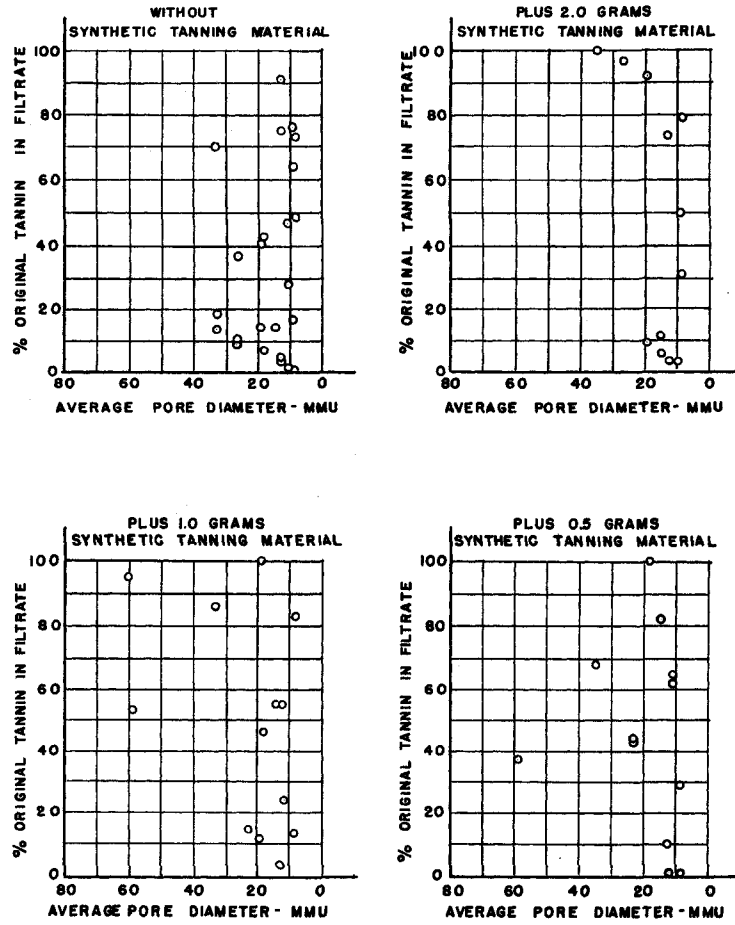


FIGURE I

Tables V and VI and Figure 2 show the results obtained on the ultrafiltration of infusions containing 10.0 g. of ordinary quebracho extract, with and without 4.0 g. synthetic tanning material, per liter.

TABLE V

ULTRAFILTRATION OF ORDINARY QUEBRACHO INFUSION

10.0 g. Quebracho Extract Per Liter

0.545 g. tannin /100 ml.		0.530 g. tannin /100 ml.	
Average Pore Diameter	% Original Tannin in Filtrate	Average Pore Diameter	% Original Tannin in Filtrate
60.5	70.0	14.1	58.0
59.0	96.0	12.3	6.5
15.1	1.4	11.5	100.0
10.0	0.2	10.8	2.0

Limiting Pore Diameter 9 - 12 millimicrons

TABLE VI  
ULTRAFILTRATION OF ORDINARY QUEBRACHO-SYNTHETIC

TANNING MATERIAL INFUSION

10.0 g. Quebracho Extract Plus 4.0 g. Synthetic Tanning Material Per Liter

0.662 g. tannin /100 ml.		0.655 g. tannin /100 ml.	
Average Pore Diameter	% Original Tannin in Filtrate	Average Pore Diameter	% Original Tannin in Filtrate
14.1	28.0	62.7	97.0
12.8	26.0	60.5	100.0
11.1	70.0	15.1	7.4
10.0	27.0	13.3	8.4
		11.7	7.0
		10.8	4.5

Limiting Pore Diameter 9 - 12 millimicrons

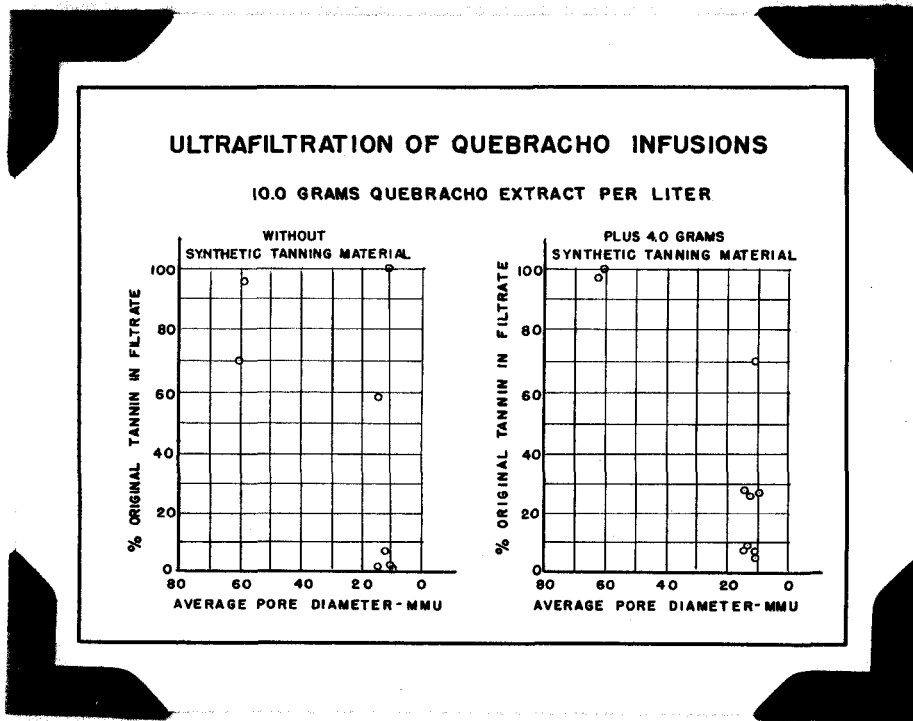
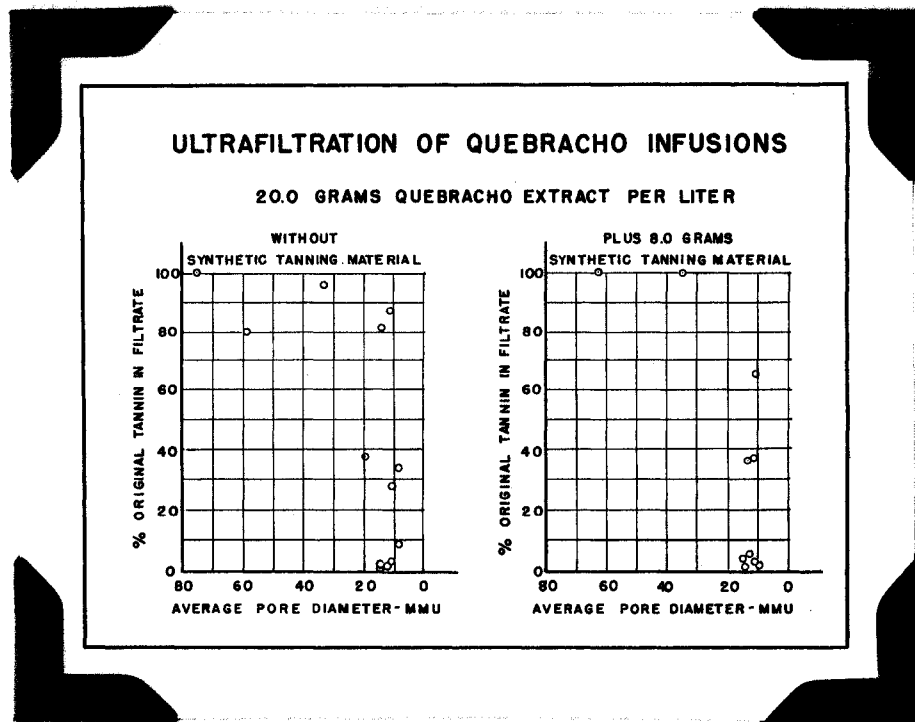


FIGURE II

Tables VII and VIII and Figure 3 show the results obtained on the filtration of infusions containing 20.0 ordinary quebracho extract, with and without 8.0 g. of synthetic tanning material, per liter.



**FIGURE III**

TABLE VII  
ULTRAFILTRATION OF ORDINARY QUEBRACHO INFUSION.

20.0 g. Quebracho Extract Per Liter

0.922 g. Average Pore Diameter	tennin /100 ml. % Original Tannin in Filtrate	1.05 g. Average Pore Diameter	tennin /100 ml. % Original Tannin in Filtrate	1.05 g. Average Pore Diameter	tennin /100 ml. % Original Tannin in Filtrate
14.4	0.4	75.5	100.0	59.0	80.0
12.6	1.4	19.8	37.6	33.6	96.0
11.0	27.8	14.3	1.6	14.1	81.0
8.4	8.7	11.0	2.8	11.2	87.0
		8.7	33.9		

Limiting Pore Diameter 9 - 12 millimicrons

TABLE VIII  
ULTRAFILTRATION OF ORDINARY QUEBRACHO-SYNTHETIC

<u>TANNING MATERIAL INFUSION</u>		<u>1.41 g. tannin /100 ml.</u>	
		<u>Average</u>	<u>% Original</u>
<u>20.0 g. Quebracho Extract Plus 8.0 g. Synthetic</u>		<u>Pore</u>	<u>Tannin in</u>
<u>Tanning Material Per Liter</u>		<u>Diameter</u>	<u>Filtrate</u>
<u>1.22 g. tannin /100 ml.</u>		14.7	1.7
<u>Average</u>	<u>% Original</u>	12.8	5.7
<u>Pore</u>	<u>Tannin in</u>	11.7	2.8
<u>Diameter</u>	<u>Filtrate</u>	10.0	2.0
62.7	100.0		
35.0	100.0		
15.1	4.0		
13.3	36.0		
11.7	37.0		
10.8	65.1		

Limiting Pore Diameter 9 - 12 millimicrons

### Discussion of Results

The filtration end-point curves have not been plotted because the experimental data do not lie close enough to a smooth curve to permit such a procedure.

The variations evident in the experimental results arise from one or more of these factors:

1. non-uniformity of membranes.
2. non-uniformity of quebracho infusions prepared at different times.
3. heterogeneity of particle sizes in quebracho infusions.
4. deposition of phlobaphenes on the membrane.
5. leaks around the membrane.

Although the results are not regular enough to permit plotting of the filtration end-point curves they do designate a narrow range of Limiting Pore Diameter. In all cases studied the Limiting Pore Diameter was found to be 9-12 millimicrons. The fact that the Limiting Pore Diameter is not decreased by the addition of synthetic tanning material lends support to the hypothesis that the particle size of a vegetable tannin is not decreased by the addition of synthetic tanning material. However, this lack of change in Limiting Pore Diameter does not necessarily indicate that there is no change in the vegetable tannin particle size on addition of synthetic tanning material.

It is quite possible that the synthetic material might act as a capillary active substance (2) for the quebracho tannin or for a possible quebracho tannin-synthetic tanning material complex. Such a condition would permit a particle larger than the original tannin particle to pass through a membrane having an Average Pore Diameter equal to or less than the Limiting Pore Diameter for the original tannin.

The results show a decided discrepancy when membranes with Average Pore Diameter's below 10 millimicrons are used. Other investigators have had much the same trouble. Elford (5,6) in reporting factors for calculating particle diameters from Limiting Pore Diameters states that the factor, which tends to decrease as the Average Pore Diameter decreases, appears to increase for membranes below 10 millimicrons. Ferry (7) suggests that Poisseulli's Law may fail for capillaries less than 10 millimicrons in diameter. He believes this possible failure may be due to these three factors:

1. electrokinetic effects.
2. steric effects.
3. water in such small capillaries cannot be considered as a continuous medium.

There is no apparent change in Limiting Pore Diameter for ordinary quebracho infusions in the range 5.0

to 20.0 grams of ordinary quebracho extract per liter.

Conclusions

If the assumption is made that particle size is directly proportional to Limiting Pore Diameter (2) ultrafiltration shows no change in the effective particle size of ordinary quebracho tannin, either with change in tannin concentration or addition of synthetic tanning material, over the range of concentration used in this study.

NOTE: The synthetic tanning material used in this study was Mertanol D, a product of the Monsanto Chemical Company.

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