LEATHER INDUSTRY

IN TRE

NEAR EAST

By

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#### PREFACE

The chemistry of leather manufacture is progressing more rapidly now than at any previous time. Therefore the purpose of this thesis is :- First, the attempt to solve some of the problems of the Leather Industry in the Near East arising as a result of the war. Second, the scientific investigation of the effects of pH and neutral selts on the rates of diffusion in gelatin - jellies and the amounts of combination with collagen ( hide - powder ). Third, the correlation together of facts on the Leather Industry in the Near East.

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#### HISTORY

Thirty thousand years or more ago there existed in Spain, and in fact Western Europe generally, a race of primitive human-beings now known as the "first true men ". During the glacial periods, which we are told threatened to exterminate every human creature on the face of the earth the life of man must indeed have been fearful beyond imagination. At such a time man needed clothes, and it is reasonable to suppose that the only covering he possessed was made up of the skins of animals that he had killed.

The prehistoric man dried his skins and used them as such for clothing after having noticed that wet skins putrefy and decay, while dry ones do not. But dry ones being hard and horny he must have tried to remedy this hardness by rubbing the dry skin with the fat of the animal, of which he must have noticed the softening effect on his own skin. By this means he was able to produce softer and more durable leathers; some of the greesy and albuminous matter used were fat, brains, milk, butter and egg-yolk, separately or mixed together, even now adays we practically use some of these same processes.

In the Fourth Glacial Age the prehistoric man must have early noticed that wood-smoke had an antiseptic and preservative effect on skins which were dried in it.

The use of vegetable tennins, though prehistoric was not

so exclust on the spoke encodes, but it may have had its origin

so ancient as the smoke process, but it may have had its origin before the use of clothing and may be when people tried to introuce dyes into the skins, by using certain bark extracts as dyes.

And it happened that some barks also contained tannins, as a result found that this has a superior quality over the bark which did not contain any ( of course they did not know that ) and so began using barks which gave also the effect of vegetable tannins. That is how tanning skins with vagetable tannins originated.

The art of tanning with alum and salt was still a latter introduction, and must have originated in countries where alum is found as a natural product. This art was not known in Europe or perhaps it was lost during the dark ages until introduced into Spain by the Moors.

while the savages of the West were intent upon the mere satisfaction of their animal desires, the Egyptians were considerably advanced in technical knowledge. In the tomb of Tutankh-Amen a considerable amount of leather was found, in the form of harness, seats of stools, and of sandals. Unfortunately, the damp and heat of the tomb destroyed the leather, in fact rendered it black brittle and almost pitch-like.

The discovery of parchment paper was a result of the rilvalry between the libraries of Alexandria and Pergamum.

Let us pass now to the Roman civilization, which the old chronologeis state was founded in 753 B.C., we find that the

leather industry was in a flourishing condition. It would be remembered that the eight gilds of the seventh century were those of the flute players, goldsmelters, smiths, dyers, cordwainers, curriers, brassworkers, and potters.

In Antioch during the Hellenistic Age we are told from an ancient inscription that tanneries used to manufacture Leather shields for the army.

England was very backward in leather manufacture up to the end of the eighteenth century, owing to the fossilising influence of much paternal legislation, and of certain exciseduties, which were only repealed in 1830. But since this time the art has made rapid strides.

The past fourty years have been marked-in many parts of the world, such as Germany, France, England, U.S.A. and many others - by very considerable advance, and the application of science to the manufacture has been very noticeable.

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#### INTRODUCTION

since the dawn of civilization, leather has been one of the world's most important commodities. It has become so much a part of our everyday life that we should find ourselves in a dilemma if it were taken from us. And yet, after thousands of years of daily use, its properties remain but poorly defined. Leather is not a simple and homogeneous material of definite properties, on the contrary, it is of very variable composition; it has an exceedingly compex structure; and every variation in composition or structure causes some corresponding change in the properties and serviceability. Unfortunately, the relations involved in the leather manufacture are not yet well understood.

The manufacture of leather is undoubtedly an extremely complicated chemical process. The leather industry was developed like many other great industries by man who had no chemical training whatsoever. When chemists started putting their sharp and sensitive moses in this industry—as they did in many others a sharp conflict arose between the "theoretical "and the "practical "minds. Although a practical man possessed no knowledge of chemistry, nevertheless knew how to make a serviceable and salable piece of leather. On the other hand, the theoretical man who had a good knowledge of the fundamental principles of chemistry, and with a good record in all his subjects when in college, usually spoiled every lot of leather that he tried to improve. Thus it was but natural then that the practical man

developed a contempt for the theoretical man, regarding them as ignorant meddlers and their experiments as a waste of time and money.

But it happened that the practical men got into difficulties which proved very costly and, even after these difficulties were overcome, there was no guarantee that they would not recur. Thus chemists would not have been tolerated had it not been to these difficulties that the practical man got into. Furthermore. the public taste changes with time - especially those of the ladies - forcing tanners to change their methods. The manufacture of leather involves many extremely complex processes. all of which must be in perfect balance to produce a salable product. If one of these operations is changed in any way, the balance is upset and, unless compensating changes are made in the other operations, the leather may be completely ruined. The cut - and try method was usually employed in making these compensating changes and, because of the seemingly infinite number of possible changes, it was a matter of good fortune for the tanner to succeed before the spoilage was so great as to ruin him. For this reason he was reluctant to throw away any possible chance of assistance, and so he kept his chemist in the hope that he might prove vauable in times of distress, even if only in a small way. Although the chemist might prove a great help if allowed to meddle with the processes, he often had suggestions which, coupled with the tanner's own knowledge of leather manufacture, got the tanner out of his difficulties. Nevertheless we find glaring

examples of the farreaching effects of our ignorance in this respect. I shall cite only one of them:-

We know that the great majority of people suffer unnecessary foot discomfort because of the methods employed in tanning the leather used in making their shoes. The discomfort being due to an axcessive shrinkage and expansion of the leather with changing atmospheric conditions, which can be overcome to a very considerable extent by changing the method of tanning the leather. That is by increasing the temper, elasticity, flexibility, and resilience of the leather, which is brought about by incorporating greater amounts of oil into the leather, and also the great expansion and shrinkage with change of weather conditions can be much decreased by using upper-shoe leathers tanned with vegetable tannins and not with chrome tannins, because chrome leathers increase in area by an average of about 18% when going from a dry to a moist atmosphere, while the tannin-leathers increase in area only by an average of about 6%. Also they shrink in area correspondingly when the relative humidity falls. The shoe upper is thinner and tends to reach equilibrium with the air much more quickly than the very thick sole, and so the changing size is much more effective when the upper is chrome-tanned. Nearly everybody in the Near East now wear shoes with chrome tanned uppers, because tanners are mostly preparing chrome-tanned shoe uppers, which are subject to these great size changes with atmospheric conditions. For this reason many people here suffer unnecessary foot - discomfort.

The reason for this change in size with change in atmospheric conditions ( according to Wilson ) is that the basic groups of the proteins take up water from the atmosphere more readily than the acidic groupe. In chrome leather most of the basic groups are still free, in vegetable-tanned leathers the acid groups are free and therefore the tannin occupies the position that the water would otherwise take, and so the power of the leather to take up water and change in size is correspondingly diminished. The public can have whatever it demands, but it will probably be a long time before it is educated to the point of knowing what is possible to get in the way of foot comfort. Leather plays a very important part in the daily life of nearly every civilized human-being, and therefore a great service can be rendered to mankind by the development of a scientific control of all the important properties of leather.

A control of all the important properties of leather involves studies of the materials used in making leather and of their
chemical reactions, as well as measurements of properties of
leather which are not well defined. Animal skin contains a number
of different properties, fats and other materials in variable
proportions. Few materials known to the chemist are so complex as
the proteins and the tannins which are employed to convert protein
matter into leather. In the manufacture of leather, one also
encounters bacteria, molds, enzymes, complexorganic salts, emulsions of various kinds of oils, dyestuffs, and finishing materials,
including waxes, gums, resins, e soluble proteins, and lacquer

and varnish materials. To solve the basic problems, of leather chemistry actually requires the elucidation of the basic problems of most other branches of chemistry.

However, the outlook is far from being hopeless. During the last fourty years leather chemistry has kept pace with the unprecedented speed of development of other branches of sciences, for example:-

- 1. The unhairing of skins was done by lime which required from 1 3 weeks to cause the hair to slip easily, during which time a considerable amount of collagen beams hydrolysed, especially in old liquors or in liquors not kept completly saturated with lime at all times. With increasing demand for speed of operation and conservation of the skin collagen, "sharpening agents" have been used, the principle ones being As<sub>2</sub>S<sub>5</sub> and 0.01 M Na<sub>2</sub>S. The judicious use of these materials, in conjunction with lime, has reduced the time required to unhair skins from 1 3 weeks to 1 3 days.
- 2. The use of artificial bating material instead of dung of dogs. The latter giving rise to fowl smells, and making the process more difficult to comtrol.
- 3. The use of organic acids instead of bran in the drenching process. When the bran ferments it gives rise to several
  organic acids ( which bring about the drenching of the skins and
  hides ) and many other gases and bacteria, thus making the process
  dangerous and more difficult to control.

In the task of producing a more serviceable leather under

scientifically controlled conditions, a few definite results have been obtained and we may confidently look forward to further important developments in the near future.

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#### STATUS OF THE LEATHER INDUSTRY

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## STATUS OF THE LEATHER INDUSTRY IN THE NEAR EAST.

The leather industry has not developed in the Near East except in certain parts of Palestine and in Beirut due to the presence of specialists from Europe as refugees and because people started to realize the great future that lied in front of the Leather - Industry in this part of the world and so some had the great luck of getting machinery before the war started. It is true that we have many more tanneries than twenty years ago, but the methods employed and the leather produced in most tanneries are but slightly improved.

#### 1. STATUS OF THE LEATHER INDUSTRY IN PALESTINE

Palestine offered between 1920 and 1939 a good market for imported leather and manufacture of leather goods. Though the country had a fair supply of raw materials, yet owing to the lack of modern tanneries and factories for the manufacture of leather goods, it was compelled to export a certain percentage of undressed hides and skins, and re-import them in the form of manufactured leather, boots, saddlery, bags, etc... The demand was mostly for manufactured goods of average quality and cheep prices.

In 1927 Pelestine started to export sole and finished leather but not in great quantities, which was dropping every year, so that it dropped from 96,000 Kgs. in 1929 to 5,000 Kgs. in 1938.

The chief competitors before 1922 were between high priced

English, French, American leather goods, and the cheap Egyptian kind. The Egyptian was cheeper by 50% and of course of poor quality, but holded the market, and the value of its imports into Palestine was greater than the combined imports from other countries. But in 1922 Germany appeared in the market, due to the low rate of exchange of the mark and credit facilities and commercial enterprise, this country was prominent in the import of leather and shoemakers grindery.

In 1936 there were several fairly large tanneries using modern machinery and considerable number of smaller undertakings. The principal factories working in 1936 were: Lekovitch Bros., Tel-Aviv; the Anglo-Palestine leather Co, Yazur, with a capital of £. P. 20,000; the Levathian Tannery Co., Yazur, with a capital of £. P. 15,000; Wadie Dorkhum, Jaffa; and Kiriako Kiriazi, Jaffa. They manufacture mostly sole leather, principally from local hides. Attempts to produce high - grade upper leather have not been successful, owing to the fact that local hides are usually damaged by insects.

The Leather Industry in Pelestine is cenered around Tele

Aviv, Abu-Gosh (near Jaffa ) and Hebron. The best leather now 
adays is produced around Tel-Aviv in Raenana and in Nathanya,

while in Abu-Gosh and Hebron the old methods are still prevalent.

Raenana is mainly specialized in the production of Furs and has to

few machinery, while in Nathanya and other tanneries around Tel-Aviv like the Lekovitch Tannery and the Anglo-Palestine LeatherGo. Produce mainly upper-shoe leather and sole leather and use mostly machineries. Hebron and Abu-Gosh produce mainly sole and sheep leather and use mostly vegetable tennins.

In 1928 there was a Government census, a census which is not very reliable and from that time on there were no census until 1940 and 1941, but they are military secrets and therefore ecunot be published.

#### GOVERNMENT CERSUS OF 1928, FOR LEATHER AND CANVAS.

Ente	rpris	s Per	rsons	Employ-Capital ed Invested			Value o	of output in 1927.			
Num- ber	% of Total	Num- ber.	% of Total	%ter Price	Amount P.	% of Total	Amount P.	% of Total		Kgm. Mater- ials P.	
67	1.9	236	1.3	3.5	34,477	1.0	47,615	1.2	410,7	27,338	

#### 2. STATUS OF THE LEATHER INDUSTRY IN SYRIA AND LEBAMON.

The status of the leather industry in Syria and Lebenon is the same as that of Palestine except in production which is much greater. The quality of the Syrian leather and especially sole leather was better than that of Palestine. This is not true new for the case of the upper-shoe leather. In certain parts of Palestine especially in Reenana and Nathanya, the leather produced is as good and may be a little better than that produced in certain parts of Lebenon.

The leather industry in Lebanon is centered in two principal places: Beirut and Mashgara. In Syria they are centered in Damascus

and Aleppo.

The leather industry was important before World War I, but it was handiccapped by its crude methods of production. Since War I modern factories have been erected - mostly in the years 1930 to 1939 - especially in Damascus, Aleppo and Beirut, while old tenneries have been rapidly disappearing but some reappeared during this war because of the large profits it is bringing. Before World War II, the leather industry, with its improved methods of production, has come to satisfy the greater part of the requirements of the internal market and to do some exporting and especially now it supplies all the requirements of the internal market.

#### Leather Industry Before The World War II:-

The tanning of hides and skins of all sorts has developed greatly in the last few years. Based originally on the presence of native raw materials, it now depends to a considerable extent on foreign supplies of raw hides. Its production has greatly increased, so that in addition to supplying most of the local demand it now exports a considerable quantity of tanned hides.

In addition to local hides used for tanning, large quantities are imported from Palestine, Turkey, Egypt, India and Iraq. Some local hides are exported to Italy, France, the United s States, England and Germany.

#### The Kinds Of Leather Manufactured Are :-

1. Lebanon: - Mostly cow hides, sheep and goat skins, and

small amounts of buffalo and kid skins. The buffalo hides before the War were brought mainly from India, but now only from Irak and in small quantities.

2. Syria: They manufacture mostly sheep, goat and kid skins, and small amounts of buffalo, cow and camel hides.

#### Workers And Wages:-

The large tanneries have about 35 workers, the medium ones between 15 and 30, and the small ones about 5 workers.

The monthly wage of the best worker in Syria before the war was between 15 and 30 syrian pounds; while now the wage of a worker ranges from 150 to 300 syrian pounds per month.

Price Of Hides And Skins In Syria And Lebanon From 1924-1939

Year	Price in %of Sheep and Goat Skins.	Price in % of Cow Hides.		sterling	g pound.
-			January	July	December
1924	100	100	£. L. 4.25	£.L. 4.25	£.L. 4.37
1925	100	100		-	-
1926	150	150	6.48	10.87	6.14
1927	140	140	6.17	6.21	6.21
1928	140	140			
1929	160	160		-	_
1930	70	150			
1931	50	130	6,19	6,21	4.42
1932	35	80		-	
1933	45	75		-	
1934	50	65		_	-
1935	55	70	-		-
1936	70	75	3.73	3_80	5.26
1937	75	<b>7</b> 5	7.36	_	8,84
1938	85	80	8.84	8.84	8,83
1939	75	80	8,83	8,83	8,83

The price per kg. of sheep or goat skin in 1924 was 50 p.s. which is equivalent to 100%.

The high percentage in prices between 1926 and 1927 was due to the low rate of exchange of the franc, while between 1928 and 1931 to the low rate of exchange of the franc and also

to the world crisis.

Sheep And Goat Leather In Syria And Lebanon From 1939 to 1943

Year	Price per Kgim. in L.P (Tanned)	of an	mal	Proposed of local yearly sump	cal y con-	Price per skin in L.P	Proportion of exports
1939	125	100	%	35	%	80	65 %
1940	125	100	%	45	%	80	45 %
1941	170	75	%	60	%	120	_
1942	300	60	%	95	%	175	. 5 %
1943	325	50	%	100	%	200	

Value of Sterling pound from 1959 to 1943 was L.S. 8.83
100 % is equivalent to approximately 1,500,000 skins. The production of skins in Lebanon is approximately 3. of the total production of both Syria and Lebanon except in the production of cow hides in which Lebanon exceeds Syrian production.

Half of the production of the Lebanese tanneries is consumed in Syria, while a 4th. of the Syrian tanneries are sold in Lebanon.

Lebanon has imported for 1938 - 1939, an average of 3,500 to 4000 tons yearly of e raw hides and skins. A part of these hides and skins were tanned, then reexported at an average of 1,500 tons, yearly. Actually, there must be added a number for the local consumption of the army.

Prices of hides and skins per kgm. for August of every year:-

Sa.	Selted sheep skin with wool.		wi th	L	amb	(2) sk	ins,		Cow hides.					
1938	1939	1940	1941	1942	38	89	40	410	4241	38	39	40	41	42
60	75	45	45	185	125	150	100	135	145	50	55	220	200	175

- 1. By kgm, of sheep skin ( 4 kgm, the piece ).
- 2. By kgm. of medium lamb skin (1.25 kgm. the piece )
- 5. By kgm. of cow hide ( 6 kgm. the piece ).

Prices in 1939 for sheep and lemb were dearer than 1940, because there were no exportations and the demand was nearly the same; while in the case of cow hides, Syria and Lebanon used to import, as a result supply decreased and therefore prices went up.

Imports and exports of Syria and Lebanon: In addition to local hides used for tanning, large quantities are imported mainly from Palestine, Turkey, Egypt, India and Iraq. Some local hides are exported to Italy, France, The United States, England and Germany.

The imports consist mainly of cattle hides and, to a lesser extent, goat and sheep skins. The exports are mainly hides of goats and sheep. The imports have been increasing, while the exports have been on the decline. The large quantity exported in 1933, which exceptional, was due to large shipments of hides made to the United States. The increase in the excess of imports over

exports of raw hides is an evidence of the increasing dependence of the local tanning industry on foreign supplies. Since 1928, when modern tanning methods began to develop, there has always been a more or less large excess of imports over exports. Considering the large quantities of hides supplied locally, the increasing importance of the tanning industry is clearly revealed.

With the large decrease of imports, local production supplies the greater part of the local market. It is estimated that 75 % of the "box " leather and 85 % of the sole leather used internally are furnished by the local industry. The imports of box-calf as well as of fine leather come mainly from the United States and France. The imports of sole leather come mainly from France and Egypt. Syria may be considered self-sufficient in tanned hides, however, for certain qualities of fine leather, it is dependent on foreign supplies. In sole leather it is almost sel-sufficient for in addition to supplying 85 % of the internal market in 1934, about 105 tons of sole leather were exported, as compared to 122 tons of imports. The exports of tanned leather go mainly to Palestine and England.

Imports and experts of Syria and Lebanon during this war in tons:-

Skins and hides		- STATES OF THE REAL PROPERTY.	_	1940		194		19	42
	<u> </u>	Imp.	Ex	o. Imp.	Exp	Imp.	Exp.	Imp.	Exp.
Tanned and Untanned		9 1,	985	1,980	376	1,351	154	1,862	146

Most of the imports and exports of Syria and Lebanon during

this war are raw hides and skins, especially the exports.

#### Materials Used In Tanneries;

Most of the materials used in the tanneries are imported from outside e.g. degras oil, sodium sulfide, artificial material, chromates of sodium and potassium.

The chromates were mostly imported from Germany because it was cheaper than other countries like England and America, but nowadays it is imported from America while the degras oil is imported from England.

The tanning extracts are mostly obtained from Africa (
like quebracho ) and Izmir-Turkey ( mostly Valonia ) and in the
region of Aleppo ( Aleppo galls ).

Since the war started there were no more importations and as a result tammeries were suffering from the lack of materials, but with the coming of the Allies into Syria and the Lebanon the tammeries have been able to get some materials, thus relieving the problem slightly. Nevertheless they are not enough, tammeries are being forced, on account of this, and because of the great price of materials, to resert to the use of old methods, like the use of dung of dogs a instead of artificial bating material. This is specially done in Mashagara and Hebron.

# Comparison Of Leather Produced In The Near East With Leathers Imported From Other Countries Before The War.

The skins and hides imported from Europe and America are

of a much better quality than the ones produced in the Near East for two reasons :-

- 1. The animals are fed better and well taken care of.
- 2. Holes in the hides and skins caused by Anthranx.

The leather produced is also of a much higher quality than the one produced here for two main reasons:-

- l. Lack of specialists. In the Near East there are very few specialists and even these are not skilful, and therefore there is no control of the materials in the processes.
- 2. Lack of machinery, which constitues the difficulty of controlling the processes as the hide is tanned.

The leather produced here cannot be compared with the European, except sole leather which is done as well as in Europe for the sole reason that it needs very little technic as compared to the upper-shoe leather.

#### Sanitary Conditions

Sanitary conditions in most of the tammeries in the Near East especially in the small ones, is very poor, due to the lack of government control. The tannery is rarely cleaned and the byproducts are thrown mear-by. Even the building is not sanitary so far as ventilation is concerned.

When a men in Europe or America thinks of ereating a tennery he is forced to consider by the government and for his own good the following important points:

- 1. Specialists to control the tannery.
- 2. The possibility of drainage and disposal of effluent waste liquors and washing waters.
  - 3. Soft water supply.
- 4. commercial facilities as to nearness to markets and sources of supply of raw materials.
- 5. Erection of a building suitable for the purpose of ventilation, fire accidents, water supply, etc...

Now, what a tanner here cares for is only a good water supply and the hell with the rest. He chooses an old building devoid of ventilation, drainage system for the disposal of waste liquors, waste material and washing waters.

As a result we therefore expect the leather produced to be of a very inferior quality.

Thus, to my opinion, in order to improve our tenneries in the Near East we must have the:-

- 1. Means of destroying the flies that inferiorate our skins and hides, and here is a problem to be tackled by the biologists and the government.
- 2. We should have government control in the tenneries as regards the disposal of waste materials, ventilation, and cleanliness.
- 3. Specialists, people that do understand and have had great experience in leather manufacture and who also are chemists.

4. Machinery, in order to make the means of controlling the processes of tanning much easier.

#### Methods Used

1. Old Method: - Mashghara, Beirut, Hebron, Abu-Gosh.

Upper shoe leather: The skins are washed in a pit, then removed and put in another pit containing saturated lime and some Na<sub>8</sub>S. After three days they are taken out, dehaired, cured by a beamster and washed. They are then put in a pit containing dung of degs or hen until placid when they are taken out and put in successive pits containing bark extracts or leaves e.g. Sumach, until they are well tanned. They are dried, then slightly wetted and ironed with a piece of iron. Afterwards they are dyed and oiled, and thus our leather is ready.

2. Modern Method: - Beirut, Ranana, Nathanya.

Upper shoe leather: The salted hides are soaked with water in a pit for three days until they are soft, or if sundried a little longer.

They are then drummed with saturated lime solution containing Na<sub>2</sub>S for one day. They are afterwards unhaired and scudded in machines, put in artificial bating materials for about an hour and then pickled in a mixture of organic acids and Nagl for arround one hour. The use of bating and pickling is for the following reason:-

In the final preparation of the skin for tanning, the PH

value of the solution absorbed by the skin and with which the skin is in equilibrium must be adjusted to suit the particular method of tanning to be employed. During liming, this solution has a PH value of about 12.5, during bating a PH value of about 7.5. Before the skins can be tanned properly by any of the common methods of tanning, the PH value of this solution must be lowered considerably below the value of 7.5. During vegetable tanning, the PF value of the liquors is usually less than 5, and in chrome tanning, less than four. By using tan liquors containing the excess of acid, the adjustment of the PH value may be made in the ten liquor itself. But this is often a very difficult matter where the process is not under rigid chemical control. Consequently by using organic acids before tanning ( drenching ) the PH value can be lowered to the desired value or by the use of NaCl in conjunction with organic acids ( pickling ) in order to prevent the unnecessary swelling of the hides. They are than washed in warm water ( in a drum ) at arround 60 degrees centigrade.

The hides are then drummed for three hours with basic chrome liquor the first day, left overnight and drummed for two hours the second day. The hides are afterwards washed in the same drum with water to remove the excess chrome liquor and then dyed.

The hides are then taken to a machine, thinned as required from the flesh side and smoothed in a staking machine to remove wrinkles. They are then fat-liquored, put on rectangular frames.

streched, held in place by picks and then dried in the sun.

When dried they are again dyed with a pad on the grain side and afterwards ironed in a machine at a temperature of around 60 degrees centigrade.

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## STATISTICS ON IMPORTS EXPORTS

## AND LEATHER PRODUCTION

IN THE

NEAR EAST

#### PALESTINE

## Statics on Importation and Exportation between 1924 and 1941.

#### 1924.

Tm	Exports			
Hides and Skins Undressed Leather and Manuf. Thereof Chrome Alum Vegetable Tannins Bags, Wallets, Belts ect.	114,430 382,800 16,000 75,000	0,350	479,680 25,000	0,350
Total:	588,230	68,465	504,680	33,765

#### 1925.

	mports		Expo	rts
Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins Bags, Wallets; Belts ect.	17,000 88,915	6,670 65,710 0,400 1,700	612,465 39,200 27,750	30,050 6,010 0.750
Total	525,310	74,560	679,415	36,810

#### 1926.

	Impor	ts	脸	ports
Hides and Skins Underes. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins Bags, Wallets; Belts ect	350,437 16,000 86,354	3,395 65,360 0.350 1,760	443,518 63,600 33,750	23,645 6,715 0.915
Total	501,635	70,865	540,868	31,275

#### 

	Impor	ts	Exports		
Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins Bags, Wallets, Belts, ec	504,984 15,000 120,582	12,000 87,706 0,300 2,700	474,245 103,000 21,850	24,515 12,750 0,315	
Total	844,330	102,700	609,095	37,580	

#### 

Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins +Bags, Wallets, Belts ect	9,000	15,733 62,624 0.200 3,740	661,388 78,900 5,332	36,640 10,050 0,115
Total	553,790	82,297	745,620	46,805

#### 

Chrome Alum Vegetable Tannins +Bags, Wallets, Belts ect.	17,871 342,330	0.440 8,160	20,112	0,235
Hides and Skins Undres.	289,139	20,855	708,323	57,400
Leather and Manuf. Ther.	247,260	68,000	96,305	12,710

<sup>(+)</sup> They are included under Leather and Manuf. Thereof.

#### 

	Import	s	Expe	37,405 10,522 0.540
Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins +Bags, Wallets, Belts ect.	218,563 351,700 6,020 241,637	19,267 69,774 0,111 25,354	439,020 78,852 37,638	10,522
Total	817,920	94,506	555,510	48,467

#### 

Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins +Bags, Wallets, Belts ect.	3,040 255,690	18,527 56,790 0,052 4,130	561,766 44,900 13,000	22,445 4,820 0,240
Total	808,935	79,499	619,666	27,505

#### 

Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins +Bags, Wellets, Belts, ect	210,710 292,490 8,220 205,505	10,386 61,040 0,220 4,338	418,450 14,476 6,474	15,450 1,146 0.050
Total	716,925	75,984	439,400	16,646

<sup>(+)</sup> They are included under Leather and Manufacture Thereof.

#### 1933

	Import	8	Exports	
Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins Bags, Wallets, Eelts, ec	4,253	14,517 73,827 0,149 6,237	486,070 19,726 27,594	14,632 1,770 0,187
Total	985,760	94,730	533,390	16,589

#### 1934

Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins +Bags. Wallets. Belts. ec	9,220	22,120 102,565 0,375 8,065	837,355 29,743 15,922	22,845 8,880 0,120
Total	1,509,315	133,125	883,020	31,845

#### 1935

Hides and Skins Undres. Leather and Manuf, Ther. Chrome Alum Vegetable Tannins Bags, Wallets, Belts, e	519,518 9,000 589,740	14,220 125,330 0,350 9,570 7,854	1,334,074 25,310 7,200	48,467 7,000 0,075
Total	1437,625	157,324	1,366,584	55,542

(+) The are included under Leather and Manufacture Thereof.

## 

	Inport	8	Exports	
Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins Bags, Wallets, Belts.eet	6,220 140,880	30,272 102,600 0,193 2,570 3,147	2,326,000 10,500 4,200	108,070 0,870 0,025
Total	1241,940	138,782	2,340,700	108,965

## 

Hides and Skins Undres. Leather and Manuf, ther. Chrome Alum Vegetable Tennins		59,346 166,214 0,195 6,100	2,845,000 4,540	187,260
Bags, Wallets, Belts, e		7,500	1,620 6,200	5,720
Total	1948,650	239,355	2,857,360	193,318

## 

Total	776,875	108,710	1,877,170	91,882
Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins Bags. Wallets.Belts.ect	13,075	6,650 85,625 0,260 2,075 4,100	1,864,000 5,000 3,670 4,500	86,965 0,540 0,027 4,350

## 

Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins Bags, Wallets, Belts, Ect.	253,000 760,000 2,075 316,900 16,300	15,350 134,677 0,062 6,033 5,400	1,330,000 2,212 0,700 3,000	63,146 0,166 0,005 2,400
Total	1348,275	161,522	1,335,912	65,717

## Palestine Statics cont.

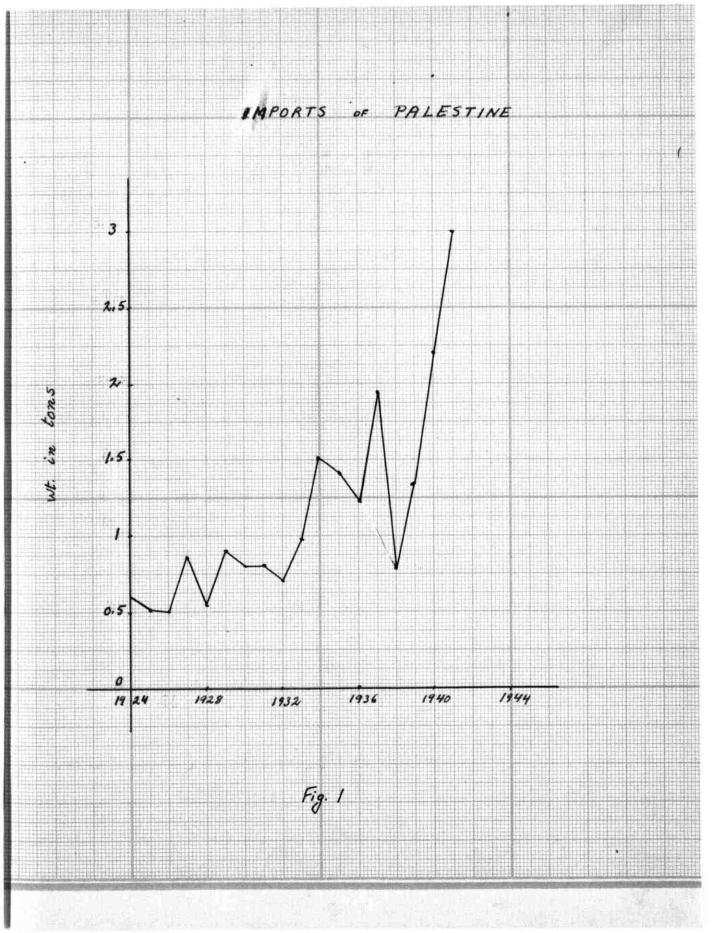
## 1940

Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins Bags, Wallets, Belts, ect.	966,000 737,000 3,730 505,085 1,350	29,708 184,314 0,144 15,925 0,777	0,735 1,110	42,375 0,360 0,006 0,826
Total	2213,165	230,868	649,045	43,567

## 1941

	According to the company of the comp	Name and Address of the Owner, where the Party of the Owner, where the Party of the Owner, where the Owner, which is the Owne	Name and Address of the Owner, where the Party of the Owner, where the Party of the Owner, where the Owner, which is the Owner,	THE RESERVE OF THE PERSON NAMED IN
Hides and Skins Undres. Leather and Manuf. Ther. Chrome Alum Vegetable Tannins Bags, Wallets, Belts, ect.	1,147,000 381,000 6,045 1,552,575 1,098	41,800 159,255 0,375 52,565 1,117	896,000 1,500  4,292	70,912 0,320 8,000
Total	3,087,718	254,112	811,792	79,232

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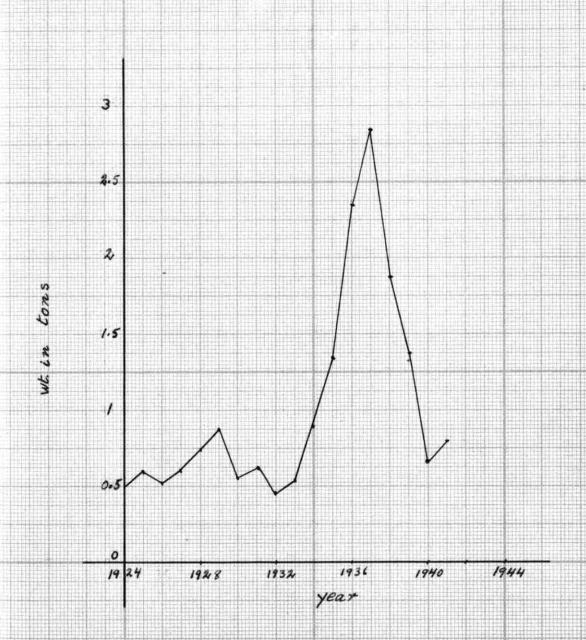


Fig. 2

#### SYRIA AND LEBANON

#### 1924

	Imp	orts	Exports	
Degras Oil W.And S. of Skins (1) P.M. for the T.I. (2) T. Extracts Chromate	194,646	46,672	319,178	67,798
Skins and hides Pieces of work in H.and P.B.or P. and Furs (3)	8.1134,231	669,743	1480176	62,758
Total	1328,877	716,415	467,354	130,556

#### 1925

COLUMN TO A SECURE A DESCRIPTION OF THE PROPERTY OF THE PROPER	Aparent and a second	-		
Degras Oil				
W.and S. of Skins P.M. for the T.I.	859,178	251,224	1,855,850	636,800
Tanning Extracts			******	
Chrometes			-	-
Skins and Hides (1) Pieces of work in HS. P.B.or P.and Furs (3)	(2)1307,088	1136,824	367,840	285,996
Total	2166,266	1388,048	2,223,690	922,796

#### 1926

Degras Oil W.and S. of Skins P.M.for the T.I. Tanning Extracts	145,000 797,910 558,000 650,000	11,500 364,340 56,300 38,000	286,890	19,087 50,500
Chromates Skins and hides, Pieces of work in HS. P.B. or P. and Furs	45,000	11,500	329,545	352,500
To tal	3614,700	2164,980	907,435	422,087

Waste and screpping of Skins.
 Primary Materials for the Tannery Industry.
 Peltry brute or prepared and Furs.

### Syria and Lebanon cont.

### 

	Jm	ports	Export	3
Degras Oil W.and S. of Skins P.M. for the T.I. Tanning Extracts Chromates Skins and Hides Pieces of work in HS. P. B. or P. and Furs	135,000 1307,563 474,000 803,100 36,000 1578, 751	10,750 101,988 570,000 51,900 9,500 295,845	149,065 445,050 533,745	4,260 62,000 153,600
Total	4634,414	1040,028	1127,860	219,860

## 

Degras Oil W. and S. of Skins P.M. for the T.I. Tanning Extracts Chromates Skins and Hides Pieces of work in HS.	114,000 1446,600 875,500 810,000 33,000	10,500 104,265 265,000 85,000 8,250 250,122	300,000 600,250 598,880	21,000 79,800
P.B. or P. and Furs Total	4178,290	203,137	1499,130	233,640

## 

	AND DESCRIPTION OF PERSONS ASSESSMENT ASSESSMENT ASSESSMENT ASSESSMENT ASSESSMENT ASSESSMENT ASSESSMENT ASSESS	THE RESERVE AND ADDRESS OF THE PARTY OF THE	the second section of the second section is the second section of the sect	Bright Street, or other Designation of the last
Degras Oil W.and S. of Skins P.M. for the T.I. Tanning Extracts Chromates	125,000 1413,900 850,000 600,000 45,000	10,600 104,124 52,000 35,056 12,000	280,600 450,000	19,005
Skins And Hides P.of Work in H.and S. P. B. of P. and Furs	891,137	1168,500	524,540	384,250
Total	3925,037	1382,280	1255,140	465,260

## Syria and Lebanon cont.

### 

	In	ports	Export	S
Degras oil W. and S. of Skins Tanning Extracts P.M. for the T.I. Chromates Skins and Hides P.of work in H.and S. P.B. or P. and Furs	100,500 1810,850 950,000 35,000 891,135	10,050 148,060 9,040 9,000 1168,500	320,000 649,000 318,410	20,058 82,050 330,162
Total	4487,485	1389,600	1278,410	432,270

#### 

Degras oil W.S. and of Skins P.M. for the T.I. Tanning Extracts Chromates Skins and Hides P.of work in H.and S. P.B. or P.and Furs	114,080 83,820 874,220 809,380 33,765 2871,205 33,985 6,390	10,556 3,818 8,635 85,278 8,030 1292,880 108,080 20,545	365,960 654,033 26,940	78,815 45,088 208,830 17,815
Total	4826,845	k537,822	1516,235	350.548

### 

Degras oil W. and S. of Skins P.M. for the T.I. Tanning extracts Chromates Skins and Hides P. of work in H.and S. P.B. or P. and Furs	137,301 15,540 474,703 650,292 41,076 1637,800 30,440 4,361	10,745 0,590 570,812 38,155 7,694 592,600 93,000 18,120	442,467  471,975 9,485 12,389	78,264  167,750 6,756 27,020
Total	2992,413	1331,716	936,316	279,790

## Syria and Lebanon cont.

### 

	Im	ports	Export	3
Degras oil W. and S. of Skins P.M. for the T.I. Tanning extracts Chromates Skins and Hides P. of work in H. and S. P.B. of P. and Furs	114,610 77,430 557,910 903,520 36,040 2208,630 32,134 12,301	8,306 2,052 56,295 52,010 5,730 579,730 98,125 13,382	3150,850 23,824 34,430	128,030 675,450 15,450 39,730
Total	3842,745	815,630	4049,170	858,660

#### 

Fanning Extracts Chromates Skins and Hides P. of work in H.and S. P. B. or P. and Furs	580,962 1146,655 44,860 2541,500 34,780 7,560	48,490 61,510 5,965 546,140 98,730 14,720	438,233 36,100 772,457 43,780 10,405	73,645 2,235 205,025 19,500 9,100
Degras oil	145,478 37,630 580,962	10,237 0,993 48,490	438,233	73,645

### 

Degras oil W. and S. of Skins P.M. for the T. I. Tanning Extracts Chromates Skins and Hides P. of work in H. and S. P.B. or P. and Furs	125,000 63,803 345,882 1309,028 45,367 3692,000 37,500 3,908	9,200 1,707 33,840 74,243 5,615 637,000 89,745 10,510	640,070 58,165 1665,660 84,020 614,060	83,835 4,010 406,125 38,780 406,125
Total	5497,488	861,860	3061,975	938,875

## Syria and Lebenon cont.

### 1936

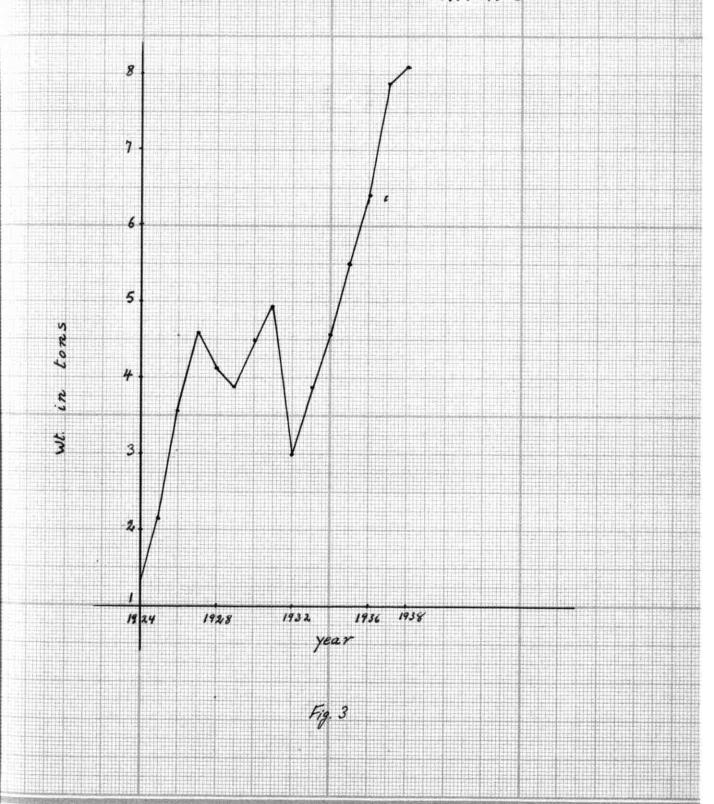
	1	mports	Exports		
Degras oil W. and S. of Skins P. M. for the T. I. Tanning Extracts Chromates Skins and Hides P. of work in H.and S. P. B. or P. and Furs	146,795 19,390 402,575 1247,600 20,900 4505,460 53,880 3,665	15,222 1,938 62,010 93,730 3,040 849,000 71,790 11,315	619,770 25,120 2300,470 38,240 13,690	76,987 2,103 631,030 19,150 9,910	
Total	6399,865	1105,045	2997,290	739,180	

#### 1937

Degras oil W. and S. of Skins P. M. for the T. I. Tanning Extracts Chromates Skins and Hides P. of work in H. and S. P. B. or P. and Furs	142,845 30,565 874,320 1571, 405 47,535 5032,160 44,160 5,310	19,540 11,910 142,900 484,500 7,260 1787,030 144,430 24,800	469,905 30,785 2806,165 20,935 17,025	
Total	7748,300	2622,370	3424,815	1724,250

1938.

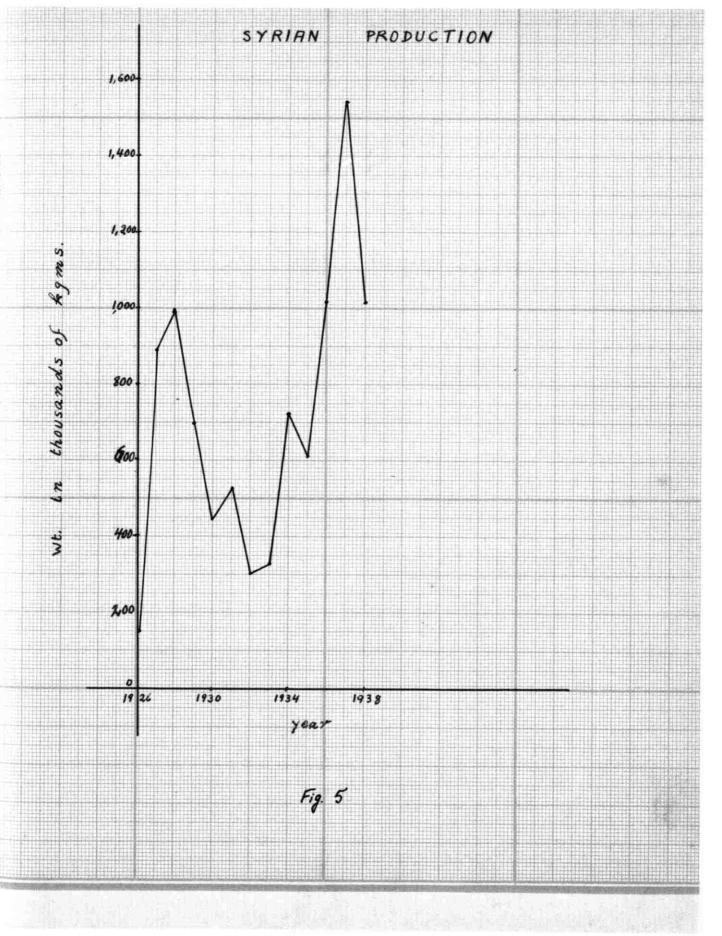
Degras oil	166,483	38,392	*****	etherras
W. and S. of Skins	82,000	19,300	122,590	2,320
. M. for the T. I.	786,522	102,458	561,780	104,760
Tanning Extracts	1787,305	308,600	37,940	11,404
Chromates	92,990	21,560		
Skins and Hides	5108,900	2117,600	2023,715	1423,830
P. of work in H. and S.	25,817	141,370	20,025	23,180
P. B. of P. and Fors	5,597	40,230	17,270	18,720
Total	8055,614	2789.510	3083,320	1584.214



SYRIAN PRODUCTION OF HIDES AND SKINS

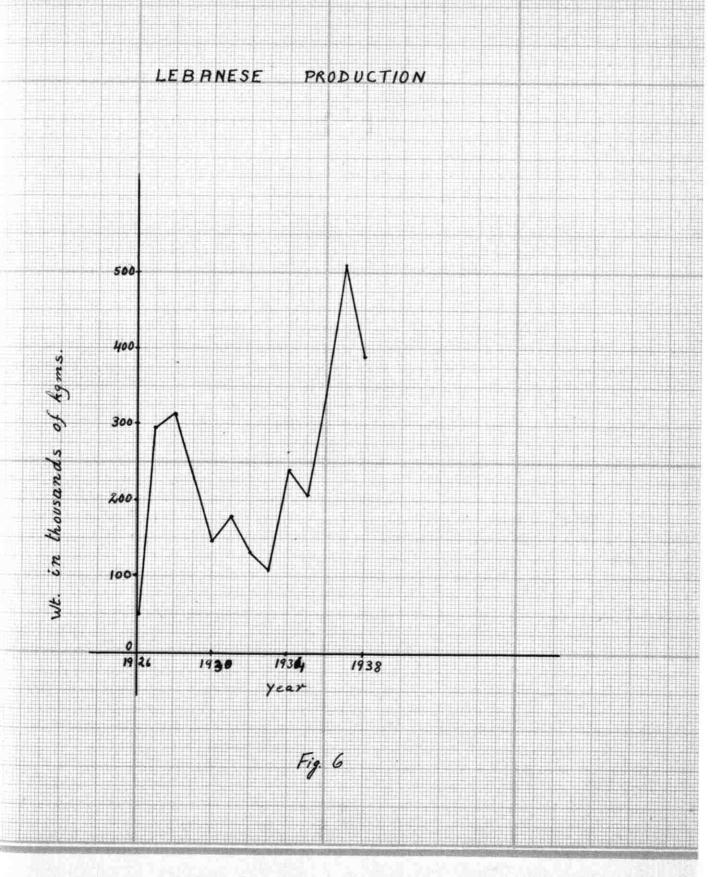
Year	Lemb	Sheep	Cow	Goat	Buffallo	Camel	Total
1926	8,550 8,550	34,900 139,600	410 2,460	+	30 180	175 1,070	44,065 151,560
1927	11,350 11,350	167,600 670,400	13,400	+	9,9 <b>50</b> 59,700	10,255	212,355 883,380
1928	+	172,200 688,800	17,250 103,500	+	15,950 95,700	8,525 <b>4</b> 9,150	213,925 937,150
1929	++	144,950 579,800	8,525 51,150	+	4,500 27,000	6,545 38,270	164,520 696,220
1930	*	100,050	3,285 19,710	* *	1,430 8,580	2,460 14,760	107,225
1931	+ +	76,650 302,600	5,405 32,430	41,200 164,800		1,116	127,156 529,236
1932	61,050 61,050	39,300 157,200	3,883 23,298	20,250		1,016	128,334 304,654
1933	35,450 35,450	43,000 172,000	3,465 20,790	21,450 85,800		483 2,898	126,563 333,228
1934	28,500 28,500	64,5 <b>6</b> 0 258,240	4,425 26,910	45,600 182,400	2,650 15,900	1,310 7,860	145,105 719,810
1935	38,300 38,300	101,000	4,535 27,210	31,730 126,520	1,560 9,360	2,060 12,360	179,187 617,750
1936	48,000 48,000	153,000 618,000	15,350 92,600	62,400 249,600	825 4,950	2,730 16,380	282,305 1023,630
1937	77,700 77,700	206,000 824,000	19,220 115,320	125,500 502,000	830 4,980	1,510	430,760 1533,060
1938	39,100 39,100	161,000 644,000	2,870 17,220	77,000 308,000	830 4,980	1,420	282,220

<sup>+</sup> Indluded under Sheep.



Year	Prieces	Kgms.
1026	15,000	50,620
1927	72,000	294,460
1928	75,050	312,583
1929	65,200	232,000
1980	35,225	147,775
1931	43,150	176,415
932	45,000	128,720
.933	43,560 Y	111,075
.934	50,105	239,950
935	60,100	205,920
936	95,305	341,010
937	150,760	511,020
.938	155,200	390,610

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VEGETABLE TANNINS FOUND IN THE

NEAR EAST

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## MOST IMPORTANT VEGETABLE - TANNINS FOUND IN THE NEAR EAST

1, RHUS CORIARA: - (Sumach )

#### Location: -

- 1. Lebanon: Top of Beruk, Abayh, Beirut.
- 2, Syria:- West of Duma.
- 3. Palestine: Jerusalem, Hebron.

Tannins: - Found in the leaves, fruits and bark.

- 2. PISTACIA LENTISCUS:- (Mestick Lentisk )
  - 1. Lebanon: South of Tripoli, Beirut.
  - 2. Syria:-
- 3, Palestine: Bayt Jibrin, Jaffa, Emmaus, Hifa, Mt. Carmel, Mt. Tabor, Wadi Kishimyal ( Jordan Valley ) Ras un Wakourah.

Tannins:- Found in the leaves.

- 5. QUERCUS INFECTORIA:- ( Aleppo Oak Vis)
  - 1, Lebenon: Prumana, Baruk Cedars, Safita.
  - 2. Syria:- Aleppo, Alexandretta, Bityas.
- 3. Palestine: Tabor, Janin, Ul-Kubaybeh, South of Safad, Mt. Karmel.

Tannins: - Found in the barks and galls.

- IV. QUERCUS CERRIS:- ( Turkish Oak راق )
- 1. Lebanon: Ain Zahalta, Cedars, Jabel Baruk, Above Ihdin, Hermon.
  - 2. Syria:-
  - 3. Palestine:- Northern Palestine.

Tannins: - found in Galls.

V. QUERCUS SESSILIFLORA:- ( Durmast Oak - )

Location:- Mountainous regions.

Tannins:- found in the bark

- VI. QUERCUS GOCGIFERA:- (Kermes Oak زان-سنریان)

  Location:- Mountanous regions.

  Tannins:- Found in the bark.
- VII. QUERCUS AEGILOPS:- ( Valonia رملول سل )

  Location:-
  - 1. Lebanon: Fundajek, Safita.
  - 2. Syria: Northern Syria.
- 3. Palestine:- Baniyas, Mt. Karmel, Mt. Tabor, Haera, Near Herzlia.

Tannins:- Found in the galls.

- VIII. PISTACIA TEREINTHUS:- ( Terebinth Butim )
  - 1. Lebanon: Widely distributed.

- 2. Syria: Widely distributed.
- 3. Palestine: Banias, Petra ( Trans Jordan ).

Tanmins: - Found in the bark and galls.

## IX. <u>PISTACIA VERRA:-</u> ( Pistachio - )

- 1. Lebanon: Beirut.
- 2. Syria: Ayn-ut-Tinah.
- 3. Palestine: Remah.

Tannins: - Found in the galls.

K. MIMOSA PUDICA:- (Sensitive Mimosa - )

Location:- Found as wild form.

Tannins: - Found in the bark.

## XI. SALIX:- (Willow - John) Location:-

- 1. Lebanon: Widely distributed.
- 2. Syria: Widely distributed.
- 5. Palestine: Widely distributed.

Tannins: - found in the bark,

# XII. CASTANA VESCA:- ( Cheshut - vi) Location:-

- 1. Lebanon:-
- 2. Syria:- In the north.
- 3. Palestine:-

Tannins: - Found in bark and cupule.

## XIII. POPULUS ALBA:- ( White poplar - /p> ) Lecation:-

- 1. Lebanon: Abayh, Tripoly, Beka'a.
- 2. Syria:-
- F. Palestine: Amman, Jarah, Hulah, Jerusalem etc. Tennins: Found in bark.

## XIV. ACACIA ARABICA:- (Gum Arabic - Je je)

- 1. Lebanon: -
- 2. Syria:-
- 3. Palestine:- Introduced in 1919 ( 10000 trees at Rishon. )

Tennins: - Found in Bark.

## XV. <u>EUCALYPTUS:-</u> (Eucalyptus - الينا) Location:-

- 1. Lebanon: Nearly everywhere
- 2. Syria: Nearly everywhere.
- 3. Palestine: Thousands of trees at Hadera, and elsewhere

Tannins: - Found in bark.

Aleppo Pine عريم Location:-

## AVI. PINUS HALEPENSIS:- (Aleppo Pine - Syrjing) Location:-

- 1. Lebanon: Everywhere.
- 2. Syria: Everywhere.
- 3. Palestine: Everywhere.

Tannins: - Bark and in fleshy part of the stem, only obtained when tree is cut.

## XVII. PUNICA GRANATUM:- ( Pommegrade - i)

- 1. Lebanon: Wearly everywhere.
- 2. Syria: Nearly everywhere.
- 3. Palestine: Nearly everywhere.

Tannins: - Found in rind of fruit, and in bark of stem and root.

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#### PERCENTAGE TANNING IN VEGETABLE TANNING FOUND IN THE NEAR EAST=

Veg. Tan.	Country	From	Percentage Tannin
Sumach	Lebanon	Fruits	6.7
п	12	Leavs	25.00 *
in .	88	Bark	
Aleppo Oak I	Syria	Galls	60.0 *
" II	Ħ	Galls	50,0 *
" III	11	Galls	38,2 *
Turkish Oak	17	Galls	45.0
Durmast Oak	Lebanon	Bark	12,0
Kermes Oak	n	Bark	15.0 #
Valonia	Palestine	Galls	35.0 *
Terebinth		Cupule	50.2 *
Pistachio		Galls	
Sensitive Mimosa	11	Bark	10.0 *
Willow	Lebanon	Bark	11.0 *
Chestaut	Personal Publisher	Bark	7.0
White poplar	Lebanon	Bark	
Alappo Pine		Bark	15.0
Ponmegranade		Rind of P	om. 14.0 *
	Palestine	Rind of Po	om. 9.8
"		Bark of S	tem 2.0
Quebracho Extra	t Africa	Bark	60.0

RESULTS

OF THE

INVESTIGATIONS

CARRIED

ON

VEGETABLE TANNINS

#### Data concerning Gelatin

- For all the investigations carried on gelatin, jellies containing 4 gms. gelatin per 100 cc. water were used
- 2, The pH of the 4% gelatin-jelly was found to be 4.4 .
- 3. The isoelectric point of the gelatin was found to be 4.9.
- 4. The ash content of the gelatin was found to be 1.2 % .

1. Rate Of Diffusion Of Tannin-Extracts Into 4% Gelatin-Jelly
With Same Percentage Of Non-Tannins But Different Percentage
Of Tannins.

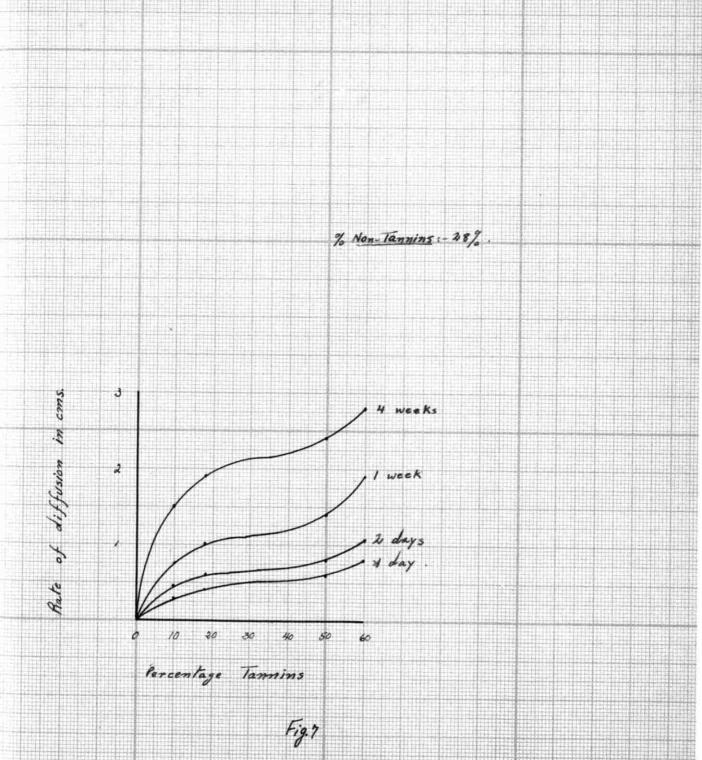
Kind of	%	1 %	Rate o	f diffus	ion in e	ms.
Tannin	Tannin	Non-Tan	1lday	2 deys	1 week	4 weeks
Aleppo-galls (quality I)	60	88	0,8	1,05	1.9	2,8
Aleppo-galls (quality II)	50	28	0.6	0.80	1.4	2.4
Sumach (seeds)	18.	28	0.4	0.60	1.0	1.9
Bark of Pom	10	28	0.3	0.45	0.75	1.5

Tannin-extracts of two kinds of Aleppo-Galls, one of Sumach and one of the bark of Pommegrenade were prepared. The percentage of non-tannins in each was made constant, but the percentage tannin was made variable.

10 cc. of each solution were poured over 4% gelatinjelly containing 0.1% Ferric chloride in test tubes of 1.6 cms. diameter and the rates of diffusion in each determined after the specified times. The results are given in the chart above (Fig. 7).

Tannin and some non-tannins react with Ferric chloride giving very deep blue colors, which served to indicate the extent of the penetration.

It is found that the rate of diffusion increases with



increase in the percentage of tannins, but the proportionality factor of diffusion is not constant.

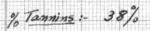
II. Rate Of Diffusion Of Tannin-Extracts Into 4% Geletin-Jelly
With Same Percentage Of Tannins But Different Percentage
Of Non-Tannins.

Kind of Tannin	%	%	% Rate of diffusion in cms.					
Iannin	Tannin Non-Tan	Non-Tan		4 days	6 days	24 days	1 mohtl	
Alep.Galls (Quality III)	38	7.6	0.5	1.1	1.5	2.5	2.8	
Alep.Gells (Quality II)	38	15.0	9.7	1.45	1.7	3.2	3.45	
Alep.Galls (quality E)	38	18.0	0.8	1.6	1.85	3.4	3.7	
Sumach (seeds)	38	60.0	1.1	2.5	3.40	5.5	5.8	

Tamin extracts of three kinds of Aleppo galls and one kind of S umach seeds were prepared. The percentage of tannin in each was made constant, but the percentage non-tannins were made variable.

10 cc. from each solution were poured over 4% gelatinjelly containing o.l % Ferric chloride and the rate of diffusion in each test-tube determined after the specified times. The results of the experiment are shown in the above chart (Fig. 8 )

It is found that the rates of diffusion increases with increase in the percentage of non-tennins, but the proportionality factor of diffusion is not a constant.



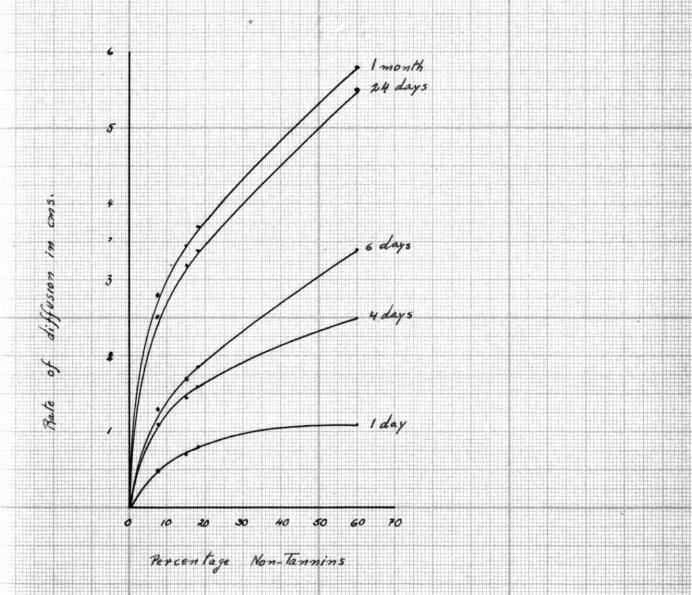


Fig. 8

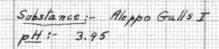
III. Rate Of Diffusion Of Aleppo Galls Extract Into 4% Gelatin-Jelly With Increase Of Tannin Concentration.

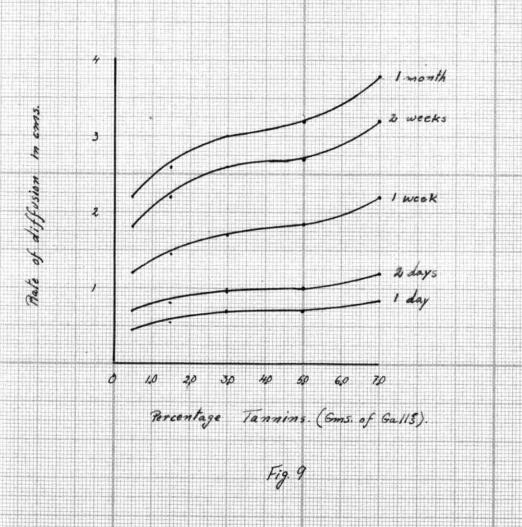
Kind of	Gms. of Galls in		Rate of diffusion in cms.				
Tannin	100 cc.	1 day	2 days	2 days 1 week		lmonth	
Alep. Galls I	0.5	0.45	0.7	1.2	1.8	2.2	
	1.5	0.55	0.8	1,45	2.2	2.6	
44	3.0	0.7	0.95	1.7	2.6	3.0	
N	5.0	0.7	1.0	1.85	2.7	3,2	
**	7.0	0,85	1.2	2.2	3.2	3.8	

Tannin extracts of Aleppo Galls (quality I) were prepared containing different amounts of the galls per 100 cc. water.

10 cc. from each solution were poured over 4% gelatinjelly containing 0.1 % Ferric chloride and the rates of diffusion in each test-tube determined after the specified times. (Fig. 9).

It is found that the rate of diffusion increases with increase in the percentage of non-tannins, but the proportionality factor of diffusion is not a constant.





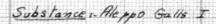
IV. Rate Of Diffusion Of Aleppo Galls Extract Into 4% Gelatin-Jelly With Increase Of Sodium Chleride Concentration In Gelatin - Jelly.

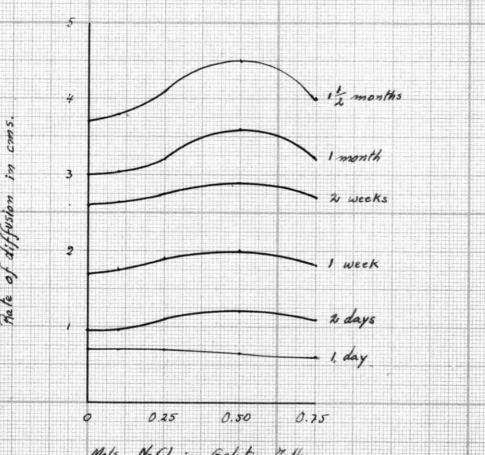
4 gms. Gel. in 100 cc. water.	Gel.	Mols	Hate of diffusion in ems.					
	NaCl 1 da	1 day	2 days	1 week	2 weeks	1 month	13 mon.	
G <b>el</b> atin	+	0.0	0.7	0.95	1.7	2.6	3.0	3.7
18	+	0.1	0.7	0.95	1.75	2,65	3.0	3,8
**	+	0.25	0.7	1.1	1.9	2.75	3.2	4.1
19	#	0.5	0,65	1.2	2,00	2.9	3.6	4.5
11	+	0.75	0.6	1.1	1.8	2.7	3.2	4.0

chloride were made 0.1 M, 0.25 M, 0.5 M, and 0.75 M. with respect to S edium chloride. They were set in test-tubes of 1.6 cms. diameter and 10 cc. of Aleppo Galls extract (quality I) containing 3 gms. galls per 100 cc. water were poured into each test-tube above the gel and the rates of diffusion in each test-tube determined after the specified times. The results are shown in the chart above (Fig. /0).

It was found impossible to prepare gelatin-jellies with concentrations higher than 0.75 M. with respect to sodium chloride in the presence of Ferric chloride due to the conglustion of the gelatin.

The maximum rate of diffusion was found to be around 0.5 M.





Mols NaCl in Gelatin-Jelly.

Fig. 10

The rate of diffusion of tannins in gelatin-jellies containing Sodium sulfate, Magnesium chloride and Sucrose were not determined due to their great power of hydration.

V. Rate Of Diffusion Of Aleppe Galls Extract Into 4 % Galatin-Jelly With Increase Of Sodium Chloride Concentration In Galls Extract.

No results were obtained due to the coagulation of the tennins by the Sodium chloride and the gelatin which was partly dissolved. Thus part of the tennins were precipitated and therefore the rates of diffusion could not be determined.

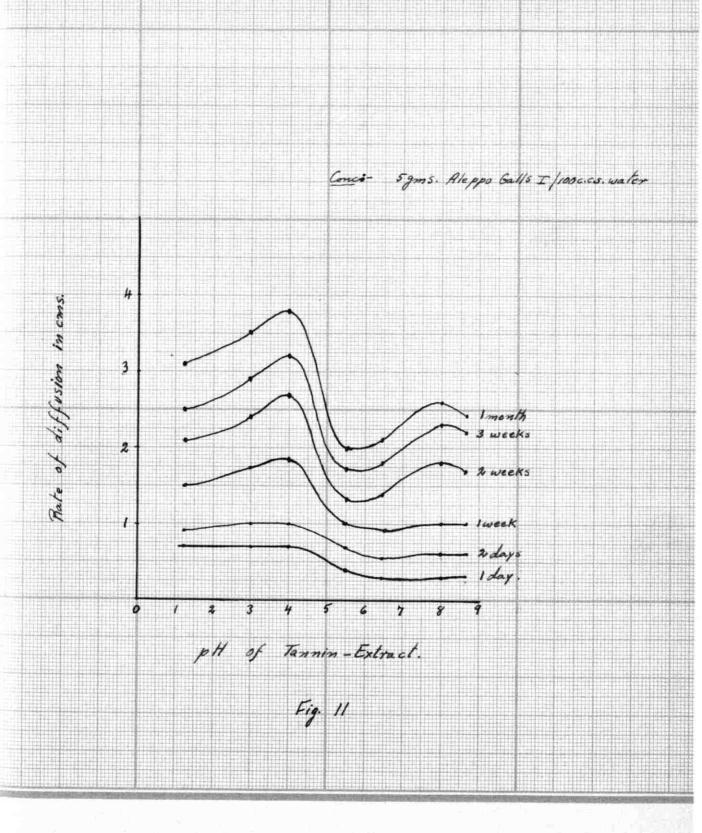
VI. Rate Of Diffusion Of Aleppo Cells Extract Into 4 % Gelatin-Jelly With Change In pH of The Extract.

Gms. in 100 cc. of water	рН	Rate of diffusion in cms.					
		1 day	2 days	l week	2 weeks	3 weekd	1 month
5 gms.	1.22	0.7	0.9	1.5	2.1	2.5	3.1
п	3,00	0.7	1.0	1.75	2.4	2.9	3.5
*	3,95	0.7	1.0	1.85	2.7	3,2	3,8
**	5.50	0.4	0.7	1.0	1,3	1.7	2.0
	6.45	0.3	0,55	0.9	1.4	1.8	2.1
77	8.00	0.3	0.6	1.0	1.8	2.3	3,1
87	8.65	0.3	0.6	1.0	1.7	2.2	2.9

Aleppe Gells extract ( quality I ) were prepared with different pHs. and containing 5 gms. of the galls per 100 cc. water.

10 cc. of each solution were poured over gelatin-jelly containing 0,1 % Ferric chloride and the rates of diffusion determined after the specified times. The results are shown in the above chart (Fig. // ).

Two maximum rates of diffusion were found, one at a pH of 3.95 and the other at a pH of 8. The rates of diffusion were found to increase as the pH increased from 1.5 to 3.95, Further increase in pH caused an decrease in the rate of diffusion until pH 5.5 was reached when it started to increase again. The reason



( according to Wilson ) being that tennin particles below pH 5 are positively charged, while between pH 5 and pH 8, and below pH 2 they are negatively charged.

Since tennin particles are negatively charged in this region and since the rate of combination increases, one may suppose that collagen may become increasingly positive with rise in pH from 5 to 8, thus increasing amount of combination.

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#### I. PREPARATION OF HIDE POWDER.

The adipose tissue was carefully cut away from the fresh skin and the skin thoroughly washed. It was then extracted with several changes of 10 % Sodium chloride solution, in order to remove the soluble protein matter. It was then treated with a Sodium sulfide (0.1 %) saturated lime solution for several days until the hair was quite loose.

The hair and epidermal matters were removed by scrapping the grain surface with a knife blade and the entire grain surface was cut away on a splitting machine. The skin was then washed thoroughly to remove most of the lime. It was then digested for 5 hrs. at 40°C, with a solution containing one gm. of pancreatin, 2.8 gms. Sodium dihydrogen phosphate and 18 cc. of 1 M. solution of Sodium hydroxide per liter. This removed all the elastin fibers. The skin was then cut into small pieces and put into a jar of water equipped with a stirring device. Dilute Hydrochloric acid solution was then added at such a rate as to maintain the solution just faintly acid to methyl orange. When no more acid was required, the pieces were left to wash in running tap water over night. Next day they were soaked in several changes of alcohol to remove the water and then in xylene, after which they were exposed to six until the xylene had evaporated. They were then grained in a mill to a fibrous powder,

Percentage esh in the Hide-powder = 0.5 %.

pH of pure Hide-powder according to Porter = 4.8

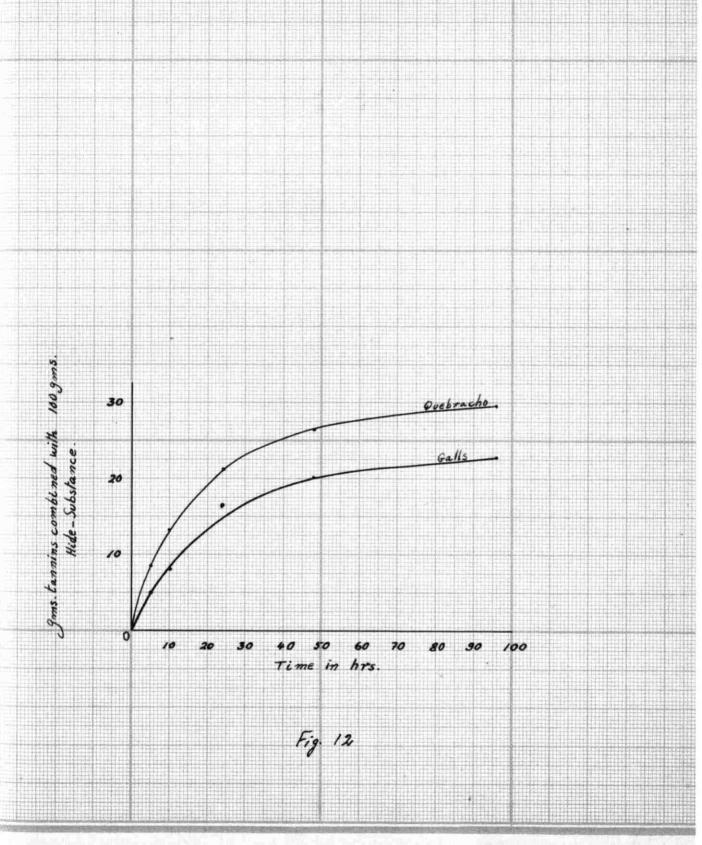
Porter observed that a point of minimum swelling of hide powder occurs at a pH value of 4.8, indicating this as its isoelectric point. Porter also found points of maximum swelling of hide powder at pH values of 2.4 in acid solution and about 12.3 in alkaline solution.

II. AMOUNT OF TANNIN ABSORBED BY HIDE POWDER FROM TANNIN EXTRACT WITH LIME.

Gms. Extract	Vegetable Tannin	Gms. Ta	nnin fix	ed by 10	O gms. H:	ide-powde
	. GIMILI	a contract of			1	96 hrs.
3 gms.	Alep.Galls	5.0	8.1	16.5	20.04	22.53
3 gms.	Quebracho	8,5	13.45	21.2	26.5	29.25

3.84 % non-tennins ) and Quebracho extract ( 52.4 % tennin and 7.6 % non-tennins ). The amounts of tennin fixed by 100 gms. of hide-powder determined after 5,10,24, 48, and 96 hrs. respectively.

Portions of purified powder equal to 2 gm. of anhydrous substance were shaken with 50 cc. of the extracts and each determined after the specified times. After the specified time the powder was washed until the wash water no longer gave a dark color upon the addition of a drop of Ferric chloride solution. The powders, freed from soluble matter were dried in a current of warm air and then completely dried in the oven. The increase



in weight of the absolutely dry material was taken as the amount of tannin fixed by 2 gm. of hide-powder. The results are given in the chart above ( Fig. /2 ).

The rate of fixation of the tannin increases as the time increases but the propertionality factor of fixation is not a constant. The reason being that as the time of fixation is increased the amount of combination is also increased, which decreases the rate of diffusion of the tannin and therefore the rate of combination is decreased.

EXTRACT AFTER TWENTY FOUR HOURS WITH INCREASE OF TANNIN CONCENTRATION.

Kind of Veg.		Gms.	Cannin 1	Fixed by	7 100 gr	ns. Hide-powd
Tennin	рН	0.5 gms Tannin	2 gms. Tennin	4 gms. Tannin	6 gms. Tannin	8 gms. Tannin
Aleppo Galls	4.0	7.0	20	13	9	7.5
Quebracho	4.3	9.0	27.5	15	10	9.0

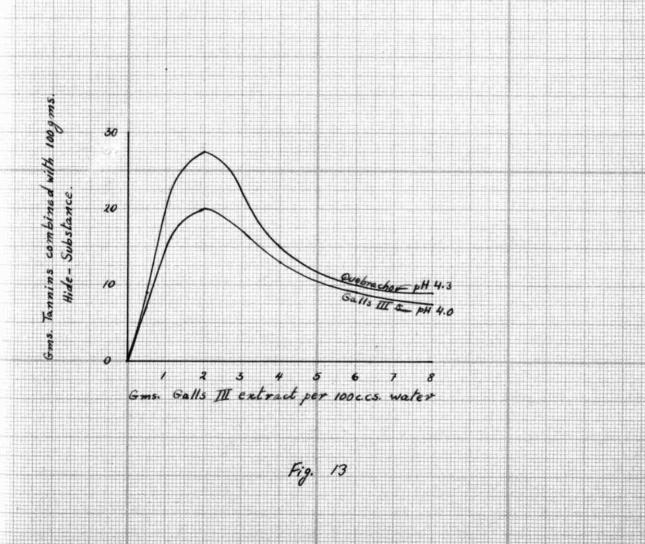
Two kinds of vegetable tannins were used, one of Quebracho extract containing 52.4 % tannins and 7.6 % non - tannins and Aleppo Galls III extract containing 56.16 % tannins and 3.84 % non-tannins.

Portions of purified powder equal to 1 gm. of anhydrous substance were shaken with 50 cc. of the tan liquor containing 0.5 gm., 2 gms., 6 gms., and 8 gms. respectively of Quebracho and Galls.

The results show how the rate of tanning varies with increasing concentration of solutions of Quibracho and Aleppo Galls extracts. Both extracts give curves of similar shape and having maximum points at the same concentration (Fig. /3)

There are two explanations given for the appearance of maximum points in the curves:

- 1. The rate of combination of tannin and hide substance increases so rapidly, with increasing concentration of tan liquor, that it soon reaches a point where the surfaces of the hide fibers quickly become so heavily tanned that they are rendered less permeable to the tannin remaining in solution. The interior of the fibers are thus prevented from tanning so rapidly, which accounts for the smaller amount of tannin fixed by the hide powder in the stronger solutions.
- 2. The second explanation is furnished by the work of Thomas and Foster, who observed that the electrical difference of potential at the surface of tannin particles decreases with increasing concentration of tan liquor. This would lessen the attraction between the tannin porticles and the protein jelly and thus cause a decrease in the rate of combination.



I believe that the second explanation is the more plausible, because a greater rate of diffusion of tan liquor into gelatin, as was shown in part VI experiment 1 and 2, is obtained when using more concentrated solutions. This means that according to the first explanation the rate of diffusion increases to a maximum and then decreases with increase of tannin concentration, which is not true, because according to experiment 1 and 2 part VI the rate of diffusion increases with an increase in the tannin concentration. Increasing the concentration increases the rate of diffusion but not the rate of combination, which supplements the second explanation.

## IV. AMOUNT OF TANNIN ABSORBED BY HIDE POWDER FROM VEGETABLE TANNIN WITH CHANGE IN pH OF TANNIN EXTRACT.

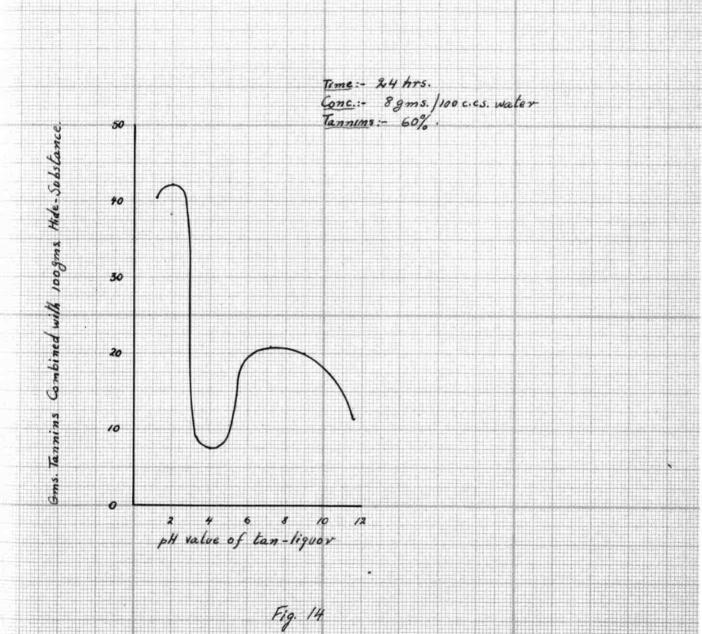
Gms. of Galls	Gms.	tannin	combi	ned wit	h 100	gms.
extract per 100 cc. of water.	pH 1.2	рН 2.02	р <u>н</u> 4.05	рН 7.2	р <u>н</u> 9.0	pH 11.55
35 gms. 80 gms.	30.2	30.15		17.53		9.25

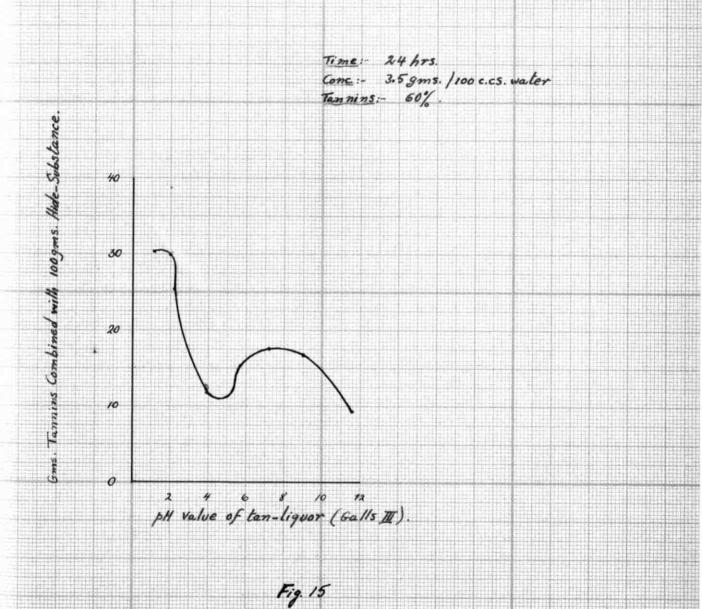
Aleppo Galls III extract was used. Portions of purified powder equal to 1 gm. of anhydrous substance were shaken with 50 cc. of ten liquer of pHs 1.2, 2.02, 4.05, 7.2, 9.0 and 11.55 respectively of the extract.

In the concentration experiments ( Exp. III ), a tan liquor containing 2 gms. of solid matter per 100cc. gave a much greater rate of tanning than one containing 8 gms. per 100 cc., but the results of this experiment show that this is dependent upon the pH value; at pH 4, the more dilute solution tans at the greater rate, while at 2 and at 8, the more concentrated solution tans at the greater rate ( Fig. /+ and /5 )

Looking at the curves one observes a steep rise in both curves to the left of pH 4.5, which is exactly what one would expect, knowing that the positive electrical charge on collagen increases as the pH value falls from the isoelectric point (pH 4.8) and that the tennins are negatively charged at pH values higher than 2.

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RESULTS

OF THE

INVESTIGATIONS

CARRIED

ON

BASIC CHROME LIQUOR

## CHROMITS ORE

OCCURENCE:- In the region of Ladikiyyah.

Qualitative Analysis:- The metals found in the chromite-ore besides chromium are the following:- 1. Iron, 2. Aluminium, 3. Magnisium, 4. Calcium and 5. Silica.

Quantitative Analysis:- Three grams of the chromite-ore were treated with 8 grams of Sodium peroxide for one hour in a percelain crucible. The crucible while hot was put in a large beaker containing 200 cc. distilled water and boiled until the mixture was completly disintegrated. The resulting mixture was filtered and the solution made up to 250 cc.

The filtrate contained Chromium and Aluminium in the form of Sodium chromate and sodium aluminate respectively, while the precipitate contained Ferric hydroxide, Calcium hydroxide, Magnisium hydroxide and Silica.

## Procedure for the Analysis of the filtrate:

- 1. Chromium: 50 cc. of the filtrate were taken and the Sodium chromate determined volumetrically by the Ferrous-permanganate method.
- 2. Aluminium: 50 cc. of the filtrate were taken, acidified with sulfuric acide and the Aluminium precipitated

as Aluminium hydrozide with dilute ammonium hydroxide. The Aluminium hydroxide was then determined gravimetrically.

Procedure for the Analysis of the Precipitate: To separate the Ferric hydroxide, Calcium hydroxide and Magnisium hydroxide from the broken pieces of the crucible and the silica, was treated with hot dilute hydrochloric acid until all the precipitate dissoved and the soln, made up to 250 cc.

- 1. Iron: 500 cc. of the filtrate were taken and made alkaline with dilute ammonium hydroxide. The Ferric hydroxide precipitated was determined gravimetrically.
- 2. Calcium exide and Magnisium oxide: To the filtrate after precipitating the iron as Ferric hydroxide, ammonium chloride and disodium hydrogen phosphate were added until there was no more precipitate. The CaO and MgO were then determined as Calcium phosphate and Magnisium pyrophosphate, (gravimetrically).
- 3. Silica:- The silica was determined separately.

  Result Of The Complete Quantitative Analysis Of The Ore

Chromic Oxide	Percentage 46.4
Aluminium Oxide Ferrous Oxide Calcium , Magnisium Oxides Silica	7.9 35.3 6.4 4.05 0.08
Moisture Total	101.05

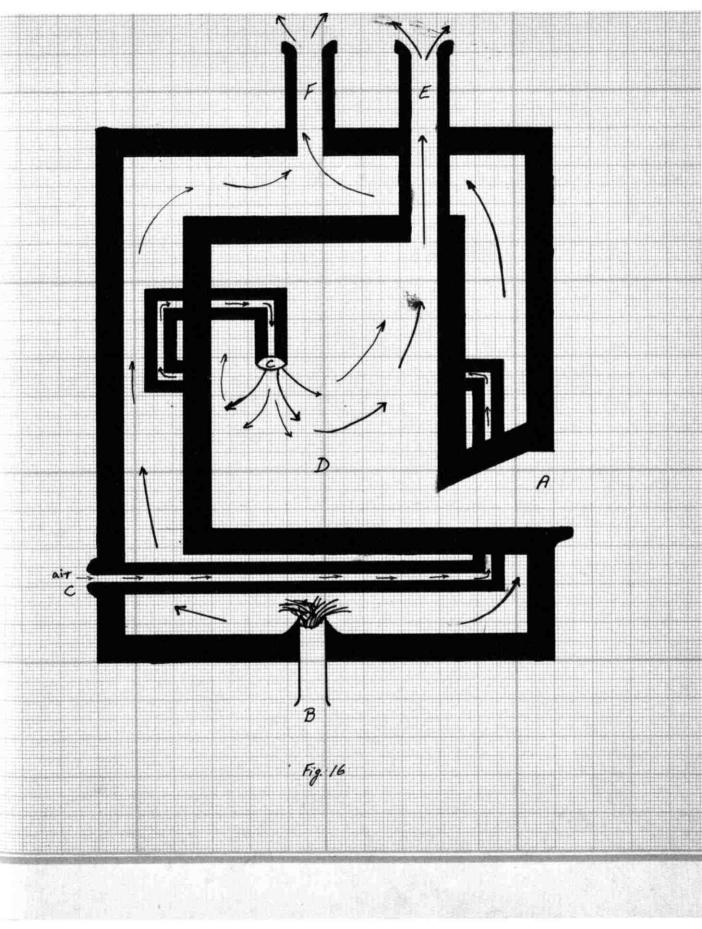
## PREPARATION OF SODIUM DICHROMATE FROM THE CHROMITE - ORE

120 parts of powdered chromite-ore were mixed together with 100 parts of sodium carbonate powder and 50 parts of powder lime, was added in order to prevent the materials from fusion, but remain in a pulverise form, in order to make it easy to leach.

The construction of the furnace is as follows: { Fig. 16 }. The whole furnace is made of fire-bricks, except the inside part which is made of refractory-bricks. The mixture is put into the chamber D through the door A. B is a masout burner and C is a tube made of fire-bricks which is being heated by the mazout burner and which conducts air into the chamber D in order to exidise the chromite-cre to the chromate. The air enters by the draft caused by the escaping gases from chamber C through the outlet E. The air coming in can be regulated so as to have sufficient exygen in chamber D. F is an outlet for the escaping gases from the mazout burner.

The temperature of the furnace should be around 1200 Co in order that the air will be able to oxidise the chromium to the chromate in the presence of the sodium carbonate. The approximate time required for the chromite-ore to be oxidized to the chromate is between 5 and 8 hours.

The resulting material now consists of sodium carbonate some calcium chromate, sodium oxide, lime, ferric oxide and other unimportant materials. The whole material is leached in



boiling water and then enough sulfuric acid is added to produce a weak reaction, the calcium being changed to the insoluble calcium sulfate and the solution now contains sodium chromate, ferric sulfate and sodium sulfate. The resulting solution is allowed to settle and decanted from the calcium sulfate, silica and other impurities. The ferric sulfate present in solution is now precipitated by means of chelk. The whole thing is allowed to settle and the solution decanted from the ferric hydroxide and the excess calcium carbonate. The solution now containing the sodium chromate is acidified with sulfuric acid to the dichromate and concentrated to the required concentration.

## PREPARATION OF ONE - CHROME BATH

There are two methods by which basic chrome-liquor can be prepared by the reduction of Sodium dichromate :-

## 1. Reduction with sugar: -

pure ) were dissolved in 800 cc. of water. To the dichromate solm. were added very slowly 115 grams of conc. sulfuric acid (95 %). Afterwords a conc. of sugar (actually Dibs was used) were added very slowly until a green solm was obtained, when the whole solm was made up to one liter. The resulting solm contained 12.6 % of basic chrome-sulfate.

The resulting soln is 0.38 M with respect to sodium sulfate.

Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + 24H<sub>2</sub>SO<sub>4</sub> + C<sub>12</sub>H<sub>22</sub>OH — 16Cr(OH)SO<sub>4</sub> + 8Na<sub>2</sub>SO<sub>4</sub> + 16H<sub>2</sub>O + 12CO<sub>2</sub>

## 2. Reduction with sulfur dimxide:-

pure) were dissolved in 800 cc. water. Sulfur dioxide was then passed through the soln until complete reduction was effected, shown by the changein color from orange-yellow to green. The resulting soln contained approximately 12.6 % basic chrome-sulf...

The resulting soln is C.38 M with respect to sodium sulfate.

 $Na_{8}Cr_{8}O_{7} + 38O_{8} + H_{8}O = _{8}Cr(OH)SO_{4} + Na_{8}SO_{4}$ 

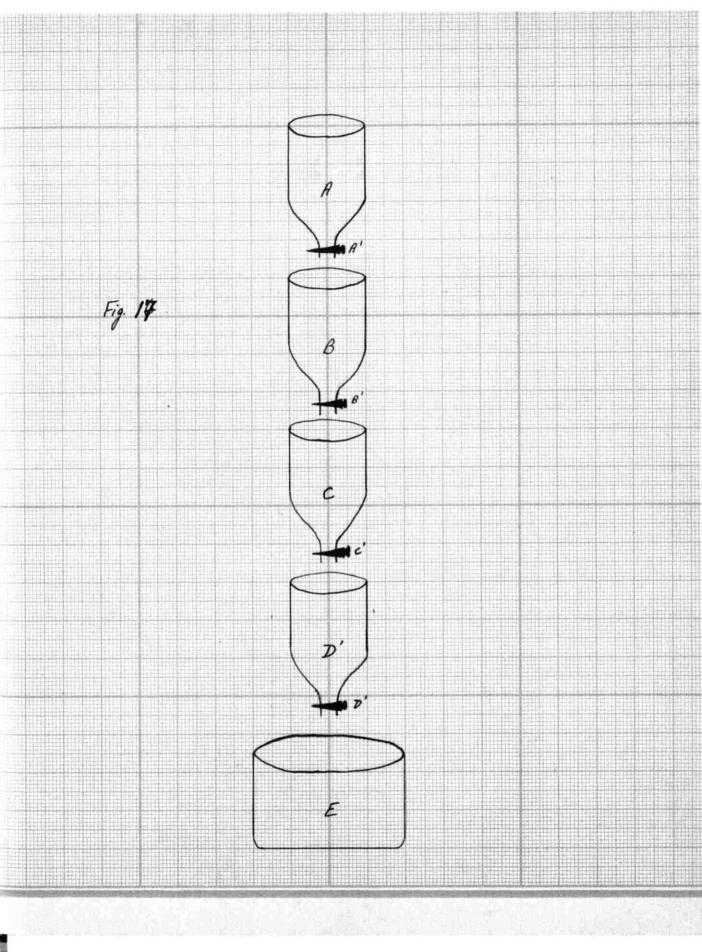
## PREPARATION OF GLUE FROM CHROME SHAVINGS

Extractor A is covered with 5 % Sulfuric acid at temperatures ranging between 50 and 70 Co. After a day tap A' was opened and solution poured over B, and left there for another day afterwards poured over C then D and finally poured into vessel E. The process was repeated until A was nearly free (required five extrations) from any green color. Then B was put in place of A, C in place of B and D in place of C and extractor A containing a new sample was put in place of D and the whole process could be continued indefinitely.

The liquor in vessel E containing chromium sulfate and excess sulfuric anid was concentrated to the required concentration and the solution treated with calcium carbonate and filtered until the right acidity was obtained, so that it will be used again for chrome tanning.

The shavings were first washed to remove the remaing acid and then dissolved in boiling water and the solution treated with sufficient lime powder to precipitate the remaining chromium sulfate as chromium hydroxide. The solution was then filtered, the excess lime was just neutralised with dilute sulfuric acid and the excess acidneutralised with calcium carbonate. The solution was then filtered from the calcium sulfate and the excess calcium carbonate.

The resulting glue solution was moncentrated and then left



to be dried under the sun.

The treatement with lime hydrolised part of the glue and degelled it.

# RESULTS OF THE EXTRACTION OF BASIC CHROME - LIQUOR FROW CHROME SHEVINGS-

## WITH SULFURIC ACID

Sample No.1

Wt. of	No. of	Conc. and	ıd					8	Chromie
sample.	Extrac-	volume c	of	solution after extraction.	after e	xtractic	·uc	ONLE	oxide for
	tions	solvent.						12.00	every
		vol. in	Sp. Gr.	Vol. in liters	Sp. Gr.	Crohso, in Soln	Gronso.	Graos in Ch.sh.	0.005 deg.
			2						
440 8.	п	20.0	1.03	1.90	1.050	1.02	4.40	3.00	0.50
	QQ	1.8	1,03	1.75	1,035	0.26	1.04	0.47	0.47
	80	1.5	1.03	1.50	1,035	808.0n	1.05	0.48	0.48
	4	1.5	1.03	1.50	1,032	0.13	0.44	0.20	0.50
	ıo	1.5	1.03	1.50	1.032	0.13	0.44	0.20	0.50
Total							7.42	3,37	Av. 0.49

## SULFURIC ACID

Semple No. 2

Wt. of	No. of	conc.	and						% chromic
sample	extrac-	volume	10 e	30.	Solution al	after ext	extraction.		oxide for
	tions	solvent	nt						GVGLY
		Vol. in liters	Sp.Gr.	Vol. in	Sp.Gr.	% CroHSO <sub>4</sub> in Sola:	Grouso. in Ch.sh.	GraOs	0.005 deg.
400 8**	4 05 to 4 18	1.9	1.035	11111 83481	1.087	0.76	22.27	1.03	0.54 0.49 0.48
			CO.T	T. 2	1.03%	0.12	0.45	0.80	0.5
Total							7.18	20. 20	0 KO9

chromic oxide remaining in the chrome shavings after extraction is equal to 0.18 gms. in the first sample and 0.33 gms. in the second sample. therefore the amount of 0.5 gms. chromic oxide in solution. The amount of chromic oxide removed from 100 gms. of chrome shavings in first sample is equal to 3.37 gms. and 3.22 gms. from second sample. Originally the chrome shavings conttained 3.55 gms. chromic oxide per 100 gms. and therefore the amount o Bvery 0.005 degree of ruse in Sp.Gr. represents approximately from 100

## I. CHANGE IN THE PH OF BASIC CHROME - LIQUOR WITH DILUTION

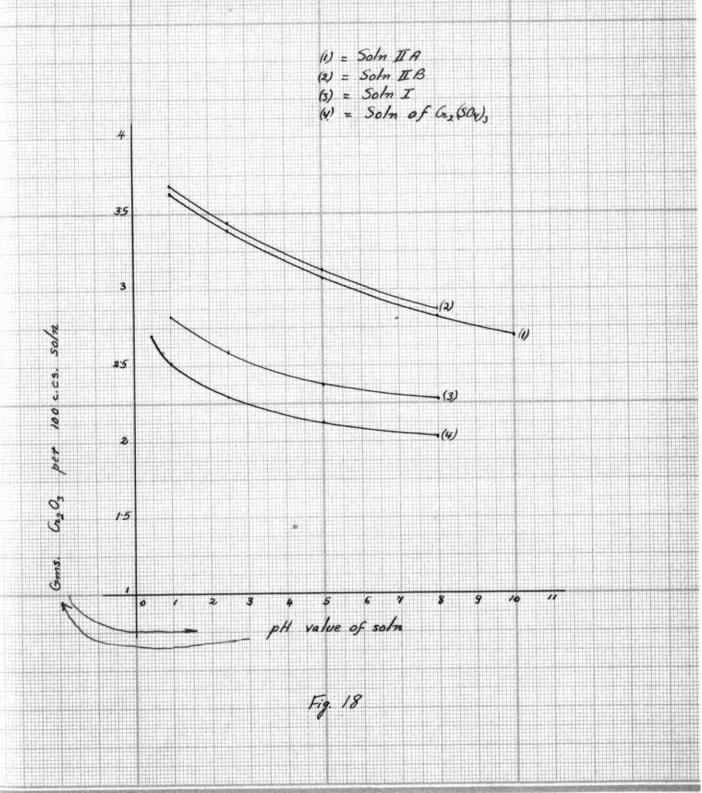
		Gr	ams	Cra0a	per	100 6	sol	ution	
Solution		рН	14%	10%	8%	5%	2.5%	1%	0.5%
Solution	I	рН			2.26	2,38	2.6	2,58	egil age
Solution	IIA	pH	2.5	2.7	2.85	3.13	3,45	3.75	
Solution	IIB	рH		2.75	2.90	3,18	3,50	3,80	
Solution Chromium		фH			2.03	2.13	2,30	2.52	2.7

Two kinds of basic chrome-liquor were used:-

- 1. The first solution (sol.I) containing 8 gms. of chromic oxide per 100 ec. of solution was used for experiments on the diffusion into the gelatin-jelly.
- 2. The second solution (scl.IIA) containing 14 gms. of chromic oxide per 100 cc. of solution was used for the experiments on the combination between it and the hide powder (collagen).

One kind of chromium sulfate solution was used, which consisted of 20.6 gms. of chromic sulfate per 100 cc. solution

For solution IIB the pH of the solutions were determined two weeks after being diluted, in order to give time for the establishment of equilibrium. The curves show that the Hydrogen-ion concentration decreases with dilution. Being a salt of a weak base and a strong acid, chromium sulfate (or basic chromium sulfate) hydrolyses to a very considerable



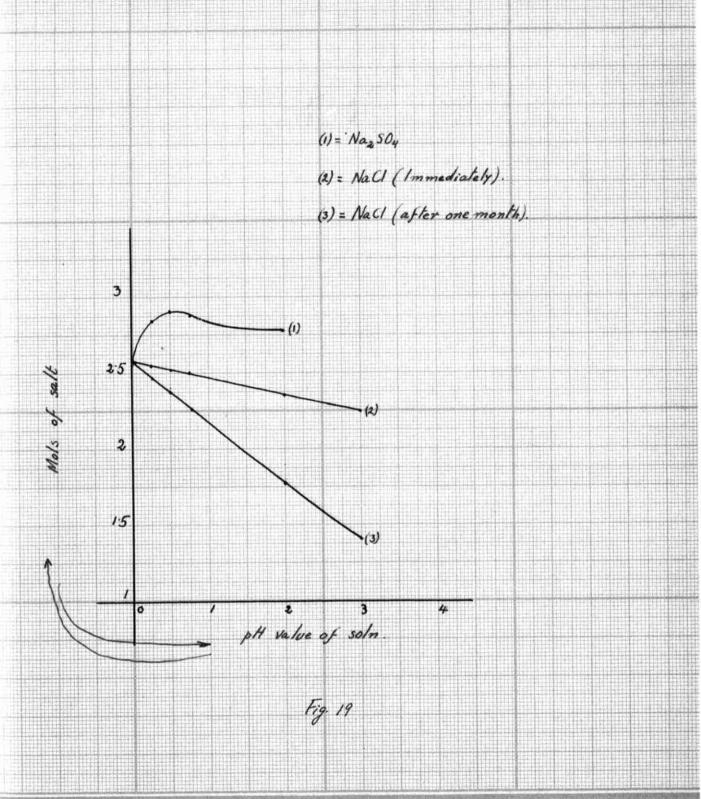
extent in squeous solutions, yielding free sulfuric acid and a series of basic chromium sulfates ( a series of higher basic chromium, e.g. Cr<sub>2</sub>(OH)<sub>4</sub>SO<sub>4</sub>), (Fig. /8).

Thus the total Hydrogen-ion concentration is increased, but the hydrogen-ion concentration per unit volume decreases on dilution, so that the resulting pH of the solution becomes higher.

II. EFFECT OF NEUTRAL SALTS ON THE PH OF THE BASIC CHROME -

Grams Chromic	Time			pH				
oxide per 100 cc. soln		Mols 0	Mols 0.25	Mols 0.5	Mols 0.75	Mols 1.0	Mols 2	Mols 3
NagSO4 selution	After 1 month	2,58	2.85	2.93	2.88	2.85	2.78	
NaCl solution	Immedia- tely	2,58	2.57	2,53	2.51	2,48	2438	2.28
NaCl solution	after 1 month	2.58		2,38		2,23	1.78	1.38

Solutions containing 3 gms. of chromic oxide per 100 cc. were made 0.25 M, 1.0 M. 2 M and 3 M, with respect to NaCl and Na<sub>2</sub>SO<sub>4</sub> and the pH of the resulting solutions determined. The results are shown above (Fig. /9). For the case of the Sodium sulfate there were no appreciable immediate changes in pH, so the pH of the solutions were determined



after one month of the addition of the sodium sulfate, while those of the sodium chloride were determined immediately, and also after one month of the addition of the sodium chloride to the basic chrome-liquor containing 3 gms. of chromic oxide per 100 cc. of water.

The pH of the acid chrome liquors were found to decrease with addition of sodium chloride and increased by the addition of sodium sulfate.

Thomas and Baldwin found that neutral chlorides lower the pH of acid solutions, while neutral sulfates higher the pH. This was found to be the case by the above experiments conducted on the basic chrome liquor. It was found by Thomas and Baldwin that chrome liquors containing more sodium sulfate required more alkali to precipitate the chromium. They suggested that this may be due to the fact that sulfates increase the stability of chrome-liquors, by forming addition compounds with the chromium salts which are less easily precipitated than the simpler salt.

III. RATE OF DIFFUSION OF BASIC CHROME - LIQUOR INTO

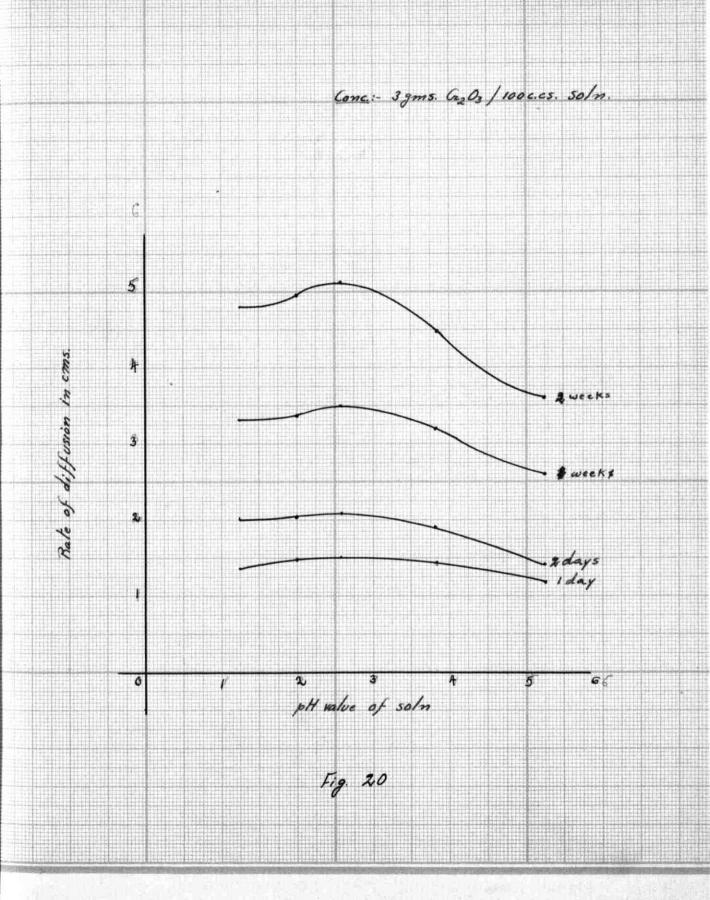
GELLATIN - JELLY WITH CHANGE IN PH OF CHROME - LIQUOR

Grai			Rate	of diff	usion in	cms.	
	selution	рH	1 day	2 days	1 week	2weeks	3 wks.
3	grems	1.25	1.35	2.00	3.30	4.80	
3	grams	2,00	1.50	2.05	3,35	4.95	
3	grams	2.50	1.50	2.10	3.50	5.10	
3	grams	3.80	1.40	1.90	3.20	4.50	
3	grams	5.25	1.20	1.40	2.60	3.60	

Basic chrome-liquors of pHs 1.25,2000, 2.58, 3.80, and 5.25 were prepared containing 3 grams chromic oxide per 100 cc. of solution.

10 cc. of every solution were taken and poured over 4 % gelatin gels in test-tubes of 1.6 cms. dimeter and the rate of diffusion in each determined after the specified times. ( [Fig. 20])

Maximum diffusion took place around pH 2.5 and an increase in the pH above 2.5 diminished tremendously the rate of diffusion of the basic chrome-liquor into the gelatin gel, white a derase in the pH below 2.5 only diminished slightly the rate of diffusion. For example, the slope of the curve above pH 2.5 is much greater than below pH 2.5 after two weeks diffusion. The reason being that an increasing pH value cause the molecule of chromium salt & form aggregates of increasing



size and therefore greatly reducing the rate at which they diffuse into the gelatin gel, ( Wilson ).

IV. PATE OF DIFFUSION OF BASIC CHROME - LIQUOR INTO GELATIN-JELLY WITH CHANGE OF CHROME LIQUOR CONCENTRATION.

Grams chromic			Rate	of dif	fusion	in cms.	
oxide per 100	рН	day	2 days	week	2 weeks	nonth	2 months
1 gram	2.85	0.70	1.00	1.70	2.40	3,20	3.50
2.5 gms.	2,63	0.85	1.20	2.05	3.00	3.90	4.25
5 gms.	2.40	0.90	1.40	2,50	3,60	4,60	5.10
8 gms.	2.26	0.95	1.45	2.80	3.90	4.85	5.40

A solution containing 8 gms. of chromic oxide per 100 cc. solution and the other solution containing, 2.5 gms., and 1 gm. were prepared by diluting the original solution. (Fig. 2/0

It was found that the rate of diffusion increases with increase in the percentage of chromic oxides but the proportionality factor of diffusion is not constant. This is due to the following causes:-

L. As the concentration of the liquor increases the Hydrogen-ion concentration increases, and therefore the rate of diffusion diminishes. The rate of diffusion increases as the pH is lowered until a point of maximum is reached when it starts to decrease. This was we shown to be true in experiment III.

<sup>2.</sup> The salt concentration increases and therefore

## Substance: - Gr (OH) SO4

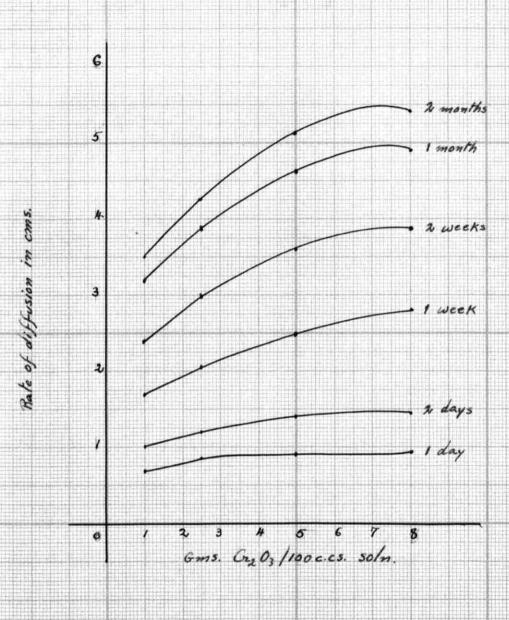


Fig. 21

the rate of diffusion of the liquor decreases.

3. The probability of the formation of additional compounds at high concentrations, increasing the molecular size of the chromium salt and therefore the rate of diffusion is decreased.

## V. RATE OF DIFFUSION OF CHROMIUM SULFATE SOLUTION INTO CELATIN JELLY WITH CHANGE OF CHROMIUM SULFATE CONCENTRATION

Grams chromic			Rat	e of dif	fusion i	n ems.
oxide per 100 cc.	pН	1 day	2 days	1 week	2 wks.	1 month
2.5 grams	2.3	0.7	1.0	1.7	2.2	3.0
5.0 grams	2.13	0.85	1.5	2.75	3.6	4.75
8.0 grams	2.03	0.9	1.7	3.3	4.2	5.5

A solution containing 8 grams of chromic oxide per 100 cc. soln was prepared. The other solutions containing 5, and 2.5 grams chromic oxide were prepared by diluting the original solution (Fig. 22).

The rate of diffusion increases with increase in the percentage of the chromic oxide in the chromium sulfate soln, but the proportionality factor of diffusion is not a constant. This is due to the same causes of the chrome-liquor with the exception of one factor which is that of concentration. We know that in the preparation of basic chrome liquors from Sodium dichromate, Sodium sulfate is formed which increases the selt concentration of the basic chrome-liquor, while in the

Substance: Cra(504)3 ٥ Gms. of G, 0, 100 c.cs. soln. Fig. 22

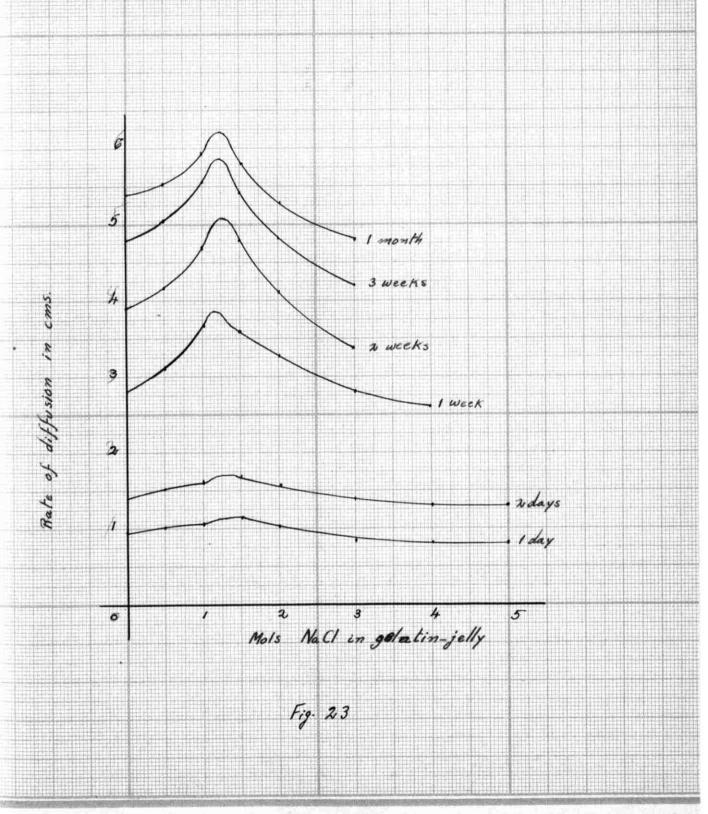
1/

that on increasing the concentration of the chromic oxide
the salt concentration is not increased as much as that of
the basic chrome liquor,. Therefore the relative decrease in
the rate of diffusion is not as much as that of the basic
chrome-liquor, especially at high concentrations of chromic
oxide. For example, a solution of chrome liquor which contains
5.6 grams of chromic oxide per 100 cc. of solution is nearly
0.4 M with respect to sodium sulfate.

VI. RATE OF DIFFUSION OF BASIC CHROME - LIQUOR INTO GELATIN-JELLY WITH INCREASE OF SODIUM CHLORIDE, SODIUM SULFATE, MAGNESIUM CHLORIDE AND SUGAR CONCENTRATIONS IN GELATIN-

JELLY

## Rate of diffusion in cms. 4 gms. gelatin Mols jelly per 100 of 1 mon. 2 days 1 week 2 wks. 3 wkd. cc. water NaCl 1 day 5.40 4.85 2.80 3.90 0.95 1.40 Gelatin-jelly 0.0 5.50 4.95 2.95 4.00 1.00 1.50 0.5 Gelatin-jelly 5.90 5.30 4.30 1.55 3.30 Gelatin-jelly 1.0 1.00 6.40 5.70 1.25 1.00 1.60 3.60 4.80 Gelatin-jelly 6.30 5.60 Gelatin-jelly 3.40 4.50 1.55 1.5 1.00 4.60 5.40 3,80 Gelatin-jelly 2.0 0.90 1.40 3.00 4.80 8.20 3.40 Gelatin-jelly 3.0 2.30 0.85 1.50 -Gelatin-jelly 4.0 0.80 1.30 2.60 -1.30 2.50 Gelatin-Jelly 5.0 0.80



1.0 M, 1.25 M, 1.5 M, 2.0 M, 3.0 M, 4.0 M, and 5.0 M with respect to sedium chloride. They were set in test-tubes of 1.6 cm. diameter and 100 cc. of basic chrome-lequor containing 8 gms. chromic per 100 cc. solution were poured into each test-tube above the gelatin, and the rate of diffusion in each test-tube determined after the specified times. The results of the experiment are shown above. In the test-tubes containing 4.0 M and 5.0 M sodium chloride the gelatin was found to be ruptured due to the great swelling caused by the high concentration of sodium chloride in the gelatin-jelly, (Fig. 23).

4 gms. gelatin	Mols	Re	te of ai	ffusion	in ems.	
per 100 cc. of water.	NagSO4	1 day	2 days	1 week	2 wks.	5 wks,
Gelstin-jelly	0.0	0.95	1.45	2.80	3,90	4.50
Gelatin-jelly	0.25	1.20	2.00	3.60	5.10	5,80
Gelatin-jelly	0.50	1.10	1.80	3.20	4.50	5,10
Gelatin-jelly	1.00	1.00	1.50	2.90	4.00	4.60

Due to the great power of hydration of sedium sulfate (10 HgO) it was found impossible to prepare gelatin-jelles with a concentration higher than 1.0 M with respect to sodium sulfate.

and 1.0 M with respect to sodium sulfate. They were set in test-tubes and 10 cc. of solutions of 8 gms. chromic oxide

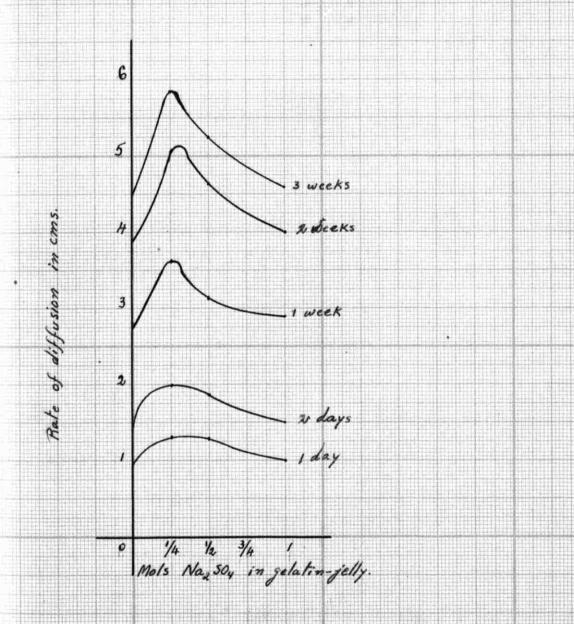


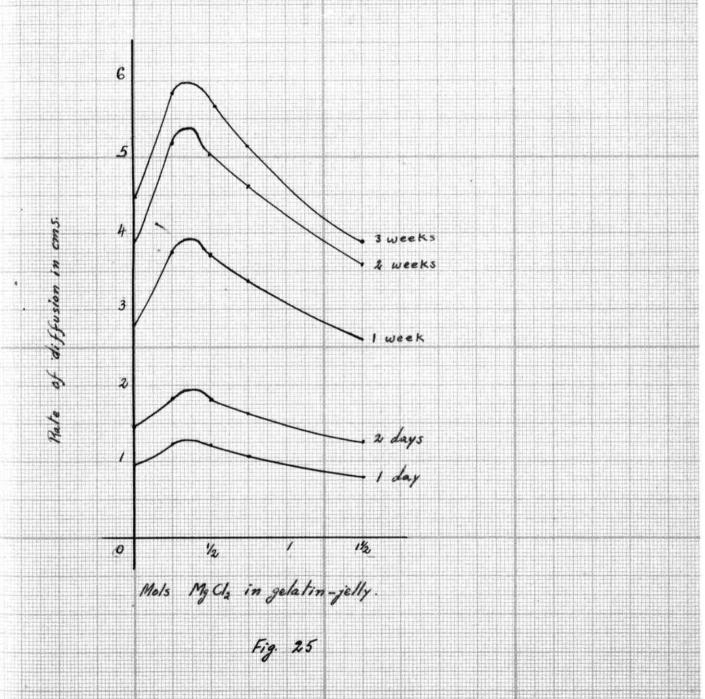
Fig. 24

were poured into each test-tube over the gel. and the rate of diffusion determined after the specified times. The results of the experiment are shown in the above chart (Fig. 24)

4 gms. gelatin	Mols	Ra	te of dif	fusion i	n ems.	
per 100 cc. of water	and agriculture on the state of	1 day	2 days	1 week	2 wks.	3 wks.
elatin-jelly	0.0	0.95	1.45	2,80	3,90	4.50
Relatin-jelly	0.25	1.10	1.80	3.75	5.20	5.80
Gelatin-jelly	0,50	1.10	1.80	3.70	5,10	3,60
Gelatin-jelly	1.00	0.90	1.50	3.10	4.30	4.75
Gelatin-jelly	1.50	0.80	1.25	2.60	3,60	3,90

Due to the great power of hydration of magnesium chloride ( not as great as that of sodium sulfate, being 6kg0 ) it was found inpossible to prepare gelatin-jellyes with a higher concentration than 1.5 M with respect to magnesium chloride.

15 cc. solutions of 4 % gelatin were made 0.25 M,
0.5 M, 1.0 M and 1.50 M with respect to magnesium chloride.
They were set in test-tubes of 1.6 cms. diameter and then 10 cc.
of solution of 8 gms. chromic oxide were poured into each testtube over the gel, and the rate of diffusion determined after
specified time. The results of the experiment are shown in
the above chart (fig. 25).



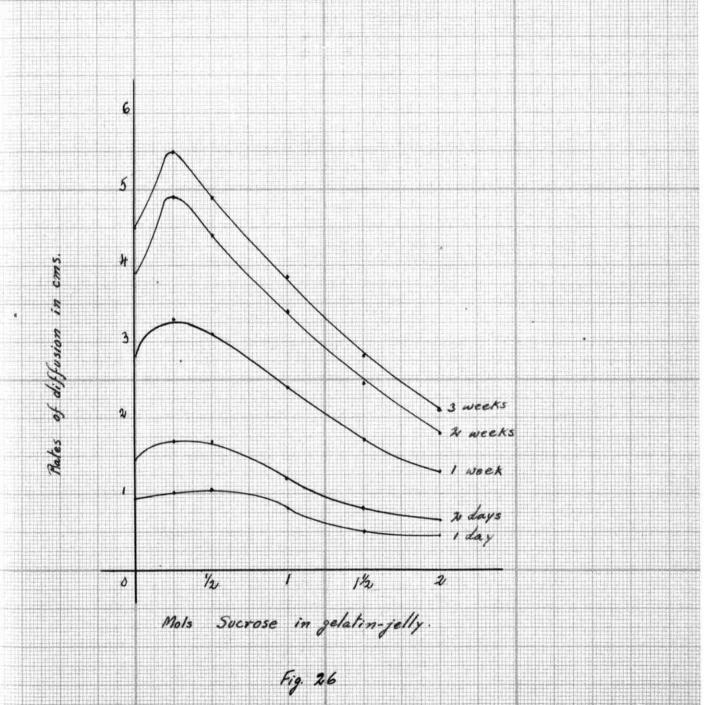
4 Grms. geletin	Mols_	Rate	of dif	fusion :	in ems.	
per 100 cc. of water	Sucrose	1 day	2 days	1 week	2 weeks	3 wks.
Gelatin-jelly	0.0	0.95	1.45	2,80	3.90	4.50
Gelatin-jelly	0.25	1,00	1.70	3.30	4.90	5,50
Gelatin-jelly	0.50	1.05	1.70	3,10	4.40	4.90
Gelatin-jelly	1.00	0.80	1.20	2.40	3,40	3,85
Gelatin-jelly	1.50	0.50	0.80	1.70	2.40	2.80
Gelstin-jelly	2.00	0.45	0.65	1,30	1.80	2.10

Due to the great power of hydration of sucress, it was found impossible to prepare gealtin-jelltes with a higher concentration than 2.0 M with respect to Surcess.

15 cc. solutions of 4 % gelatin were made 0.25 M, 0.5 M, 1.0 M, 1.2 M, and 2.0 with respect to surcose. They were set in test-tubes of 1.6 cms diameter. Then 10 cc. of a solution of 8 grams of chromic oxide were poured into each test-tube over the gel and the rate of difussion determined after the specified times. The results of the experiments are shown in the above chart (Fig. 26)

#### Explanation of the resulting charts:-

From fig. 23 it is found that the rate of diffusion of chrome-liquor into gelatin-jelly increases up to a concentration of 1.25 M, sodium chloride. Increasing the concentration diminishes the rate of diffusion of the liquor. The resistance to diffusion in gels can be considered a result of the brush-



heap structure of its internal phase. Thus the presence of sodium chloride which favours swelling up to a certain concentretion lessens the resistance to diffusion of the chrome liquor into the gelatin-jelly; swelling being regarded as a process which enlarges the spaces on the mesh-like structure of the gelatin gel. But increasing the concentration of sodium chloride in the gel brings another factor with it which is that of hydration. Thus increasing the concentration of the sodium chloride above 1.25 moles increases the concentration of the gel, counteracting the forces that act in the direction of the enlargment of the spaces in the mesh-like structure of the gelatin in gels containing less than 1.25 moles, and as a result of the hydration of the salt, the concentration of the gel is increased and therefore the rate of diffusion of basic chrome-liquor is diminished. The same is true in the cases of gelatin gels containing sodium sulfate and magnesium chloride, except that the maxima lies at the concentration of 0.25 M for sodium sulfate and at a concentration of 0.35 M for Magnisium chloride. This is due to the greater power of hydration of sodium sulfate and magnesium chloride; thus bringing the maximum point nearer to . zero concentration.

For example, looking at the curves of those of sodium chloride, sodium sulfate, and magnesium chloride after three weeks it is found that they appearimately have the same maxima, i.e. arround 5.75 M, cms, but not at the same concentration.

# VII. RATE OF DIFFUSION OF BASIC CHROME - LIQUOR INTO GELATINJELLY WITH INCREASE OF SODIUM CHLORIDE, SODIUM SULFATE, MAGNEZIUM CHLORIDE AND SUCROSE CONCENTRATIONS IN CHROMELIQUOR.

No results were obtained for chrome-liquors containing concentrations higher than 1 M with respect to the above salts, due to the gelatin being dissolved in the chrome-liquors.

## CHROME LIQUOR WITH TIME .

Gms. chromic oxide per	рН	Gms. ch	romic or	kide comb	ined with	100 gms
100 ee.		5 hrs.	8 hrs	24 hrs.	48 hrs.	96 hrs.
2 gms.	3.75	9,25	10,78	12.8	13,75	15.05

Portions of purified powder equal to 1 gm. of anhydrous substance were shaken with 50 cc. of chrome-liquor containing 2 gms. chromic oxide per 100 cc. of pH 1.53 and each determined after 5, 8, 24, 48, and 96 hrs. The results are shown above (Fig.27)

The results show that most of the combination takes place up to around 24 hr., further increase in time increases the amount of combination very slightly.

Substance: - Gr(OH) 504 Conc : 29ms, Gr203 | po 100c.cs. water. pt :- 3.75

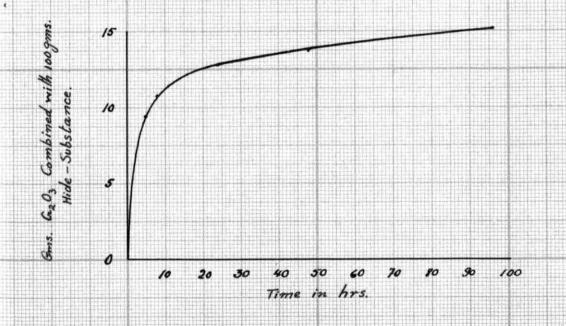


Fig. 27

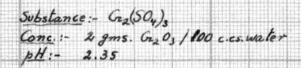
### II. AMOUNT OF CHROMIC OXIDE ABSORBED BY HIDE POWDER FROM CHROMIUM SULFATE WITH TIME.

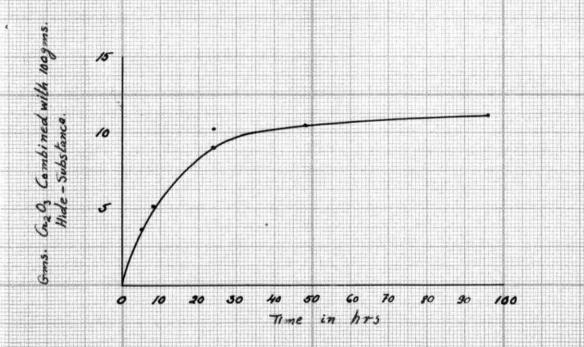
Gms. chromic oxide per 100 cc.	pН	Gms. ch	romic ox Hids	ide comb	ined with	100 cc.
		5 hrs.	8 hrs.	24 hrs.	48 hrs.	96 hrs.
2 gms.	2,35	3.52	5.13	9.01	10.54	11.20

The amount of combination of hide substance with basic chrome-liquor is greater than that of chromium sulfate.

The rate of tanning in the chromic sulfate solution is very much less than that of the basic chrome-liquor, because the hydrogen ion concentration is about 25 times as great as in the chrome-liquor. It will also be noted that the amount of chromic oxide combined with 1 gm. of skin protein is greater for the chromi-liquor after 48 hrs. than the limiting value in the case of the pure chromic sulfate which has not reached a limiting value in 48 hrs. The limiting value, seconding to wilson is 13.8 gms. chromic oxide per 100 gms. of hide substance (Fig. 28)

CHROME LIQUOR AFTER 48 Hrs. WITH INCREASE OF CHROME-

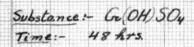




	Gms. of	chromic	oxide c	ombined wit	h 100 gms. Hid
Time	1.5 gms.	2gms.	5 gms.	10 gms.	14.gms.
	oro in	per	per	per 100 cc.	per 100 cc.
24 hrs.	13,95	13.75	11.62	7.2	4.04

The reason for the point of maximum at a concentration of 1.5 gms. of chromic exide per 100 cc. is not entirely clear, although a number of causes may be assigned to the falling off in rate of combination at higher concentrations, among which may be mentioned the increasing hydrogen-ion concentration, the increasing salt concentration, and the probability of the formation of addition compounds.

regetable tenning as a function of concentration, where both have a maximum, the chrome-liquor at a concentration of 1.5 gas. while that of vegetable tanning at a concentration of 2 gms. per 100 cc. which shows that amount of combination is greater at such concentrations than at higher concentrations. (Fig. 29



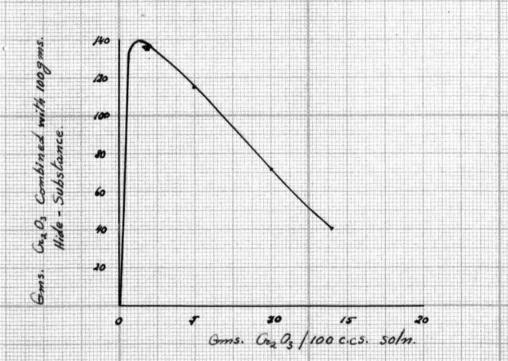


Fig. 29

## IV. AMOUNT OF CHROMIC OXIDE ABSORBED BY HIDE POWDER FROM BASIC CHROME CHROMIUM WITH CHANGE IN PH OF BASIC CHROMIUM SULFATE

Gms. chromic oxide per	Time	Gms.c	hromi	e oxide	ned wi	with 100 gms			
100 00.		pH 1.45	pH 2,5	рН 3.05	рН 3.75	рН 4.6	рН 5.25		
2 gms.	48 hrs.	3.02	8.35	12.75	13.75	11.43	10.06		

Portions of purified powder equal to 2 gms. of anhydrous substance were shaken with 50 cc. of chrome liquor of pHs
1.45, 2.5, 3.05, 3.75, 4.6 and 5.25 respectively, each containing 2 gms. chromic oxide per 100 cc. soln.

The reason for the lowering in combination below pH 3.75 is that when chromium salts contain a great excess of acid they diffuse into them very rapidly, but the rate of combination of chromium and collagen is correspondingly decreased. Thus it becomes necessary to neutralize some of the acid before the skins can become completely tanned, even though completely permeated by the chromium salt. Increasing the pH above 3.75 causes the molecules of the chromium salt to form aggregates of increasing size, greatly reducing the rate at which they diffuse into the skin, thus reducing the rate of combination between the chromium and the collagen. This was shown to be the case in VII, experiment III. Fig. 30

Substance: - Cr (OH) 50y soln Time: - 48 hrs. Conc.: - 2 gms. Cr Oz /100c.cs. soln.

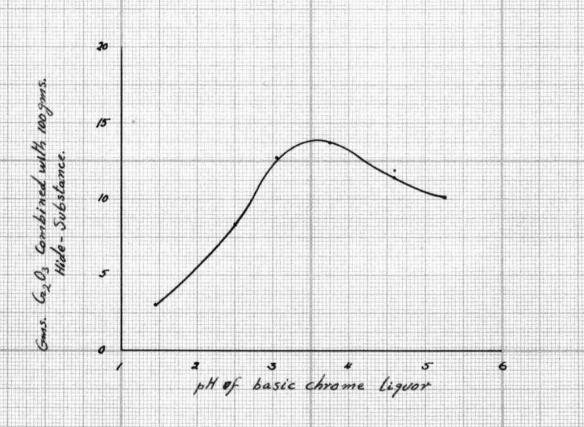


Fig. 30

#### V. RETARDATION OF CHROME TANNING BY MEUTRAL SALTS .

Gms. chro- mic oxide per 100 co.	Mols NaCl 0.0	Mols MaCl 0.5	Mols NaC1 1.0	Mols NaCl 2.0	Mols NaCl 3.0	Mols NaCl 4.0
1.5 gms.	11.54	9.51	7,5	6.24	6.67	7.55

The reason sodium chloride retards chrome tenning is that it forms addition compounds with the basic chromium salt rendering it less dissociated and, consequently, less active in combining with the skin protein. Upon increasing the concentration of the salt still further, the hydration effects a virtual concentration of the chromium ions to such an extent that the retarding action of the addition compound formation is counterbalanced by the activity of the high concentration of chromium ions and the curve therefore begins to slope upward, (Fig. 3/).

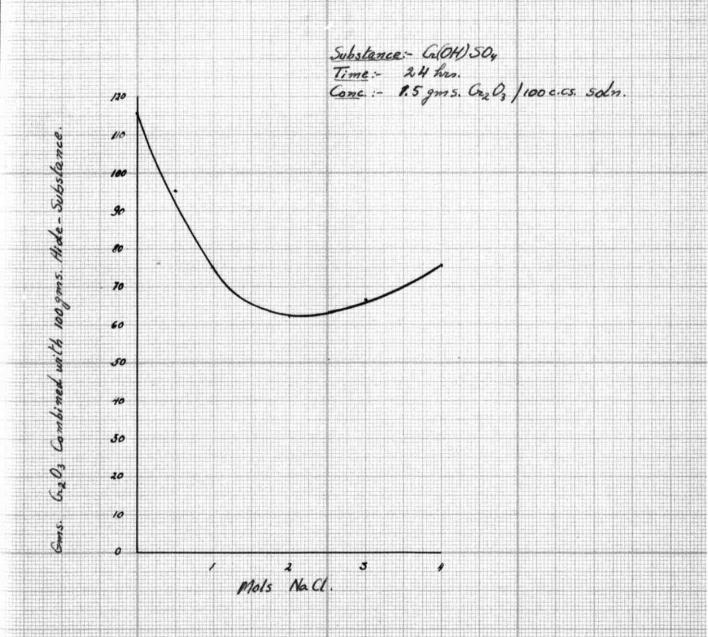


Fig. 31

#### SULFHONATED ONLS

as a constituent of fat-liquors and other preparations used in the leather trade, there is little doubt that the so-called soluble oils or sulphonated oils have assumed a place of distinct importance. Apart from the actual lubricating properties of these, they are useful as emulsifying agents for other oils and fats, and hence their widespread use in this direction.

To 100 gms. of the oil 25 gms. of concentrated sulfuric acid were added very slowly, so that it required several hours to make the total addition and the temperature kept below 10 Co. When all the sulfuric acid was added, the mixture was allowed to stand for a day, when it was ready for washing. The resulting o oil was washed with a strong solution of common salt and the whole well stirred together and the mixture allowed to stand for sepration. The oil comes to the top of the liquor and the salt solution separated. This wahing operation was repeated several times, when finally the oil was allowed to stand for a longer time than the previous washing, so that as much water as possible would settle out. The final process was neutralisation, for which dilute ammonium hydroxide was used. Dilute ammonium hydroxide solution was added in small amountsat a time, the soln being stirred after each addition, until the oil reacted neutral to litmus paper. The actual end point of the neutralisation was when the oil suddenly went quite clear. The following oils were sulfonated :- Castor oil, Olive oil, Peanut oil and Sesame oil.

#### CONCLUSION

The Leather Industry in the Near East has great possibilities - it was proved to be the case by this war. It shows that the Near East can prepare most of the materials required for the industry and instead of exporting large quantities of raw skins and hides, it can export them in the tanned form, consequently decreasing the amount of imports of tanned hids and leather works; Thus increasing the economical wellfare of the Near East.

hide-powder, show that pH of chrome-liquor in tennins), salt concentration in gelatin-jelly and in chrome-liquor, (sin tennins) and the concentration of the chrome-liquor or tennins have great effects upon the rate of diffusion of the chrome-liquor and on extracts; and on the combination between them and collagen. tannins Therefore any changes in these operations changes tremendously the final products.

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