# 华西协合大学理学院化学系毕业论文

## 烟鞣革之研究

◆马　临

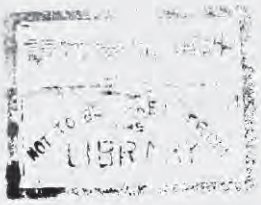
## 作者简介

马临，浙江宁波人，1924年3月生于北京，中学在香港英皇书院就读，1942年离开香港，在华西协合大学化学系学习，1947年获华西协合大学理学士学位并留校任教。后来获得奖学金赴英国利兹大学读哲学博士课程，在伦敦大学医学院从事博士后研究工作。1957年任教于香港大学，担任病理系讲师。1965年任教于香港中文大学。1978年至1987年任香港中文大学校长。1973年获选为香港中文大学理学院院长，1978年荣膺香港中文大学第二任校长。

马临是“邵逸夫奖”理事会的主要成员，协助邵逸夫捐资内地和香港，为发展教育和医疗卫生事业做了大量的工作。1978年，他被委任为香港太平绅士，曾被授予英国CBE荣誉勋衔、日本旭日勋章、德国十字勋章、香港特别行政区政府金紫荆勋章，获得英国赛克斯大学荣誉理学博士、澳门东亚大学荣誉文学博士、香港中文大学荣誉法学博士、美国纽约州立大学荣誉人文学博士、天津大学荣誉哲学博士、英国利兹大学荣誉法学博士、香港中文大学荣誉院士等称号。

据马临回忆，1942年他随父母及姐妹五人辗转到达成都。父亲马鉴在成都燕京大学任教，姐姐马彬在成都燕京大学就读，妹妹马彦在华西坝的金陵中学就读。马临考入华西协合大学化学系，开始了一生难忘的求学生涯。马临曾经撰文回忆在学校的情景：“华西栽培了我，更给我一生难忘的美丽回忆”，“华西领导们，特别是张凌高校长让人钦佩，他们的包容精神给了学生很多启发。华西坝的设施，仅仅是为一所大学所设立，但在当时，需要为五所大学所共享。这种包容精神确实伟大，正是‘海纳百川，有容乃大’。华西的领导们不仅

以身作则，而且行之有素。我们在华西不仅学到了课本上的知识，也学到他们的身教”。多年来，马临十分关心母校的建设和发展，积极促进香港中文大学与母校的交流。在华西85周年校庆时，马临等捐资设立了“校友化学奖学金”。



# 華西協合大學

## 畢業論文

題目：煙鞣之研究

理學院化學系

馬臨著

中華民國三十五年六月　日

華西協合大學

畢業論文

煙鞣革之研究

馬 臨

# A STUDY OF SMOKE TANNAGE

A THESIS

SUBMITTED TO THE DEPARTMENT OF CHEMISTRY

COLLEGE OF NATURAL SCIENCE

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OF

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THESIS DIRECTOR Paul G. Chang

CHAIRMAN OF THE DEPT. 吴绍熙

DEAN OF THE COLLEGE

ACKNOWLEDGEMENT

The writer wishes to express his gratitude to Dr. Paul C. Chang, professor of Department of Chemistry, West China Union University, who has kindly directed this piece of work, and to Mr. C. T. Wen, for his valuable helps that the present work could be performed.

To my co-workers, Miss Chi Mei-chuan and Mr. Wu Tze-cheng, chemistry student of Yen-ching Universty, I sincerely express my thanks to their enthusiasm, perseverance and co-operation to carry out this peice of work.

CONTENTS

## I. INTRODUCTION

In spite of the fact that the smoke tannage is an old and obsolete method in Chinese tanning industry, research works on this field are seldom. In China, smoke tannage is thus far still generally applied in the manufacturing of various kinds of leather, because the method is simple and rather economical. Products of smoke tannage such as shoes, boxes, boots, belts, harness and many others are widely used throughout the country.

Smoke tannage is inferior to other processes of tannage such as chrome tannage and vegetable tannage in every respect. The reason is that the method still prevailed with is that it is the most economical metnod, especially for the fulfillment of the requirement of China in war-time, when the tanning material is difficult to be obtained.

Smoke tanned leather gives poor resistivity to moisture. Therefore, in the south China, smoke leather is generally follpwed with a treatment of vegetable tannins (usually of Chinese nut gall) in order to improve the quality of the products against moisture. Mongolians

unconsciously use the sour milk as a pickling agent before tanning. The products thus obtained become better.

II. HISTORICAL

The application of smoke for the tannage of skin has long been known by Chinese perhaps two or three thousands years ago. Leather produced by the American Indians preserved in museum is recognised to be smoke tanned. The method of tannage is probably resembling that of Chinese. Among the various methods of smoke tannage some special modifications have been made althrough the general procedures are not far from one another.

The present work was carried about in order to investigate the nature of the smoke tanning in comparision with the modern scientific metnod.

III. QUALITATIVE AND QUANTITATIVE ANLYSIS.

A. ANALYSIS OF PURE AND SMOKED HIDE POWDER

1. Determination of moisture (A.L.C.A. METHOD)

About 1 gm. of hide powder was weighed and dried in an electric oven at 95°-100° C. for 16 hours. It was cooled and in a desicator for exactly 15 minutes and was weighed. The result was shown in Table (1).

2. Determination of total ash (A.L.C.A. METHOD)

The hide powder after the determination of moisture was heated in a muffle until all carbon was burnt out. It was cooled in a desicator and weighed until constant weights was obtained. Results were shown in Table (1)1

3. Determination of nitrogen content (KJELDAHL METHOD)

About 1 gm. of hide powder w s placed in a Kjeldahl flask and 10 gm. of anhydrous sodium sulfate, 0.5 gm. of copper sulfate and 25 ml. of sulfuric acid were added. The flask was placed in an inclined position and heated gen gently until the froth ing w s over; then it was boiled br briskly to a quite clear and nearly colorless liquid. It was cooled and diluted with 200 ml. of water. The liquid was m de strongly alkaline by adding sufficient amount of sodium hydroxide solution. The flask was then

connected to a bulb trap and the condenser immediately. The container was then mixed by shaking thoroughly and distilled all the ammonia over into a measured quantity of standard acid. The distillation was completed in 90 minutes. Excess of standard acid was titrated back with standard sodium hydroxide solution, methyl red as indicator. The result was shown in Table (1).

B. QUALITATIVE DETECTION OF ALDEHYDE IN SMOKE AND SMOKED LEATHER.

1. Detection of the smoke samples for aldehyde.

Smoke from the generator was collected in apparatus as in Figure (3) filled with Schiff's reagent. After about 10 minutes, the solution was changed into pink pink color and finally became deep red.

The same procedure was carried out with distilled water instead of Schiff's reagent. Smoke was allowed to bubble through gently. The sample solution was tested with Fehling's solution, to which it was positive.

2. Detection of smoke leatherfor aldehyde.

10 gm. of finely cut samples from the smoke leather were placed in a distillation flask. Dilute sulfuric acid was added and was distilled. The distillate was

lected in a testtubetube containing Schiff's reagent. After 30 minutes of distillation, pink coration was appeared.

C. QUANTITATIVE DETERMINATION OF ALDEHYDE IN THE SMOKED HIDE POWDER

10 gm. of smoked hide powder was placed in a 300 ml. distilling flask in which sufficient amount of dilute sulfuric acid was added to cover the sample(*1). The distillate was absorbed in a freshly prepared sodium bi-sulfite solution. After an hour the distillate was tested with Schiff's reagent to ensure the complete displacement of of aldehyde by sulfuric acid. The results were shown in Table (2).

TABLE 1

ANALYSIS OF PURE AND SMOKED HIDE POWDER

| CONSTITUENTS | PURE Hide Powder | SMOKED Hide Powder |
|---|---|---|
| Moisture | 16.90% | 21.58% |
| Ash | 0.15% | 00.76% |
| Nitrogen | 14.74% | 13.20% |
| % of hide substances | 82.83% | 74.18% |
| | 99.88% | 96.52% |

TABLE 2

THE QUALITATIVE AND QUANTITATIVE DETERMINATION OF ALDEHYDE

1. Qualitative detection of aldehyde:

| SAMPLES | Schiff's Reagent | Fehling's Solution |
|---|---|---|
| Smoke | + | + |
| Smoked leather | + | |

2. Quantitative determination of aldehyde in smoked hide powder: (calculated as formaldehyde.)

% of aldehyde = 0.018%/gm. of smoked hide powder.

D. RESULT AND DISCUSSION

The quantitative determination of aldehyde in smoked hide powder was shown in Table (2). From this result, it is doubtful wether aldehyde is the only tanning agent because the amount of aldhyde fixed in smoked hide powder is very small. It seems that aldehude plays a part of tanning effect in addition to the other unknown substances present in smoke. Since the quality of smoke tanned leather is poor, probably the smoked leather is in partially tanned condition.

From the result obtained in the analysis of smoked hide powder shown in Table (2), the total amount of mois-

ture, ash, and hide substances is not equal to 100%. The deviatin is probably due to the ignition lost, because some adsorbed material (such as tar, carbon particles etc. present in smoke.) which was unwashable would be ignited.

The best way of solving the compounds present in smoke is to analyse the smoke samples. In the present work, analysis has not been made due to the following difficulties:

1. The component of smoke is very complex.

2. The difficulty of separartion of the composite substances.

3. The composition of smoke varies with the origin, and moisture of straw.

5. The smoke generated is hard to handle.

For the above difficulties and also because only the tanning property of smoke is interested, we are not going to analyse smoke. Combined tannage and swelling will be studied in order to search the actin of smoke upon hide powder.

IV. SMOKE TANNIG

General detail of the Chinese smoke tanning is described exactly according tothe meth od adopted by the tanneries. Apiece of pelt, after liming and washing, is soaked in common salt solution. Then it is placed over a puffof smoke in the wet condition. Care must he taken to prevent over heating of the pelt which would otherwise be baked into gelatine. Generally, the pelt must be wet and flesh side of the pelt must be placed toward the smoke frequent moving. In actual practise, this work is performed by hand. The pelt is smoked twice daily and the period for smiling and tanning is about 10 minutes in case of cow hide. After thus working for five or six days, the tanning process is finished. The cross section of the leather should be yellow throughout. The apparatus used is shown in Figure 1.

The smoke generator is constructed of the common brick with an opening at the top of the generator. When the wet straw was put in and set to fire, a dense smoke was rushed out fromthe opening due to the incomplete combustion. The production of smike is intermittent. After each operation, the pelt was set aside for aging.

A. Preparation of Smoked Goat leather.

1. Apparatus

The smoke generator was constructed simply of a stove of the size 2.5X1X1, with a hole of 4-inch diameter on the top as shown in Figure 2. An alcohol burner was placed under the fire bridge to set the combustion of straw to produce the smoke columes for tanning.

2. Procedure

A piece of goat skin after liming was washed thoroughly and then was soaked in 10% NaCl solution, Straw was added frequently into the generator from the top and the the pelt was moved to and fro over the thick smoke in order to ensure complete reaction by smoke. It was wetted with salt solution before each treatment in order to reduce the unnecessary swelling of the pelt and to avoid the drying of the pelt. After tanning, the leather was air dried. A piece of light yellow smoked leather was obtained as shown in the following sample:

Method of Tannage: Smoke tanning
Species: Chinese goat skin
Date: August, 1945.



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一. Preparation of Smoked Hide Powder.

1. Apparatus

The construction of the smoke generator was quite similar to that employed in the manufacturing of smoke leather. The stove was modified by inverting a large funnel over the top to collect the smoke. An alcohol burner was placed under the fire bridge for the combustion of straws. A long rubber tubing was connected between the funnel and three large glasstubings s arranged in series in which the sample was placed. Long rubber tubing wasemployed to avoid the overheationg of the hide powder during smoking. Further more, a loop formwas provided by means of bending the rubber tubing in order to collect the condensed vapor from the combustion of straw, which usually contains a large amount of moisture. Suction was applied to increase the draft of the generated smoke.

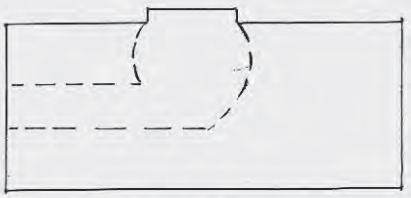
2. Procedure

200 gm. of standard pure hide powder were soaked in 0.001 N NaOH solution and was squeezed with a linen cloth. The hide powder was divided and distributed to large glass tubings. Smoke was then allowed to passe

for about 20 minutes, after that, the sample was then taken out for aging. The process was repeated twenty times, and at each time, the sample was crushed by a glass rod into small pieces and mixed thoroughly after soaking in NaOH solution. Then it was washed with water and stired in stoppered bottle in an air dried condition. The apparatus used was shown in Figure 4.

C. Result and Discussion.

The smoke tanned leather was shown on page 10. The leather is yellow in color. The yellow cross-section indicates that the smoke had completely worked in throughout the pelt during the tanning process. The resistivity of moisture is very poor porbably due to partial tannge of smoke. Oiling will deferior the quality of the smoke tanned leather.



FRONT VIEW LEFT SIDE VIEW

FIG.1. INDUSTRIAL SMOKE GENERATOR.

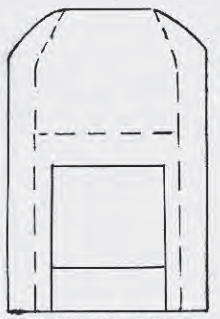


FIG. 2. LABORATORY SMOKE GENERATOR

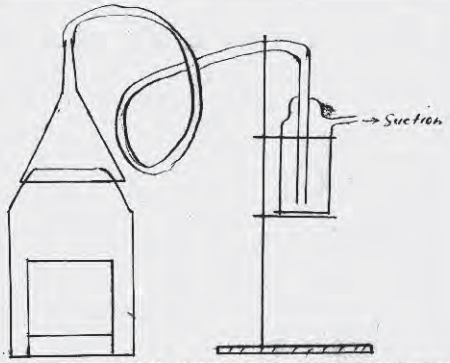



FIG. 3. APPRATUS FOR QUALITATIVE DETERMINATION OF SMOKE.

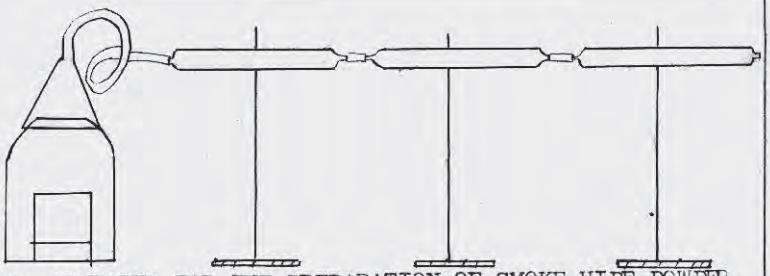


FIG.4. APPRATUS FOR THE PREPARATION OF SMOKE HIDE POWDER.

V. RETANNING OF THE SMOKE TANNED HIDE POWDER.

A. THE TAKE*UP OF TOTAL SOLUBLES FROM CHINESE VALONIA LIQUOR BY SMOKED HIDE POWDER.

Most of the local smoke tanners treat the smoked leather with valonia extract to improve it's quality, because the valonia is one of the most available tanning material obtainable from the area.

1. Preparation of tannin liquor from valonia cups.

Four kilograms of the crushed valonia was placed in a series of eight vessels and extracted with tap water. The extraction was based on the counter-current principle. The final extracted liquor was filtered to remove the suspended solid particles, phenol in a ratio of 1:1400 (2*) was added to the filtered liquor to prevent the growth of mold etc.

2. Adjustment of the sampled liquor.

A series of eight different concentrations was prepared by diluting the original extracted liquor of which the concentration was determined by both Lowenthal (3*) and gravimentric method. The concentrations of the different sample-liquors were determined by Lowenthal method only.

3. Adjustment of the pH value of the sampled liquor.

The pH value of the liquor was determined by a potentiameter using quinhydrone electrode. Sufuric acid was added to adjust the pH to 3.

4. Tanning.

Portions of one gr. of collagen of pure and smoked hide powder were weighed, each was tanned with 100 ml. of sampled liquor of different concentrations in large tubes. The tubes were lightly stopped and set in a shaking machine. The machine was continuously rotated for 24 hours. After the shaking, the liquor was filtered and each 5 ml.portions were diluted to 100ml. in volumetric flask. 10 ml. of the diluted ~~to 100 ml.~~ liquorwere taken out to be ananlysed according to Lowenthal mentod. The results were shown in Figure 5 and Table 4.

5. Result and Discussion.

The fixation curve of valonia by pure and smoke hide powder was shown in Figure 5. The up take of valonia by smoke hide powder was less than that by pure hide powder. Theis can be easily explained because a part of the amino group in the collogen had been blocked off by the aldehyde. The fixation in-

with increasing concentrations.

TABLE 3

THE EFFECT OF CONCENTRATION UPON THE FIXATION

OF VALONIA BY PURE HIDE POWDER

| Original conc. in gms. total solubles/100ml. | Equil. conc. in gms. total soluble/100 ml. 'C' | Gms. total solubles fixed/ gm. collagen 'X/M' | $\frac{C}{X/M}$ |
|---|---|---|---|
| 0.5644 | 0.1836 | 0.3808 | 0.4821 |
| 0.7480 | 0.2720 | 0.4760 | 0.5715 |
| 1.0268 | 0.4080 | 0.6188 | 0.6594 |
| 1.2580 | 0.5814 | 0.6766 | 0.8594 |
| 1.4280 | 0.6596 | 0.7684 | 0.8584 |
| 1.7136 | 0.8704 | 0.8432 | 1.0320 |
| 2.1692 | 1.2104 | 0.9588 | 1.2620 |
| 2.3262 | 1.3532 | 0.9730 | 1.3910 |

TAPLE 4

THE EFFECT OF CONCENTRATION UPON THE FIXATION

OF VALONIA BY SMOKED HIDE POWDER

| Original conc. in gms. total solubles/100ml. | Equil. conc. in gms. total soluables/100ml. 'C' | Gms. total solubles fixed /gm collagen 'X/M' | $\frac{C}{X/M}$ |
|---|---|---|---|
| 0.5644 | 0.2108 | 0.3536 | 0.5961 |
| 0.7480 | 0.3062 | 0.4454 | 0.6794 |
| 1.0628 | 0.4760 | 0.5508 | 0.8642 |
| 1.2580 | 0.6052 | 0.6528 | 0.9272 |
| 1.4280 | 0.7582 | 0.6698 | 1.1320 |
| 1.7136 | 0.9520 | 0.7616 | 1.2500 |
| 2.1692 | 1.2784 | 0.8908 | 1.4350 |
| 2.3262 | 1.4416 | 0.8846 | 1.6300 |

FIGURE 5

THE EFFECT OF CONCENTRATION ON THE UPTAKE OF TOTAL SOLUBLES BY PURE & SMOKED HIDE POWDER FROM CHINESE VALONIA LIQUOR AT pH = 3.

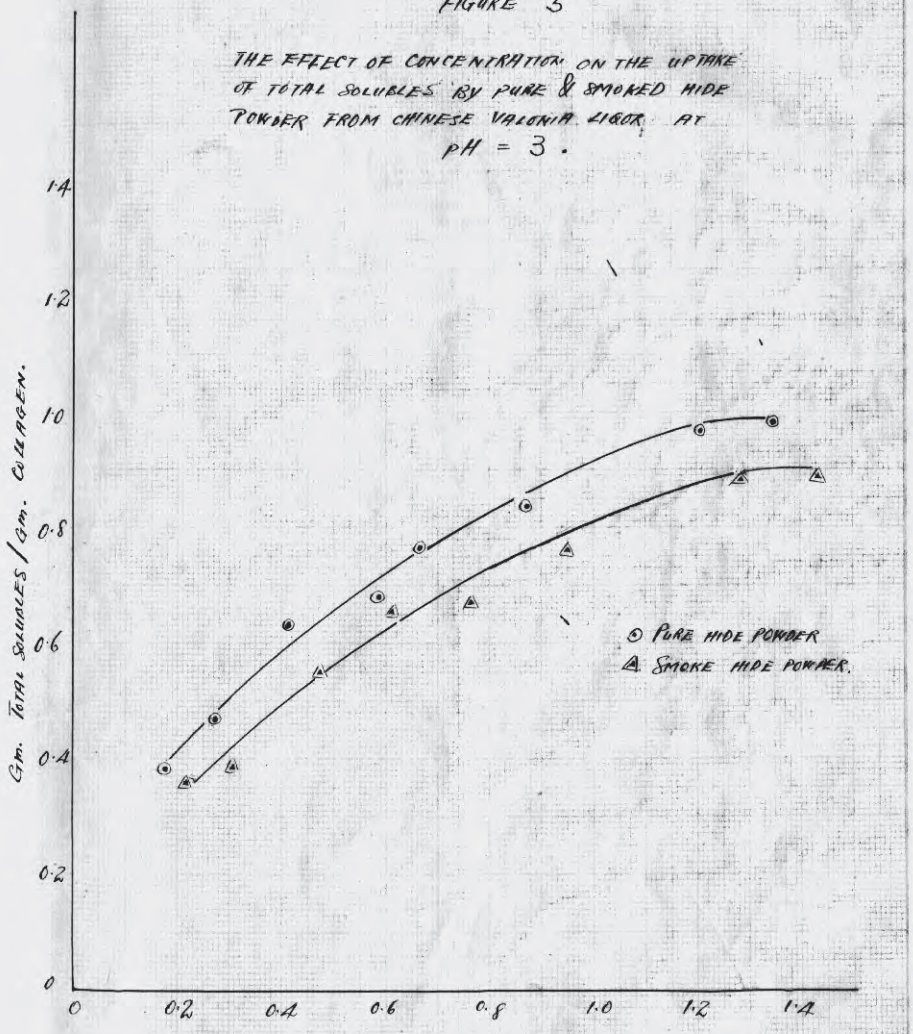
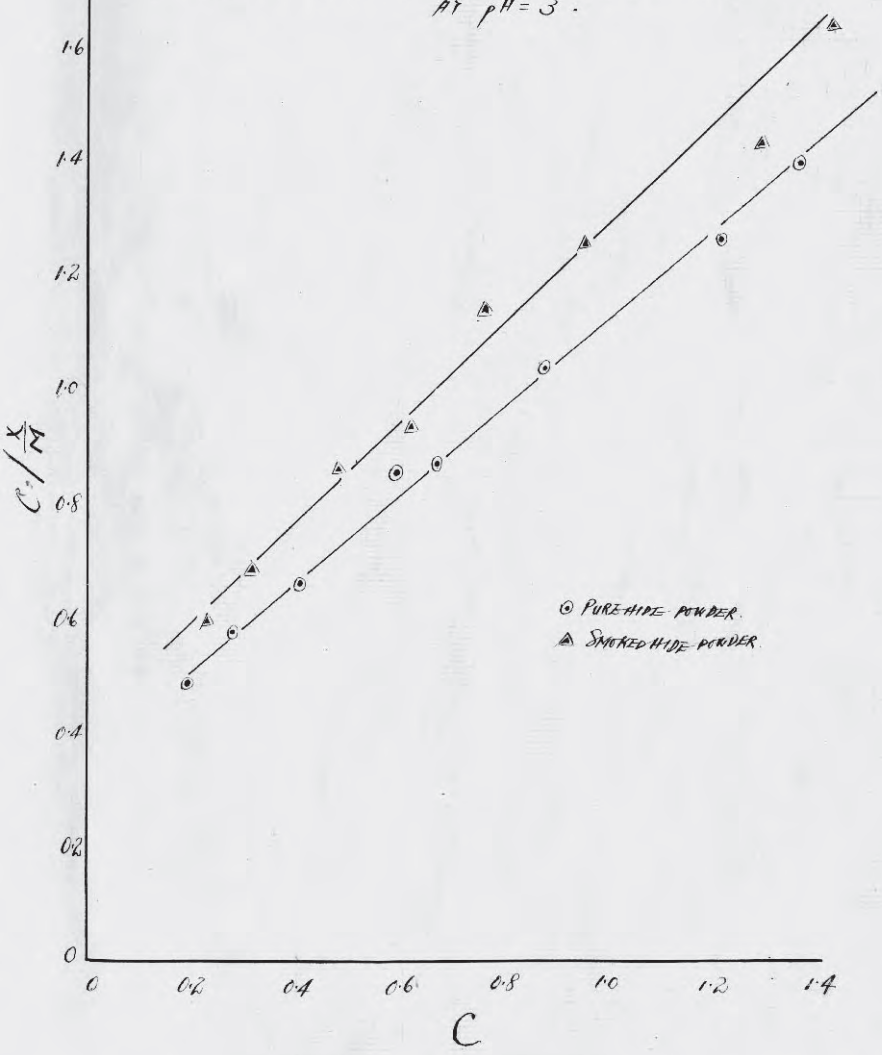


FIGURE 6

THE EFFECT OF CONCENTRATION ON THE UPTAKE OF TOTAL SOLUBLES BY PURE & SMOKED HIDE POWDER FROM CHINESE VALONIA LIQUOR AT pH = 3.

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B. THE UPTAKE OF CHROMIC OXIDE FROM BASIC CHROMIC SULFATE BY SMOKE HIDE POWDER.

The tanning property of chromic salt is due to the action of chromic complex salt on the skin protein. When chrome alum is dissolved in distilled water, with the additionof sufficient amount of NaOH, it give rise the basic chromic complex salts. Olation takes place instantly which results the tanning power.

In this experiment, the smoke tanned hide powder is subjected to be tanned with a series of chrome liquor in order to find out the fixation of chromic oxideupon the smoke collogen so as to compare the result with that the pure hide powder.

1. Experimental

a. Preparation of smoke tanned hide powder.

Refer to page 11.

b. Preparation of tanning liquor

100 gm. of chrome alum were dissolved in a liter of distilled water, in which 7.9 gm. of NaOH were added The concentration and the basicity were tested to be suitable. Seven different concentrations of chrome liquor ranging from 0.5 to 6 gm. per liter were prepared

by dilution of the original liquor. The pH value, basicity and chromic oxide content of the tan liquor were detmined separately after standing for a couple of days. Results were shown in Table5.

TABLE 5

ORIGINAL CONCENTRATIONS OF CHROMIC OXIDE IN TAN LIQUOR

| Original conc, in gm. $Cr_2O_3$ /liter C | Log C |
|---|---|
| 0.7361 | $\bar{1}$.8670 |
| 1.288 | 0.1100 |
| 1.469 | 0.1671 |
| 1.823 | 0.2608 |
| 1.981 | 0.2769 |
| 4.074 | 0.6100 |
| 6.099 | 0.7582 |

c. Tanning

Both smoke and pure hide powder were placed in 120 ml. test tubes separately. A series of tan liquor of 100 ml. were placed in each test tubes. After well corking, the tubes were rotated in a shaking machine for 24 hours until equilibrium was reached. The pH values,basicity and chromic oxide content of the chrome liquor were again analysed and was recorded in Table 6 and Table 7.

TAPLE 6

FIXATION OF CHROMIC OXIDE ON PURE HIDE POWDER

| Original conc. in gm. $Cr_2O_3$/L. C. | Gm. $Cr_2O_3$ fixed/gm. collagen | % Of fixation x/m | Log x/m |
|---|---|---|---|
| 0.7361 | o.o612 | 6.12 | 0.7868 |
| 1.288 | 0.0599 | 5.99 | 0.7774 |
| 1.469 | 0.0656 | 6.56 | 0.8169 |
| 1.825 | 0.0932 | 9.32 | 0.9694 |
| 1.981 | 0.1132 | 11.32 | 1.0539 |
| ----- | ------ | ------ | ------ |
| 4.074 | 0.1544 | 15.44 | 1.1886 |
| 6.099 | 0.1661 | 16.61 | 1.2204 |

TABLE 7

FIXATION OF CHROMIC OXIDE ON SMOKED HIDE POWDER

| Original conc. in gm. $Cr_2O_3$/L. C | Gm. $Cr_2O_3$ fixed/ gram collagen | % of fixation. x/m | Log x/m |
|---|---|---|---|
| 0.7361 | 0.0112 | 1.12 | 0.0492 |
| 1.288 | 0.0305 | 3.05 | 0.4843 |
| 1.469 | 0.0432 | 4.32 | 0.6355 |
| 1.823 | 0.690 | 6.90 | 0.8388 |
| 1.981 | 0.1054 | 10.54 | 1.0229 |
| 4.074 | 0.1163 | 11.63 | 1.0666 |
| 6.099 | 0.1563 | 15.63 | 1.1939 |

d. Result and Discussion

When the concentrations of $Cr_2O_3$ were plotted against the percentage of fixation with collagen, curves were drawn as Figure 7 and Figure 8.. From these curves, it is known that the fixation of $Cr_2O_3$ in smoked hide powder is less than that in pure hide powder.

When the value log C was plotted against log x/m, stright lines were produced, as in Figure 8. It was also shown that the fixation of $Cr_2O_3$ in both the pure and the smoked hide powder was increased with increasing concentrations.

The basicity of the first and the last chrome liquor was comparatively high (around 40), which caused the higher fixation of $Cr_2O_3$ in collagen.

Since smoke tannage is a partial tannage probably due aldehyde and other unknown tanning agents present in smoke. The fixation of these tanning agents reduced the fixation of $Cr_2O_3$ from basic chromic salt in collagen. This is easily interpreted by the curves which show that the fixation of $Cr_2O_3$ in smoke hide powder is always less than that in pure hide powder.

The fixation of $Cr_2O_3$ in lower concentrations was higher in this paper. It is explained thus:

1. The concentration of the tan liquor was easily changed when the air-dried hide powder was placed in it due to the adsorption of the solvent, cause of the increase of concentration.

2. The basicity was a little higher.

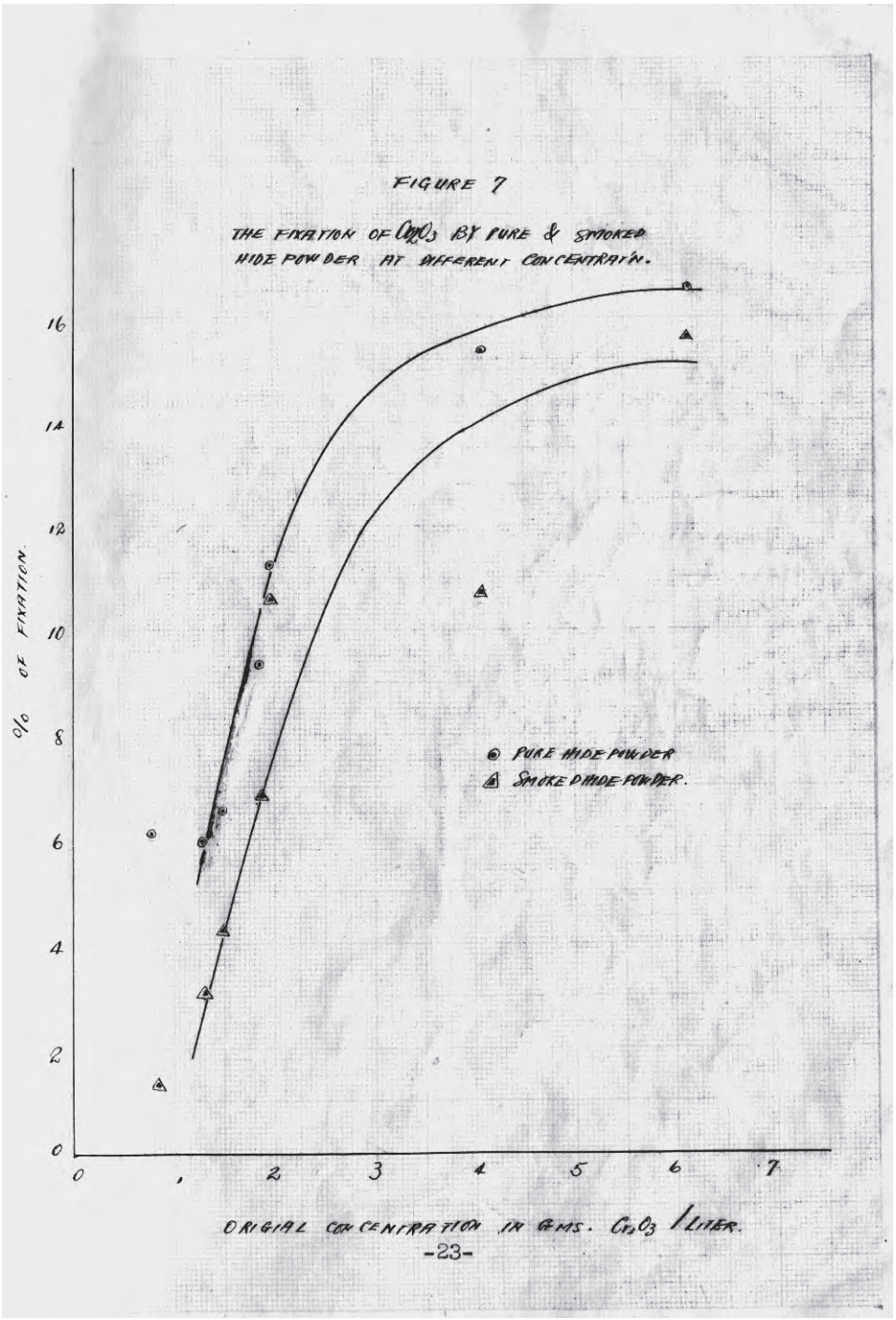
FIGURE 7
THE FIXATION OF $Cr_2O_3$ BY PURE & SMOKED HIDE POWDER AT DIFFERENT CONCENTRATION.
% OF FIXATION.
0
2
4
6
8
10
12
14
16
0
1
2
3
4
5
6
7
PURE HIDE POWDER
SMOKED HIDE POWDER.
ORIGIAL CONCENTRATION IN GMS. $Cr_2O_3$ / LITER.

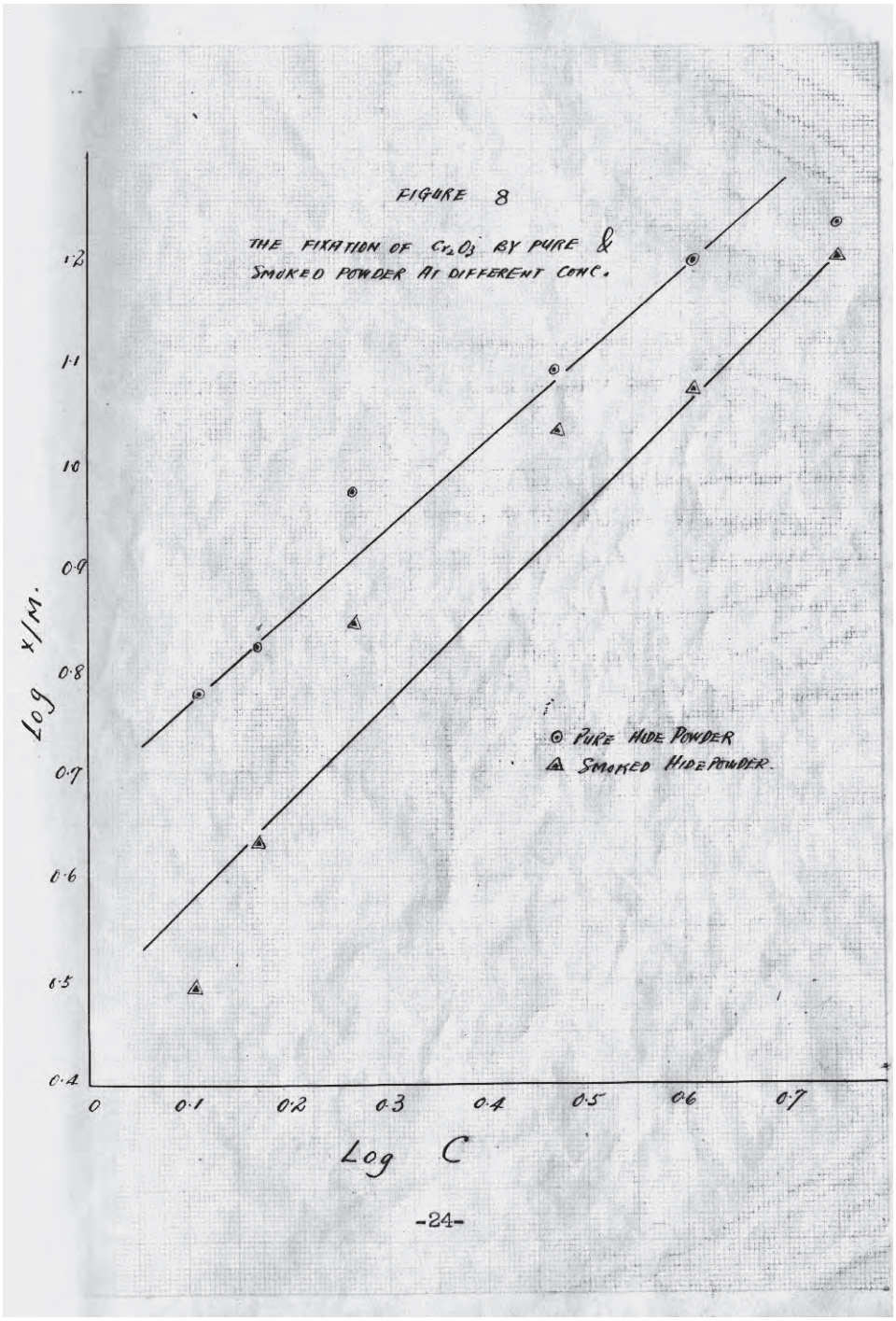
FIGURE 8
THE FIXATION OF $Cr_2O_3$ BY PURE & SMOKED POWDER AT DIFFERENT CONC.
Log x/M.
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
Log C
⊙ PURE HIDE POWDER
△ SMOKED HIDE POWDER.

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VI. THE SWELLIG EFFECT OF SMOKED HIDE POWDER

The mechanism of swellig effect is based on the Donnan's equilibrium thory. The infuence of swelling upon tanning was brought about in the previous paper by Mr's. Chang, Yen, Pan and Wu (4*). The present work was carried out inorder to obtain more information concerning the mechanism of smoke tannage.

A. EXPERIMENTAL

Samples of pure hide powder and smoked hide powder passing thru 40-mesh sieve were weighed on the basis of one gram collagen each sample. They were put into clean swelling tubes. Duplications were carried out for the smoked hide powder.

100 ml. of dilut sulfuric acid solution with a series of adjusted pH were added to each tube. The contents were allowed to stand for 24 hours with constant stirring. At the end of the 20th hour, the hide powder was stirred once and then left to settle till the end of 24th hour. The volume was calibrated with distilled w ter from a burette and the equilibrium pH value of the supernatent solution was detmined by means of the quihydrone electrode. Results were shown in Table 8, Table 9 and Table 10.

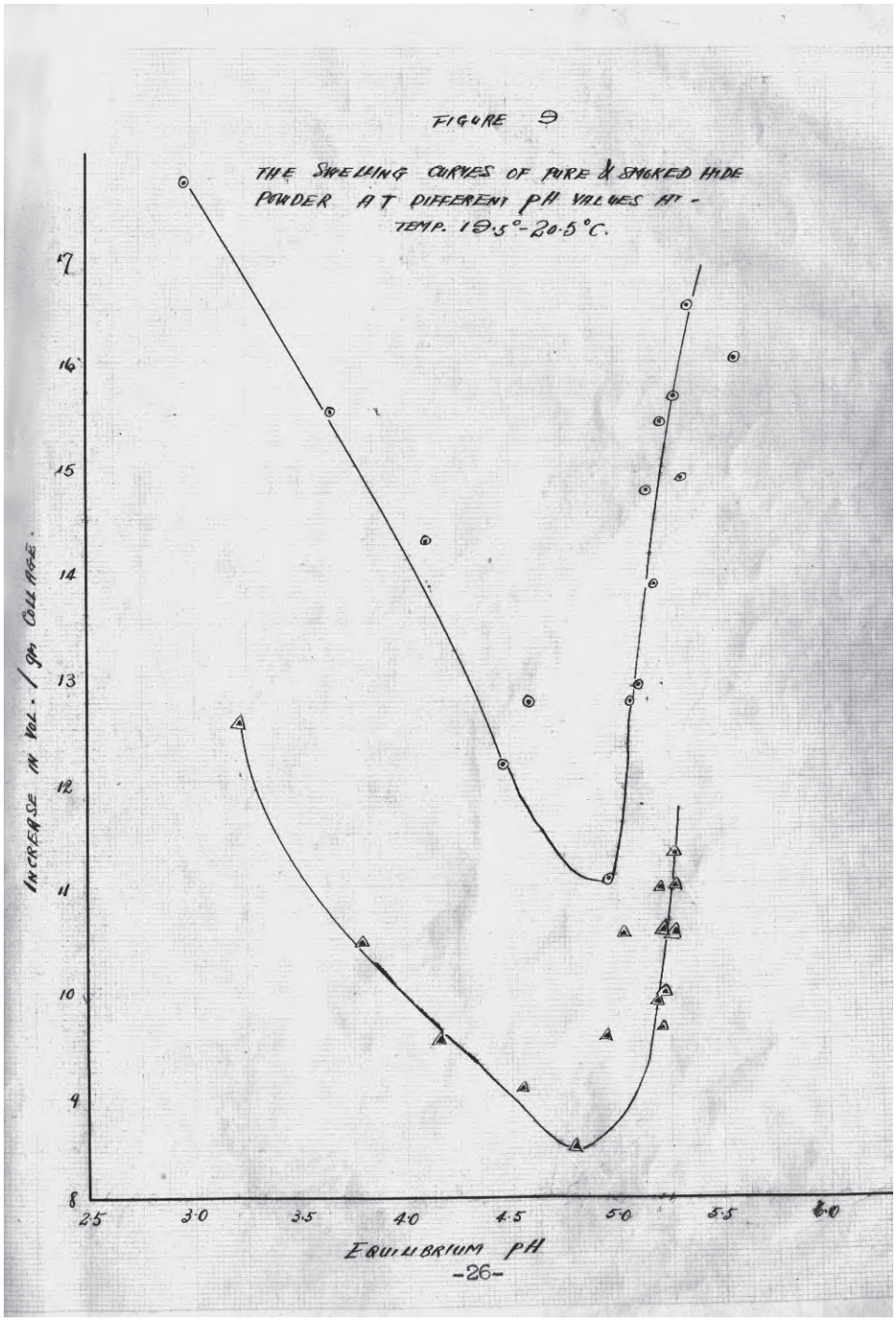
FIGURE 9
THE SWELLING CURVES OF PURE & SMOKED HIDE POWDER AT DIFFERENT pH VALUES AT - TEMP. 19.5°-20.5°C.
INCREASE IN VOL. / gm COLLAGEN.
17
16
15
14
13
12
11
10
9
8
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
EQUILIBRIUM pH
-26-

TABLE 8

SWELLING EFFECT OF PURE HIDE POWDER

| Initial pH | Equilibrium pH | Increase in Vol (ml.) |
|---|---|---|
| 2.38 | 3.02 | 17.80 |
| 2.63 | 3.62 | 15.62 |
| 2.90 | 4.10 | 14.36 |
| 3.29 | 4.45 | 12.18 |
| 3.40 | 4.59 | 12.80 |
| 3.83 | 4.92 | 11.08 |
| 4.00 | 5.10 | 12.80 |
| 4.30 | 5.12 | 12.90 |
| 4.65 | 5.15 | 14.80 |
| 4.95 | 5.17 | 13.86 |
| 5.20 | 5.20 | 15.46 |
| 5.35 | 5.27 | 15.74 |
| 5.60 | 5.29 | 14.92 |
| 5.82 | 5.33 | 16.80 |
| 5.95 | 5.58 | 16.12 |

1.2070 grams pf pure hide powder = 1 gram of collagen. This value was ontained by calculating from the percentage of hide substance.

TABLE 9

SWELLING EFFECT OF THE SMOKE TANNED HIDE POWDER

| Initial pH | Equilibrium pH | Increase in vol. (ml.) |
|---|---|---|
| 2.38 | 3.20 | 12.40 |
| 2.63 | 3.38 | 10.40 |
| 2.90 | 4.18 | 9.40 |
| 3.29 | 4.58 | 9.02 |
| 3.40 | 4.80 | 8.52 |
| 3.83 | 4.96 | 9.36 |
| 4.00 | 5.04 | 10.02 |
| 4.30 | 5.17 | 9.80 |
| 4.65 | 5.20 | 9.76 |
| 5.95 | 5.23 | 10.60 |
| 5.20 | 5.23 | 10.50 |
| 5.35 | 5.27 | 10.56 |
| 5.60 | 5.23 | 10.96 |
| 5.82 | 5.30 | 11.12 |
| 5.96 | 5.35 | 11.20 |

1.3480 grams of smoke tanned hide powder -e- 1 gm. of collagen. This value was obtained by calculation from the percentage of smoke tanned hide substances.

Table 10 (B)

THE SWELLING EFFECT OF THE SMOKE TANNED HIDE POWDER

| Initial pH | Equilibrium pH | Increase in vol. (ml.) |
|---|---|---|
| 2.38 | 3.22 | 12.86 |
| 2.63 | 3.78 | 10.48 |
| 2.90 | 4.14 | 9.72 |
| 3.29 | 4.58 | 9.12 |
| 3.40 | 4.80 | 8.60 |
| 3.84 | 4.96 | 9.82 |
| 4.00 | 5.04 | 11.06 |
| 4.30 | 5.17 | 9.96 |
| 4.65 | 5.20 | 9.56 |
| 4.95 | 5.23 | 9.86 |
| 5.20 | 5.23 | 10.66 |
| 5.35 | 5.27 | 10.76 |
| 5.60 | 5.23 | 11.08 |
| 5.82 | 5.27 | 10.58 |
| 5.95 | 5.33 | 11.36 |

B. Result and discussion.

The result of the swelling of pure and pure and smoked hide powder were shown in Table 8, 9, 10, plotted on Figure 9. The minimum swelling curve of pure hide powder was shown at pH 4.9 and that of smoked hide powder at pH 4.8. The shift of the minimum of the smoked hide powder to the acid side is probably due to the block off of some active groups by smoke tanning. The curve for smoke hide powder was lying below that of the pure hide powder because some active groups were rendered inactive by smoke and the swelling capacity of hide powder was decreased.

The minimum volume of the swelling was less than that as pointed out by that paper (5*), probably the difference is due to:

1. the hide powder was left to settle for 2 hours more;
2. the difference in the effect of temperature;
3. the uniform size of hide powder.

## VIII. SUMMARY

1. The amount of aldehyde fixed in smoked hide powder was found to be 0.018% equiv lent to formaldehyde on the basis of air dried smoke hide powder.

2. The uptake of Chinese valonia by smoked hide powder is less than that by pure hide powder probably due to the tanning effect of aldehyde by smoking.

3. The uptake of chromic oxide from the basic chromic salt by smoke hide powder is less than that by pure hide powder which againg confirms the presence of tanning effect in smoking.

4. The swelling curve of pure hid powder in sulfuric acid solution has a minimun at pH 4.9 and that of smoked hide powder at pH 4.8. The swelling of smoke hide powder is less than that of pure hide powder.

VIII. CHINESE ABSTRACT

(1) 卷烟中含有醛，烟梗烟粉中含有其重量0.018%之醛。

(2) 烟梗烟粉中所吸收橡椀子丹宁之量较纸皮粉所吸收者为少。

(3) 烟梗烟粉中所吸收铬盐之量亦较纸皮粉所吸收者为少。

(4) 纸皮粉在硫酸溶液中膨胀，于pH=4.9时为最小；烟梗烟粉则于pH=4.8时为最小。

## IX BIBLIOGRAPHY (*)

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(3) Atkin W.R. & Thompson F.L. "Procter's Leather Chemist's Pocket Book." 3rd. edition, pp.204-206.

(4) Paul C. Chang, C. T. Yen, S.T. P'an and W. C. Wu: "The Effect of pH value upon the Swelling of Pure and Chrmed Hide Powder."

X. DATA AND CUALCULATIONS.

A. QUANTITATIVE ANALYSIS OF HIDE POWDER

1. Analysis of Pure Hide Powder

a. Determination of Moisture.

| No. of sample--------- | #1 | #2 | #3* |
|---|---|---|---|
| Wt. of sample--------- | 1.0022gm. | 1.0008gm. | 1.0020gm. |
| Loss of wt.---------- | 0.1694gm. | 0.1692gm. | 0.1689gm |
| %of moisture---------- | 16.91% | 16.89% | 16.85% |

Calculation:

#1. % of moisture $\frac{0.1694 \times 100}{1.0022}$ 16.91%

#2. % of moisture $\frac{0.1692 \times 100}{1.0008}$ 16.89%

Average 16.90%

#3. % of moisture $\frac{0.1689 \times 100}{1.0020}$ 16.85%

b. Determination of total ash.

Data:

| No. of sample-------- | #1 | #2 | #3 |
|---|---|---|---|
| Weight of sample----- | 1.0022gm. | 1.0008gm. | 1.0020gm. |
| Weight of ash-------- | 0.0014 " | 0.0015 " | 0.0015 " |
| % of ash---------- | 0.14% | 0.15% | 0.15% |

Calculation:

#1. % of ash $\frac{0.0014 \times 100}{1.0022}$ 0.14%

#2. % of ash $\frac{0.0015 \times 100}{1.0008}$ 0.14%

Average: 0.15%

#3. % of ash $\frac{0.0015 \times 100}{1.0020}$ 0.15%

c. Determination of nitrogen content, % hide substance.

Data:

| No. of sample ------ | #1 | #2 |
|---|---|---|
| Wt. of sample------- | 1.0024gm. | 1.0042gm. |
| Wt. of Nitrogen----- | 0.1476 " | 0.1482 " |
| % Of Nitrogen---------- | 14.72% | 14.76% |

Calculation:

(1) #1. % of Nitrogen $\frac{0.1476 \times 100}{1.0024}$ 14.72%

#2. % of Nitrogen $\frac{0.1482 \times 100}{1.0042}$ 14.76%

Average: 14.74%

(2) % of hide substance 14.75 X 5.62 -- 82.83%

2. Analysis of Smoked Hide-power.

a. Determination of Moisture.

Data:

| No. of sample------- | #1. | #2 | #3 |
|---|---|---|---|
| Wt. of sample------- | 1.0259gm. | 0.9890 | 1.0100gm. |
| Loss of wt.--------- | 0.2214 " | 0.2131 | 0.2184 " |
| % of moisture---------- | 21.58% | 21.54% | 21.62% |

Calculation:

#1. % of moisture $\frac{0.2214 \times 100}{1.0259}$ 21.58%

#2. % of moisture $\frac{0.2131 \times 100}{0.9597}$ 21.54% Av.: 21.58%

#3. % of moisture $\frac{0.2184 \times 100}{1.0100}$ 21.54%

b. Determination of total ash.

Data:

| No. of sample----- | #1 | #2* | #3 |
|---|---|---|---|
| Wt. of sample----- | 1.0259gm. | 0.9897gm. | 1.0100gm. |
| Wt. of ash-------- | 0.0078 " | 0.0070 " | 0.0077 " |
| % of ash----------- | 0.76% | 0.71% | 0.76% |

Calculation:

#1. % of ash $\frac{0.0078 \times 100}{1.0259}$ 0.76%

#2* % of ash $\frac{0.0070 \times 100}{0.9897}$ 0.71%

#3. % of ash $\frac{0.0077 \times 100}{1.0100}$ 0.76%

Average:0.76%

C. Determination of Nitrogen content, hide substance.

Data:

| No. of sample----- | #1 | #2 |
|---|---|---|
| Wt. of sample----- | 1.0036 gm. | 1.0126 gm. |
| Wt of Nitrogen---0 | 0.1323 " | 0.1338 " |
| % of Nitrogen---------- | 13.18% | 13.21% |

Calculation:

1) #1. % of nitrogen $\frac{0.1323 \times 100}{1.0036}$ 13.18%

#2. % of nitrogen $\frac{0.1338 \times 100}{1.0126}$ 13.21%

Average:13.20%

2) % of hide substance-- 13.20 X 5.62 -- 74.18%

NOTE: Those which possess an arterist (*) are to be discarded.

3. QUANTITATIVE ANALYSIS OF ALDEHYDE IN SMOKED HIDE POWDER.

| Data: No. of sample---- | I. | #1 | #2 |
|---|---|---|---|
| Wt. of smoked H.P. | | 10.2553gm. | 10.2553gm. |
| Wt of sample titrated | | 1.0255 " | 1.0255 " |
| Vol of iodine used | | 0.84 ml. | 0.82 ml. |
| Conc. of $I_2$ solution | | 0.01476N. | 0.01476N. |
| % of aldehyde | | 0.013% | 0.013% |

Calculation: % of aldehyde $\frac{0.01476 \times 0.84 \times 0.015}{1.0255}$ 0.013%

% of aldehyde $\frac{0.01476 \times 0.82 \times 0.015}{1.0255}$ 0.013%

NOTE: 1 ml. of 0.1 N. $I_2$ ≙ 0.0015 gm. HCHO.

B. THE EFFECT OF CONC. UPON THE FIXATION OF VALONIA BY PURE AND SMOKED HIDE POWDER.

1. Determination of the original conc. of tan-liquor begore tanning. (pH=3. 1 ml. $KMnO_4$ ≙ 0.0017gm. total solubles.)

| Original conc. in gm. total solubles/100 ml. | ml. of $KMnO_4$ used for titration. |
|---|---|
| 0.5644 | 1.66 |
| 0.7480 | 2.20 |
| 1.0268 | 3.02 |
| 1.2580 | 3.70 |
| 1.4280 | 4.20 |
| 1.7136 | 5.04 |
| 2.1692 | 6.38 |
| 2.3282 | 6.84 |

2. Determination of the equilibrium conc. of tan liquor after tanning with pure and smoked hide powder for 24 hours. (pH --3. 1 ml. $KMnO_4$ -O- 0.0017 gm total solubles.)

A. Pure Hide Powder.

| Equil. conc. in gm. total solubles/100ml | ml. $KMnO_4$ uses for titration. |
|---|---|
| 0.1836 | 0.54 |
| 0.2720 | 0.80 |
| 0.4080 | 1.20 |
| 0.5814 | 1.71 |
| 0.6596 | 1.94 |
| 0.8704 | 2.56 |
| 1.2104 | 3.56 |
| 1.3532 | 3.98 |

b. Smoked Hide powder.

| Equili. conc. in gm. total solubles/100ml | ml. $KMnO_4$ used for titration. |
|---|---|
| 0.2108 | 0.62 |
| 0.3026 | 0.89 |
| 0.4760 | 1.40 |
| 0.6052 | 1.78 |
| 0.7582 | 2.23 |
| 0.9520 | 2.80 |
| 1.2784 | 3.76 |
| 1.4416 | 4.24 |

3. Method of calculation.

ml. of $KMnO_4$ used for original solution x 0.0017 x 200 -- X. gm. of total solubles/100 ml. of origi. sol'n.

ml. of $KMnO_4$ used for equil. sol'n. x 0.0017 x 200 -- Y gm. of total solubles/100ml. of equil. sol'n.

X - Y -- gms. total solubles fixed /gm. collagen.

C. THE EFFECT OF CONCENTRATION UPON THE FIXATION OF $Cr_2O_3$ FROM CHROME LIQUOR BY PHRE AND SMOKED HIDE POWDER.

1. The pH value, $Cr_2O_3$ conc. and acid content in tanning liquor begore tanning.

| Basicity | Conc. in gm. $Cr_2O_3$/ liter of Cr-liquor | pH |
|---|---|---|
| 40.12 | 0.7361 | 4.14 |
| 34.22 | 1.288 | 2.95 |
| 33.12 | 1.469 | 3.07 |
| 33.30 | 1.823 | 2.74 |
| 33.18 | 2.981 | 3.00 |
| 33.12 | 4.074 | 2.31 |
| 39.54 | 6.099 | 3.24 |

The pH values, concentrations and acid contents in tanliquor after tanning.

a. Pure Hide Powder.

| Basicity | Conc. in gm. $Cr_2O_3$/ liter of Cr-liquor. | pH |
|---|---|---|
| 24.18 | ------ | 4.36 |
| 23.22 | ------ | 4.22 |
| 25.62 | 0.6811 | 3.16 |
| 26.43 | 0.6976 | 4.28 |
| 20.18 | 0.8123 | 4.45 |
| 21.08 | 0.7809 | 4.26 |
| 20.36 | 0.8958 | 4.23 |
| 23.44 | 0.8851 | 3.92 |
| 19.45 | 1.8480 | 3.84 |
| ----- | ------- | ---- |
| 29.44 | 2.4310 | 4.54 |
| 20.62 | 2.628 | 3.12 |
| 21.22 | 4.437 | 4.06 |
| 20.46 | 4.437 | 4.12 |

b. Smoked Hide Powder.

| Basicity | Conc. in gm. $Cr_2O_3$/ liter of Cr- liquor | pH |
|---|---|---|
| 26.24 | 0.6352 | 4.56 |
| 27.43 | 0.6117 | 4.72 |
| 25.44 | 0.9813 | 3.09 |
| 26.62 | 0.9803 | 3.18 |
| 29.45 | 1.045 | 3.22 |
| 32.13 | 1.026 | 3.86 |
| 30.29 | 1.132 | 3.92 |
| 31.27 | 1.132 | 3.54 |
| 29.26 | 1.922 | 3.44 |
| 29.23 | 2.946 | 3.32 |
| 31.62 | 2.933 | 4.01 |
| 30.95 | 4.534 | 3.92 |
| 31.62 | 4.529 | 4.13 |

3. Method of calculation.

Before tanning

ml. of 0.1027 N $Na_2S_2O_3$ used/ml. sample $=$ 2.83 $=$ a'
ml. of 0.1828 N NaOH used/ ml.of sample $=$ 0.95 $=$ b'

After tanning
ml.of 0.1027 N $Na_2S_2O_3$ used /ml. of sample $=$ 2.40 $=$ a"
ml. of 0.1828 N NaOH used/ ml. of sample $=$ 0.99 $=$ b"

a' $=$ 2.91 ml. $-0-$ 0.1 N $Na_2S_2O_3$ $=$ $a'_1$
a" $=$ 2.46 ..... ..... $=$ $a''_2$
b' $=$ 1.74 ml. $-0-$ 0.1 N NaOH $=$ $b'_1$
b" $=$ 1.81 ..... $=$ $b''_2$

a. Basicity $=$ $\frac{a'_1 - b'_1}{a'_1} \times 100 = \frac{2.91 - 1.74}{2.91} \times 100 = 40.12$ Ba,

b. Conc. $= a'_1 \times 0.002533 \times 1000 = 0.7361$ gm. $Cr_2O_3$/L.

c. % of $Cr_2O_3$ fixed/gm. collagen $= \frac{a'_1 - a''_2}{a'_1} \times 0.002533 \times 100$

$= \frac{2.91 - 2.46}{1} \times 0.002533 \times 100 = 1.12\%$.

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D. SWELLING EFFECT OF PURE AND SMOKED HIDE POWDER IN DILUTE SULFURIC ACID SOLUTION.

1. Determination of intial pH value for swelling of pure and smoked hide powder.

| Potentiometer Reading | Temperature °C. | pH |
|---|---|---|
| -315.0 | 19.5 | 2.38 |
| -304.3 | 19.5 | 2.63 |
| -284.9 | 19.5 | 2.90 |
| -262.0 | 19.6 | 3.29 |
| -256.0 | 19.6 | 3.40 |
| -230.4 | 19.6 | 3.83 |
| -221.0 | 19.6 | 4.00 |
| -203.4 | 19.8 | 4.30 |
| -183.0 | 19.8 | 4.65 |
| -165.5 | 20.0 | 4.95 |
| -151.2 | 20.0 | 5.20 |
| -142.4 | 20.0 | 5.35 |
| -127.6 | 19.9 | 5.60 |
| -117.4 | 19.9 | 5.82 |
| -107.4 | 20.0 | 5.95 |

2. Determination of equilibrium pH for swelling of Pure hide powder. (19.5°C - 20.5°C.)

| Potentiometer Reading | Temperature °C. | PH |
|---|---|---|
| -277.7 | 20.5 | 3.02 |
| -242.7 | 20.4 | 3.62 |
| -215.0 | 20.5 | 4.10 |
| -194.6 | 20.5 | 4.45 |
| -186.6 | 20.4 | 4.59 |
| -167.4 | 20.4 | 4.92 |
| -157.0 | 19.8 | 5.10 |
| -155.3 | 19.8 | 5.12 |
| -153.9 | 19.8 | 5.13 |
| -153.2 | 19.8 | 5.17 |
| -151.0 | 19.8 | 5.20 |
| -147.0 | 19.6 | 5.27 |
| -145.8 | 19.8 | 5.29 |
| -143.2 | 19.6 | 5.33 |
| -129.0 | 19.5 | 5.53 |

3. Determinatio·n of the Equilibrium pH for the swelling of Smoke tanned Hide Powder.

| Potentiomenter Reading | Temperature °C. | pH |
|---|---|---|
| -207.4 | 20.5 | 3.20 |
| -232.4 | 20.4 | 3.80 |
| -210.4 | 20.5 | 4.18 |
| -137.6 | 20.5 | 4.58 |
| -174.4 | 20.4 | 4.43 |
| -165.0 | 20.4 | 4.96 |
| -.160.4 | 19.8 | 5.04 |
| -153.0 | 19.8 | 5.17 |
| -151.2 | 19.8 | 5.20 |
| -148.8 | 19.8 | 5.23 |
| -148.4 | 19.8 | 5.23 |
| -147.0 | 19.6 | 5.27 |
| -148.4 | 19.8 | 5.23 |
| -145.0 | 19.6 | 5.30 |
| -142.4 | 19.5 | 5.35 |

b. 2nd. Series.

| Potentiometer Reading | Temperature °C. | pH |
|---|---|---|
| -266.0 | 20.5 | 3.22 |
| -233.4 | 20.4 | 3.78 |
| -212.7 | 20.5 | 4.14 |
| -187.6 | 20.5 | 4.58 |
| -174.4 | 20.4 | 4.80 |
| -165.0 | 20.4 | 4.96 |
| -160.2 | 19.3 | 5.04 |
| -153.0 | 19.8 | 5.17 |
| -151.4 | 19.8 | 5.20 |
| -143.6 | 19.3 | 5.33 |
| -148.4 | 19.8 | 5.23 |
| -147.0 | 19.60 | 5.27 |
| -148.6 | 19.8 | 5.23 |
| -147.0 | 19.6 | 5.27 |
| -143.2 | 19.5 | 5.33 |