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THE PROPER UTILIZATION OF BY-PRODUCTS FROM HIDES AND SKINS, LEATHER AND LEATHER PRODUCTS INDUSTRIES 1/

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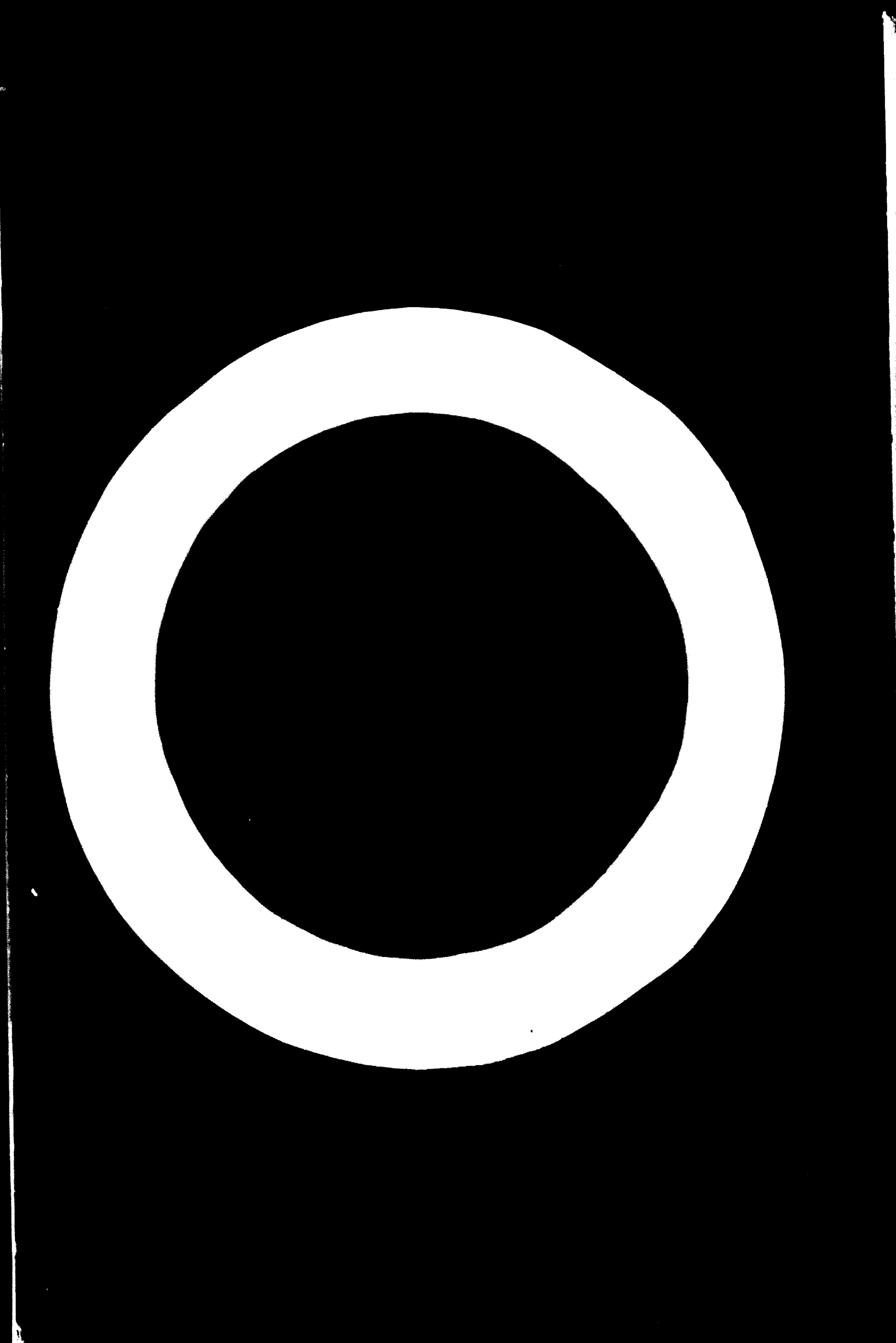
NATIONAL RESEARCH INSTITUTE FOR SHOE,

LEATHER AND ALLIED INDUSTRIES GOTTWALDOV - CSSR

Dr. Ing. Cyril Halámek :

INTRODUCTION TO
THE PROPER UTILIZATION OF BY-PRODUCTS FROM HIDES AND SKINS, LEATHER AND LEATHER PRODUCTS INDUSTRIES



THE PROPER UTILIZATION OF BY-PRODUCTS FROM HIDES AND SKINS, LEATHER AND LEATHER PRODUCTS INDUSTRIES

Introduction

Shoe and leather industries are characterised by a high amount of wastes because they use non-homogenous raw material as its shape, thickness and quality are concerned. A high amount of waste is produced not only due to the necessary correction of the pattern in hide processing, but also due to the need of producing different products from raw materials of different provenience, age, sex, race and histologically different structure. Also the influence of different production technologies used in the manufacture of special types of leather, footwear and leather goods is an important factor.

In the preparation of leather and leather articles various kinds of wastes are produced which mostly consist of hide substance, i.e. proteinous material which can be utilised for the preparation of other products being sometimes economically very interesting. Besides the main proportions of waste from hide substance which is not tanned and is produced in the manufacture of leather, or which is tanned and is produced in processing leather or in the manufacture of final products, a great number of other wastes of a quite different character is produced in the manufacture of leather and leather goods.

In converting hides to leather, and then, leather to the final product - footwear - a high amount of raw material is lost as waste compared with other industrial branches. The most serious losses occur in hide substance. If we count together these losses, occured in the production of leather and in the production of footwear, we get the value of total losses between 50 and 70% counted per content of hide substance in the original hide. Thus, it is obvious that it is necessary to pay the greatest attention to the utilization of these wastes.

However, all types of hide and leather wastes are not utilisable to the same extent. While in untanned wastes we know a great number of economically interesting utilisations (e.g. the production of artificial casings, gelatines and glues, fibrous materials for the production of semi-synthetic leather and technical fats, in tanned wastes we know only one economically interesting utilization, i.e. for the production of fibrous leather. It should be noted that also a number of economically less attractive processes exist which, however, from the economic standpoint are very interesting: preserving hair and bristles, production of fodder, fertilisers, auxiliary shoemaking materials, technical glues and wetting agents.

However, in the processing of hide and leather wastes we must take in consideration not only the problems of economical utilisation of hide substance, but also the problems of keeping the cleanness of living conditions. Improper methods of liquidating the wastes (burying, throwing in rivers, burnishing , free fouling in dumps) are a dangerous source of possible poisoning the soil, water or air by products of putrefaction with no respect to unpleasant odour and support of the existence of rodents.

Another aspect in considering the effective possibilities of processing tannery and shoemaking wastes is the problem of their centralization (total amount of occurence, possibilities of collecting and costs of their transportation) which is the condition of their economic processing.

With respect to above mentioned facts we pay our attention, in the following texts, to the problems of utilisation of tannery and shoemaking wastes, to the economically most interesting sections:

Chapter I gives a total survey on the occurence and utilisation of wastes and is mostly devoted to the interesting methods of using non-tanned wastes and to a short specification of the occurence and processing of tanned wastes and by-products of leather and shoe industry.

Chapter II is specialised to economically most interesting method of utilising tanned wastes in tanneries, i.e. to the production of fibrous leather.

Chapter III deals with the most modern and most effective methods of processing the tanned and non-tanned wastes for the production of semi-synthetic leather.

In studying the mentioned materials it is necessary to consider that the conditions for the evaluation of wastes from leather and shoe industries are not identically convenient in every country. Many of the mentioned methods of utilising the wastes are sometimes nearly unrealisable due to too sporadic occurence, unsuitable climate, insufficient degree of the development of other industrial branches, etc. Thus, these papers should serve for general information about the most modern methods of utilising the tannery and shoemaking wastes and cannot be considered for an exhausting instruction.

CONTENTS

NATIONAL RESEARCH INSTITUTE FOR SHOE,

LEATHER AND ALLIED INDUSTRIES GOTTWALDOV - CSSR

Dr. Ing. Cyril HALÁMEK :

CHAPTER I : THE SURVEY OF OCCURENCE AND USE OF TANNERY AND SHOEMAKING WASTES

The Survey of Occurence and Use of Tannery and Shoemaking Wastes

CONTENTS

2.3. Processing of other wastes

2.3.1. Characteristics of wastes

2.3.2. Basic methods of processing

2.3.2.1. Utilization of effluents

2.3.2.2. Production of felt

2.3.2.3. Production of reclaims

2.3.2.4. Unprocessed wastes

3. Economic aspects of processing tannery and shoemaking wastes

3.1. Collection of raw materials

3.1.1. Expected trends of development in the occurence of wastes

3.1.2. Possibilities of transportation and storing

3.2. Comparison of the effectiveness of individual methods of processing

3.2.1. Consumption of energies and costs of building

3.2.2. Coefficient of evaluation

3.3. Insidence of waste utilization in the national economy

1. Occurence and Division

With respect to the processability, tannery and shoemaking wastes are divided into three groups: untanned collagen wastes, tanned collagen wastes and other wastes.

1.1. Untanned Wastes

Untanned wastes are most valuable for the subsequent processing and can be also well processed because their contain well utilizable native protein. Untanned proteinous wastes are divided according to the type and occurence in the following way:

Type of Waste:	Occurence in % per Weight of Soaked Hides	
Trimmings		1
Hair		2
Machine glue stock from the production of sole leather	33	
from the production of upper leather	26	29
from the production of calf leather	27	
Hand glue stock from the production of sole leather	4.5	
from the production of upper leather	4.5	4.5
from the production of calf leather	6.0	
Split glue stock from side leather		14

In collecting these wastes it is necessary to take care of their good curing because proteinous material is a very favourable medium for the life of microorganisms and putrefies very easily. Liming is the mostly used method of curing.

Drying, salting and freezing are less usual methods. Freezing is especially problematical because the frozen material is nearly unprocessable and defreezes slowly. Properly limed waste can be stored even outside the building if it is protected from rain.

1.2. Tanned Wastes

Tanned wastes make more difficulties in the processing than untanned wastes because it is very difficult to release the bond of tanning matter with collagen without the simultaneous deeper destruction of collagen molecule. Therefore, these wastes can be practically processed only to fibrous articles or to deeply hydrolyzed products. For example, wastes of leather tanned by natural or synthetic tanning materials cannot be used at all for the production of fodder because tanning materials being hydrolyzed are decomposed to lower phenols which must not be present in the fodder even in traces.

According to the occurense and quantity the tanned wastes are divided as follows[1]:

Type of Waste	% per Weight of Wet Hide	% per Weight of Finished Leather
Chrome tanned shavings of sides	11	-
of pigskins	9	-
Chrome tanned split	x)	-
Vegetable tanned shavings	x)	-
Vegetable trimmings	x)	-
Waste in clicking vegetable tanned sole leather	-	28.9
Waste in clicking chrome tanned leather	-	26.4
Waste in clicking vegetable tanned upper leather	-	14-16
Leather dust from leather buffing	-	fragments

x) Data on an average quantity of wastes cannot be given because the quantity changes severly depending on the used technology of leather production. The present situation in the technology of leather splitting heavily influences the mutual proportion of tanned and untanned wastes because in individual plants the leather is split either in the pelt condition or in the tanned semi-product.

1.3. Other Wastes

From the other wastes in the leather and shoe industries the most important wastes with respect to their quantity are tannery effluents and non-proteinous wastes from the production of footwear.

1.3.1. Tannery Effluents

Various amount of effluent is produced according to the production technology in the plant and according to the situation in water supply. Consumption of water needed for the processing of 1 kg of hide ranges from about 60 to 100 lt depending on the kind and conditions of the production. This amount sharply increases if the wastes are processed directly in the tannery. For example, in the production of glue about 700 to 1,000 lt of water is needed for 1 kg of the product and in the production of gelatine the consumption of water increases to 1,000 up to 3,000 lt. In the production of fibrous leather the consumption of water is 150 to 400 lt per 1 kg of the product depending on the used production technology.

1.3.2. Wastes from the Production of Non-leather Footwear

These wastes are divided into rubber wastes, rubber coated fabrics, fabrics, mixed wastes, wastes from synthetic materials, paper and wood.

In the greatest quantity we meet porous and compact rubber wastes in clicking the shoe parts, then, wastes from moulding and wastes from synthetic leather. In clicking shoe parts the wastes ranges from 15 to 20% of the area or weight of the processed materials.

1.4. Survey of Losses of Proteinous Material

With respect to very different dry matters in hide and leather wastes and with respect to the fact that proteinous material is the most utilizable part of wastes, the balance of nitrogen loss which is the factor of hide substance gives us the clearest survey on the occurence of wastes in converting the hide and leather to footwear. According to Pektor and col.[2] the balance of nitrogen in converting the cattle hides into footwear is as follows:

Operation	Nitrogen Loss from the Original Dry Matter of Hide Substance in %
Soaking - liming	6.6
Machine fleshing	2.7
Hand re-fleshing	1.4
Splitting in pelt condition	6.8
Deliming - bating	21.4
Tanning - pre-finishing	7.8
Shaving	5.5
Splitting of tanned leather	13.0
Waste in clicking	7.7
Other losses	3.7
Utilized for footwear	23.4
Total	100.0

Of course, from the mentioned wastes some are returnable, i.e. they can be used for other purpose in the tannery or in the shoemaking plant, e.g. the split from tanned leather and a proportion of shavings. Thus, the utilizability of hide substance increases to about 40%.

2. Processing

In the processing of hide and leather wastes the latter can be also divided into three basic groups:

- wastes containing native collagen
- wastes containing denaturated (pre-tanned) collagen
- other wastes

2.1. Processing of Wastes Containing Native Collagen

2.1.1. Qualitative Dependences

In the processing of these wastes we know that the obtained products are the more valuable, the less decomposed or changed are proteins in their structure. This preserving of the proteinous structure depends not only on the sharpness of the used technology of waste processing, but also on the quality of wastes. From the combination of these conditions we have compiled the following sequence of the most valuable wastes and the most economic methods of processing:

Material	Product
Split pelt glue stock	Fibrous material for semi-synthetic leather
	Surgical materials
	Artificial casings
Split + hand glue stock	Edible and photographic gelatine
	Technical gelatine
Hand glue stock + cuttings of fur leather	High-viscous glues
Machine glue stock	Low-viscous glues
	Fodder
	Fertilizers

It is obvious that according to the given survey it is possible to obtain also less valuable products even from the materials of the highest quality. Of course, the reverse combination does not exist. The mentioned survey enables also a great number of inter-stages owing to various quality and combination of the given kinds of materials.

2.1.2. Basic Methods of Processing

2.1.2.1. The Production of Semi-Synthetic Leather from non-tanned wastes will be dealt with in Chapter III.

2.1.2.2. Production of Artificial Casings

This production needs a highly specialized machinery and equipment and from this reason the capital costs are high. Chart of the production is approximately the following:

/Pre-cutting and sorting/ /Liming/ /Washing/ /Acidifying/

/Cutting/ /Squeezing/ /Cross-linking/ /Conditioning/

/Shaping/ /Tanning/ /Drying/ /Washing/ /Adjusting/

The production of artificial casings is limited only to technically most developed countries, such as the U.S.A., Germany, Sweden (Trade Mark Naturin), Czechoslovakia (Cutisin), Spain (Fibran), Swiss (Elastin). In the near future the artificial casings shall be produced also in Yugoslavia and the U.S.S.R.

Finished products are adjusted to the widths from 200 to 10 mm and length per approx. 25 m. The artificial casings must withstand the boiling test, it must be sterile, it must be tanned with hygienic tanning matters (aldehydes, wood distilates) and in the production exclusively drinking water must be used. The raw material must be hygienically perfect (content of anthrax!). Split glue stock for the production of artificial casings must also have a great number of standardized properties.

2.1.2.3. Production of Surgical Materials

In the production of these material the processes are basically identical with the technology of the production of artificial casings. However, the production is more complicated because care must be taken of a greater hygienic perfectness of the products and their perfect assimilability in the human body. To the most known products belong surgical threads, implantation articles, artificial aorta. The most known manufacturer of these products having the greatest experience is the American Ethicon Corp., Sommerville, N.Y., U.S.A. Though the price of these products is considerably higher than that of other products from tannery wastes, this production does not utilize a more substantial proportion of tannery wastes.

2.1.2.4. Production of Gelatines and Glues

At the present this utilisation of collagen wastes represents quantitatively the most important method of liquidating the untanned wastes. It is because the used production technology is simple and the production is relatively cheaper with respect to the investments and machinery. Another reason is that the products are demanded for a great number of important industrial branches.

In the production of gelatine and glue a basically identical principle of production is used: the cleaned and prepared raw material is thermally hydrolyzed at the presence of water. The obtained protein solutions are thickened and dried. The differences depend only on the kind (quality) of the processed raw materials. While from glue stock with a high content of pure collagen we can obtain the highest-grade gelatine using a more complicated production technology, from inferior raw materials (machine glue stock) we can obtain only the lower-grade glues even if we take the greatest care of the production. The properties of the used raw materials are approximately the following:

Glue Stock of Different Provenience and Weight Classes	Split Glue Stock	Hand Glue Stock	Machine Glue Stock
Water content in %	72.0	73.5	79.4
Fat content in %	0.3	0.9	7.7
Ash content in %	2.3	2.9	3.3
Proteinous matter in % (nitr gen x 6.25)	27.5	25.6	10.0

Diagram of gelatine production:

/Pre-cutting/ /Washing/ /Acidifying/ /Boiling/ /Filtration/

/Preserving/ /Thickening/ /Cooling/ /Drying/ /Finishing/

/Packing/

In this production diagram we can consider also other elements (instead of thickening the solutions only direct cooling to gel condition, boiling by circulation method, pressure boiling, etc.). However, from the modern methods of drying the gelatine and glue plants have not accepted drying by pulverising because the products are too voluminous and for the use they cannot be macerated at all.

In the production of gelatine and glue we must take in consideration also the local influences. The production needs a great amount of water, in high-grade gelatine it must be drinking water which is soft and has a low iron content. The production is difficult in countries with high temperatures, and mainly, with high relative humidity of air causing troubles in drying and storing hygroscopic products. The yields in the production of gelatine and glue are approximately the following: from split glue stock we get 14 to 18% air-dried product, from hand glue stock 14 to 17% and from machine glue stock 8 to 10%. In processing the machine glue stock we get also approx. 3 to 5% of technical hide fat. The products are sensitive to the action of decomposing bacteria and it is necessary to preserve them. In the technical products it is carried out by zinc sulphate of phenol. In case of high-grade gelatine we use sulphurous acid for edible gelatine and phenol for photographic gelatine.

In the production of lower-grade products (technical gelatine and glues) the technology is changed in such a way that the raw material need not be so perfectly limed and washed, the raw material is boiled with lower care, i.e. at higher temperatures and more quickly, and due to lower quality the solutions must be always thickened before cooling. It is necessary to know that the differences in quality occur very slowly and continuously in a number of products, so that it is impossible exactly to define the quality line between gelatine and glue. We give some quality criteria, however, from the above mentioned reason they must be considered only for a framework and it is possible that some product with certain properties could at one time correspond with two quality classes.

Survey of Some Quality Factors in Gelatines and Glues

Factor	Edible Gelatine	Technical Gelatine	High-Viscous Glue	Low-Viscous Glue
Max.water content in %	16	17	17	17
Max.ash content in %	3	2.5	2	4
Min.viscosity in cP of 17.75% solution at 40°C	5.0x	39	63	12.5
Max.viscosity decrease after 24 hours in %	-	30	15	30
pH of 1 % solution	4.0-7.0	5.0-7.0	5.0-7.5	5.0-7.5
Min.stickiness in kg/cm²	-	-	100	75
Min.melting point in °C	28	-	-	-
Max.content of mechanical impurities in %	-	-	0.1	0.2

x = for 6.67% solution,

Besides this, in edible gelatine they also standardize smell, colour, content of liquefying microbes, content of sulphur dioxide and content of toxic metals.

In the processing of glue stock, especially of machine glue stock, much fat is obtained in boiling the raw material. Fat is very valuable product and is sold for processing in other industrial branches (production of soaps, fatty acids, greasing agents). Fat is such a valuable part of glue stock that sometimes the glue stock is boiled directly only for obtaining fat and the proteinous remainders are not utilised. However, from the hygienic and economic reasons we cannot agree with it.

The specialists have paid a considerable attention to the problems of fat obtaining. In the last years several quite new methods of fat obtaining appeared. The most important is the method of Lyciol Inc., Kansas City, U.S.A., in which the glue stock is processed thermally and by centrifugation. Other works were paid to mechanical methods of removing fat especially in cases in which the degreased and undenatured hide substance shall be obtained.

Utilisation of glues and gelatines is very manifold. A certain survey can be obtained from the following Table:

Product	Consumer Industry
Gelatine	Pharmaceutical, edible grade, photographical industries
Technical gelatine	Polygraphic, decoration goods, textile industries
High-viscous glues	Production of matches, scouring papers, pencils
Low-viscous glues	Flotation of ores, painter's dyes, wood-processing industry, paper industry

Despite all effort for more effective utilisation of proteinous fibrous material contained in glue stock and other untanned wastes, the production of glue and gelatine is always an economically interesting processing of wastes because it is a source of still very needed products. Despite the greatly developed industry of artificial materials, we have not yet succeeded in finding a suitable substitute for photographic gelatine, technical gelatine for the preparation of printing cylinders, high-grade glues for the production of matches, pencils and scouring papers. Also the interest of consumers in edible gelatine has the always rising trend.

2.1.2.5. Production of Fodder

The production of fodder from untanned tannery wastes is possible because the preteinous proportion of glue stock is formed nearly exclusively by the collagen protein which is composed like other proteins from a number of amino acids:

Amino Acid Composition of Collagen

Essential Amino Acids		Other Amino Acids	
valine	1.71	hydroxy proline	13.02
leucine	3.22	asparagic acid	2.68
isoleucine	1.03	glutamine acid	5.01
thionine	0	treonine	1.47
methionine	0.40	serine	3.60
lysine	4.10	proline	15.16
arginine	7.05	glycine	26.62
phenyl alanine	1.83	alanine	9.14
tryptophan	0	tyrosine	0.74
histidine	0.67		
cystine	0		

Collagen is digestible and represents the edible protein. Despite the deficiency in certain essential amino acids (there are amino acids which the animal body must get in fodder because it cannot produce them itself in the transformation of proteinous food), namely thionine, tryptophane and cystine, collagen represents a valuable feeding element if being completed with other full-value proteins. With the deficiency of feeding proteins in the world, the fodder from collagen wastes are, therefore, a demanded product. The feeding value is increased by the contained fat which is well degestible.

Fodder can be produced with respect to the price of the raw material (glue stock) only from machine glue stock. Other kinds of glue stock are identically convenient for the production of fodder too, but they are too valuable with respect to the fact that it is possible to obtain more valuable products from it than the fodder.

In the processing of untanned hide wastes we must take care that the raw material is properly removed of calcium salts and other impurities. From this reason unlined glue stock is a more suitable raw material. Further, it is necessary to take care of the hygienic perfectness of the raw material, especially, to be free of anthrax, though the proper technological processes are usually carried out in such a way that they limit the spores of anthrax survival to a lowest possible extent.

We know two methods of fodder production from untanned hide wastes: liquid fodder and dry fodder. Both methods have their advantages and disadvantages. The main advantage of processing for the liquid fodder is that thickening and drying solutions or drying the obtained fibrous materials is eliminated. However, this advantage is reduced with the fact that the liquid foddor cannot be properly preserved, and thus, it cannot be stored for a long period, and that in its distribution we must transport a greater proportion of water than is the weight of feeding material.

A typical example of well solved processing of machine glue stock for liquid fodder is the production of proteinous fodder in Wünschendorf, German Democratic Republik[4]. A principle of the production is approximately the following:

/Washing/ /Cutting/ /Acidifying/ /Pressure boiling/

/Mixing with other proteins/ /Distribution/

Liquid fodder is regularly distributed to local pig feeding stations and is fed without troubles with the addition of the needed admixtures (starch, vitamines). The produced fodder contains approx. 8 to 10% of digestible proteins and 20 to 25% of nutritious matters.

An example of glue stock processing for dry feeding flour is the process according to the French Patent. The production is considerably difficult, however, the product can be stored long. As to its nutritious value it is compared with ordinary feeding flours of the vegetable or animal origin because from essential amino acids it does not contain only tryptophan.

The principle of the production is as follows:

/Homogenisation/ /Chemical processing/ /Dewatering/

/Defibring/ /Hydrolysis/ /Washing/ /Dewatering/

/Desintegration/ /Drying/ /Milling/

Besides the mentioned method of processing also other methods are known, e.g. the preparation of liquid fodder types from fur wastes by acidic hydrolysis, the preparation of dry pelletized fodder types for poultry by treating the glue stock with steam, centrifugation and drying, boiling the glue stock with phosphoric acid and extraction, alkali treatment in cold condition and pressing, pre-tanning by alum in acid medium, pressing, neutralizaction and other.methods.

The mentioned methods of processing untanned hide wastes for fodder means that this utilization of proteinous matter is technically and agriculturally interesting and if the needed economic conditions are given, it represents one of the perfect utilizations of hide wastes.

2.1.2.6. Production of Fertilisers

When Using untanned hide wastes for fertilising fields we cannot talk about the production of fertilisers but only about the "utilisation as fertiliser". For fertilizing we can use the glue stock of cuttings either directly or we can use only their remainders which have been previously treated. Fertilizing by original glue stock is interesting because the glue stock transfers, according to its dry matter, about 1.6 % of easily decomposable nitrogen into soil. However, this is not practically done because the glue stock can be processed more economically. Further, in fertilising 50 to 80% of water would be transported on the field, and at second, the glue stock must be immediately ploughed because otherwise it would be a source of odour and sanitary infection.

The use of remainders after glue stock processing (sludges and unboiled remainders from the production of gelatine and glues) is more convenient due to their zero residual value. However, throubles with the transportation of needles water and odour are not eliminated, and moreover, another trouble occurs, i.e. an increased content of fats in glue remainders. Sludge in this case can contain up to 32% of fat which is hard assimilable. In such cases it has also very low content of nitrogen.

2.2. Production of Pre-Tanned Wastes

2.2.1. Value of Pre-Tanned Wastes

Wastes from leather, which has been tanned with vegetable tanning materials, chromium, fats, alum, formaldehyde or with other methods, are much more difficult to be lixiviated when compared with untanned wastes. It is caused by the fact that the tanned collagen is denaturated collagen which has become, due to a chemical change of its molecules, non-boilable, non-digestible and very hard bacterially degradable. These wastes cannot be processed to glues and gelatines, to valuable fodder or fertilisers.

Practically, the only method of utilising the tanned wastes in the shoe and leather branches is the utilisation of their fibrous structure for the production of fibrous sheets bound by macromolecular agents. Chrome tanned wastes can be relatively most easily de-tanned,and therefore, they are partially used for the production of glues, fodder and fibres for semi-synthetic leather.

In the processing of wastes from finished leathers there are other influences affecting the processing, namely nearly full chemical inability to degrade the grain side and, at second, the content of some veterinary inadmissible metals contained in the used tanning or finishing baths.

A partial advantage of the tanned wastes is their lower cost, bacterial resistance and a low moisture content if they are stored under a roof. This enables their more economical transportation and storing. Another advantage of these wastes is that after their drying we have at our disposal nearly in every place an emergency method of their liquidation, i.e. combustion directly in the places of occurence. However, the net caloric value of dry pre-tanned wastes equals only the net caloric value of less-grade brown coal. In combustion these wastes the disadvantage is an unpleasant odour of flue gases.

Survey of some properties of tanned wastes:

Waste	Water Content in %	Hide Substance Content in %	Ash Content in %
Vegetable tanned clicking waste	14.0	41.0	2.0
Chrome tanned clicking waste	14.0	42.0	6.4
Chrome tanned shavings	58.0	21.0	13.6

2.2.2. Basic Methods of Processing Tanned Wastes

2.2.2.1. Production of Semi-Synthetic Leather

This production will be dealt with in more details in Chapter III.

2.2.2.2. Production of Fibrous Leather

This production will be dealt with in more details in Chapter II.

2.2.2.3. Production of Glue

From tanned wastes only chrome tanned shavings can be processed to glue because owing to their small pieces they have a sufficient surface for de-tanning to proceed in an acceptable time and intensity. De-tanning is done by alkali with the required basicity and ion power. In the practice it is above all magnesium oxide. Then, the raw material is washed and boiled and is processed in an ordinary glue producing method. Yield is usually lower than in the processing of glue stock and the quality of products is also lower because the raw material is denaturated. Maximum viscosity of the obtained glues is approximately 2°E. However, the obtained glue has a very nice bright light-yellow colour.

In the literature a great number of methods is patent covered how to process chrome tanned shavings to gelatine, e.g. according to Steigmann[5]. However, the methods are considerably difficult to be realised. Up to the present the preparation of gelatine from this raw material has not been realised in a greater extent.

2.2.2.4. Production of Fertilisers

The theoretical fertilising material of tanned wastes does not differ much from other proteinous fertilisers. Content of nitrogen in tanned and finished leather is about 7.4%. However, the use for fertilisers is considerably unfavourable and unusual because the tanned collagen decomposes very slowly by microbial processes, so that the fertilising effect is low.

In order to improve the quality of these fertilisers the tanned wastes are sometimes partially hydrolysed by steam or acids, favourably by phosphoric acid, or by mixing them with lime or exhausted vegetable tanning material in order to increase the loosening effect in hard soils. However, despite the mentioned improvements the fertilising effect of those fertilisers is low and their price after further processing is unacceptably high when calculating the nitrogen content in comparison with other fertilisers, especially with artificial ones.

2.2.2.5. Production of Fodder

When using the tanned wastes for fodder it is necessary to de-tan the waste well. De-tanning of vegetable tanned wastes is possible for example by alternating influence of weak acids and bases, or only of bases, but the method is two expensive. Moreover, it cannot be used with leather tanned by syntans because even after detanning, the residual amounts of phenols would remain in the raw material. Better situation exists in the de-tanning of chrome tanned wastes. By an intensive influence of alkali (e.g. at temperatures above 100°C) the bonds between chromium salts and collagen are destroyed, however, also with the simultaneous deep hydrolysis of collagen. The released chromium can be removed as a sediment of practically unsoluble chromium hydroxide. With this method we can obtain the solutions of hydrolyzed proteins, mostly in the state of digestible peptides. Solutions can be neutralised, thickened and dried to digestible fodder.

The mentioned system of processing the chrome tanned wastes is the basis of the most modern method how to utilize the tanned wastes in Czechoslovakia for the preparation of fodder. However, thus obtained fodder has a certain residual stickiness. From this reason the product is considered for additive fodder only and its use is permitted only in the maximum addition of 2% to dry feeding mixtures. Properties of the fodder - the so-called hydrolysate of glutin - are as follows:

Water	7.0 %
Nitrogenous matters (N x 6.25)	83.0 %
Fat	0.2 %
Ash	9.0 %
Fibrous material	0 %
From nitrogenous matters:	
Proteins	18.9 %
Amides	64.1 %
Coefficient of digestibility of proteins	99.8

Yield of the fodder is 32% from the weight of chrome tanned clicking wastes or waste chrome tanned split leather, or 23% in the processing of chrome tanned shavings.

However, the application of this method of urilizing the tanned wastes is possible only in countries which have at their disposal greater amounts of chrome tanned waste which is not re-tanned by syntans, and where the product can be applied in the preparation of dry feeding flours in the mixing plants of fodder.

2.2.2.6. Production of Saponates

Hydrolyzates of the proteinous material from tanned wastes can be used also for the preparation of various condensation products with other chemicals[7]. In a certain extent they practically use a combination of alkaline hydrolysate of chrome tanned shavings with higher alcohols. The products have good wetting properties and are used as active saponates of various trade marks.

2.3. Processing of Other Wastes

2.3.1. Characteristics of Wastes

In the leather ans shoe industry there are the following other wastes:

Hair

Hair is obtained in processing hides in the stage of unhairing. It is destroyed in rapid liming, but remains if careful methods of liming are used, and in processing furs. In the production of leather the amount of hair is approximately 2 % per soaked weight of hides. In the production of furs the hair is wasted simultaneously with proteinous wastes. Hair represents a valuable raw material for the manufacture of other products, which is similar to wool. Typical is the content of keratinous protein which contains a higher amount of sulphur amino acids and in hydrolysis it is more resistant than collagen.

Tannery Effluents

Every tannery produces a great amount of highly contaminated effluents the treatment of which is difficult. In converting hides to leather or furs we know that in the processing of 1 kg of raw material for vegetable tanned leather approx. 60 lt of water is wasted, and for chrome tanned leather it is approx. 80 lt of water. In some tanneries this water amount is more increased with effluents from the processing of wastes. So, for the production of 1 kg of gelatine we need 1,000 to 3,000 lt of water, for 1 kg of glue we need 700 to 1,000 lt of water and for 1 kg of fibrous leather we spend 150 to 500 lt of water.

Average contamination of effluents is high especially with respect to the content of putrefactive matters (expressed by five-day biochemical oxygen demand with aerobic effluent digestion), content of insoluble matters and content of soluble salts. The composition of effluents in leather industry is approximately the following[8].

Insoluble matters	1,700 mg/lt
Annealing loss	900 mg/lt
Total solids	5,000 mg/lt
Annealing loss	2.500 mg/lt
BOD_5	1,100 mg/lt
Total nitrogen	190 mg/lt
Chlorides	1,800 mg/lt
Calcium	400 mg/lt
Chromium as Cr_2O_3	25 mg/lt
pH value	9 - 11
Sulphates	300 mg/lt
Sulphides as H_2S	50 mg/lt

In industrially highly developed countries the rivers of which are much contaminated with waste water from living centers or industrial plants, or in countries in which the tanneries must canalize effluents into rivers having little water, the effluents must be treated. The reason of this provision is not only the effort to keep a certain minimum cleanness of rivers but also the effort to reduce the charges for the contamination of rivers which the tanneries must pay in some countries. Effluent treatment is a net loss for the tannery which, however, is economically needed action in those cases where the tannery already pays for the contamination of rivers with effluents.

According to the kind, the tannery effluents are divided as follows:

effluents from soaking,
liming,
washing, de-liming and bating,
vegetable tanning,
pickling, chrome tanning and neutralization,
dyeing and greasing,
washing of vegetable tanned leather,
social facilities and cleaning the production rooms.

The greatest troubles in effluent treatment make the waters from vegetable tanning and liming processes. As far as possible, in new plants they are specially canalised and are subjected to a special pre-treatment.

Wastes from the Production of Non-Leather Footwear

There are wastes of synthetic materials (polyvinyl chlorides, polyurethanes, polyethylene, polystyrene, synthetic rubbers, etc.), natural rubber, textile and wood.

Some types of polyvinyl chloride, polystyrene, polyethylene and synthetic rubbers are well reclaimable, and thus, they can be again processed and used in the factory. Textile can be used again as fibres only for the processing in textile industry, but only if it is not rubberized. Practically unusable and mostly combusted are the wastes of rubberized fabrics, wood, fibrous leather and synthetic upper materials.

Waste Bark

It is found rarely only in those factories that prepare the tanning materials from bark or wood of tannin containing plants. The waste would be usable for example for the production of wood fibre boards, for the production of filling to flooring materials, etc., but its price is inconvenient with respect to the need of drying it, at least partially. In cases, that it is impossible to be dried and combust without charge, it is a troublesome waste.

2.3.2. Basic Methods of Processing

In this part we give only the methods of processing those collagen wastes which are economically important.

2.3.2.1. Utilisation of Effluents

Tannery effluents are treated in two stages: The first simpler stage is a mechanical pre-treatment, homogenization and discharging of rough insoluble materials. In this first stage about 80% of insoluble materials are removed from effluents, further 30 to 50% of organic matters determinable according to BOD_5 and about 5% of the present sulphides. The second stage of treatment is chemical or biological re-treatment. Chemical treatment is basically precipitation of soluble proteinous impurities by coagulation with ferrous sulphate in doses of 1 to 2 g of $FeSO_4.7$ per 1 lt of water. In biological treatment they use natural methods, such as biological ponds, irrigation of soil, soil filtration, or artificial methods such as aeration of water in biological filters or treatment with activated sludge. The most effective is the treatment with activated sludge. With the mentioned methods of re-treatment it is possible to reduce the content of harmful matters, determinable according to BOD_5, by 60 to 70% with chemical treatment and by up to 90% with biological treatment. According to the present experience it is necessary or convenient in the biological re-treatment to dilute the effluents by the addition of municipal waste waters which supply the system with the needed nutritious matters.

Solid impurities caught during the mechanical pre-treatment on screens are transported on to heaps and used as fertilizer. The value of fertilizers is low. There are relatively low amounts of these wastes.

Sludges both from the rough sedimentation or after the biological re-treatment are dewatered up to the excavatable stage and are used as fertilizers. Composition of sludges from the mechanical re-treatment is for example the following:

Moisture content in %	70
Ash content in % of dry substance	50
Organic matters in % of dry substance	50
Total nitrogen in % of dry substance	4
Chromium in % of dry substance	1.5
Calcium oxide in % of dry substance	up to 20

(Average of the values of 8 samples taken at random)

Fertilizing value of these sludges is not too high, and moreover, a possibility of over-dosing the fertilizer exists with respect to the content of chromium, because with more often repeated doses of the fertilizer which are higher than 1,000 kg per 1 ha a danger of excessive accumulation of chromium in soil exists. Considerable amount of sludges is wasted. From 1 m^3 of effluents about 2 kg of sludges is produced (dry substance approx. 30%) after dewatering to excavatable stage. Sludges from chemical re-treatment are worse usable for their high content of iron (up to 20% of Fe in dry substance).

The last utilizable material obtained from tannery effluents are proteins from liming waste waters. In 1 lt of these waters there are approximately 10 g of proteins which can be obtained by precipitation with suitably adjusted acidity. However, a proper use of these proteins has not yet been developed.

The most suitable method of liquidating tannery effluents is the reduction of their occurence. Therefore, the problem of effluent treatment is closely connected with the problem of saving technological water in tanneries (rationalization of washing, recirculation of less contaminated water, modern methods of liming and unhairing hides, etc.).

2.3.2.2. Production of Felt

The production of technical felt, hats and felts for textile machinery is a convenient processing of hair. Hair is sorted according to the length and colour, it is washed and dried. Then, it is placed in uniform sheets, it is desintegrated and carded. The produced fleece is folded, thermally shrunk and felted. Then, it is mordanted, milled, dewatered, dressed, dried and pressed.

Sorted bristles are obtained in theprocessing of pigskins. They are a valuable raw material for the production of brushes.

Wasted hair from furs is not processed because it is wasted together with the hide wastes. An exception is hair which is cut off for the production of hats. Wastes in the fur industry are processed without further sorting either to proteinous feeding hydrolysates from higher-grade raw materials or to low-grade fertilisers from inferior row materials.

2.3.2.3. Production of Reclaims

From non-leather wastes in the production of footwear they reclaim nearly fully the porous polystyrene rubber. The waste is crushed, binders and plasticizers are added and under temperature the compound is processed again to a semi-product. Wastes of suitable types of compact rubber are processed in the same way.

2.3.2.4. Unprocessed Wastes

From the above mentioned reasons and from economic reasons which will be discussed later on, only the following wastes have remained rationally unprocessed in the leather and shoe industry:

Extracted tannin containing materials,
Rubberised textile wastes,
Vegetable tanned split cuttings,
Wastes of fibrous leather,
Wastes of synthetic and semi-synthetic leathers.

3. Economic Aspects of Processing Tannery and Shoemaking Wastes

3.1. Collection of Raw Materials

3.1.1. Expected Trends of Development in the Occurence of Wastes

The main change in the future tens can be expected in that the proportion of untanned wastes and hair will decrease and the proportion of tanned wastes will increase. This change will occur because in the occurence and processing of hides a trend to bulk pre-processing hides in slaughterhouses is being taken place. The method of processing wastes from raw hides in slaughterhouses has been developed above all in the U.S.A.[9] because it depends on the concentration of meat industry. This will result in the situation that especially machine glue stock and trimmings will remain in slaughterhouses in the unlimed condition, i.e. in the condition which is convenient for the production of high-grade proteinous fodder. With respect to the world-wide deficiency of proteinous fodder it will be necessary preferentially to process the wastes to fodder instead of glue and to similar products. Another reason for the decrease of untanned wastes is the fact that due to the increasing mechanisation and precisioning the hide pattern, as well as due to the development of the own processing capacities in the developing countries, the proportion of wet blue will increase, so that splitting in pelt condition will be eliminated, and thus, the highest-grade untanned types of wastes will be also eliminated. For example, according to the literature[9] in the present time the wet blue counts already about 30% of the total export.

Another change of the present situation in the processing of wastes is expected from the technologies of the production of semi-synthetic leathers being developed. This production evaluates the wastes in tannery in the most effective way, and therefore, in the future it will process even the increased quantities of wastes (untanned and tanned split portions of hides, and marginal portions of raw hides which are of a lower value). From this reason it is cenecessary to consider the decrease in the quant.ty of wastes for other methods of processing.

With respect to problems in the nutrition of people it can also be expected that the production of artificial casings and edible gelatine will be increased. For this use the demand for split untanned glue stock will increase.

In the end it can be said that the total quantity of untanned tannery wastes will be reduced. The increased demand for first-grade untanned wastes on the other hand will result in their deficiency and the untanned tannery wastes will be much more valuable than they are at the present.

Besides the present types of wastes, in the future a problem will arise how to process the increasing quantities of clicking wastes from synthetic and semi-synthetic materials (leather) in the most effective way.

3.1.2. Possibilities of Transportation and Storing

The reasons mentioned in the above paragraphs will force the leather and shoe industry more and more to the collecting and processing all accessible wastes. Collecting in the places of their occurence is no problem as far as the wastes are properly preserved (untanned wastes by thorough liming, wet tanned wastes by spraying or washing in the solution of disinfectants), and as far as the mechanization of their loading has been solved together with a suitable place protected against climate influences.

However, the main problem is their concentration to one place of the processing, namely with wet untanned wastes. In their transportation also their moisture content is being taken with (content from 50 to 85% according to the type of waste) which causes troubles with the putrefaction of wastes in worm weather or, on the other hand, with freezing in cold weather. This always unfavourably increases the costs of transportation. These problems have not yet been favourably solved.

The non-rentabil and difficult transportation of untanned wastes reduces sharply the economy of their processing. Makeshift processing equipment must be built which in a great majority of cases work little effectively because of a small extent of production.

3.2. Comparison of the Effectiveness of Individual Methods of Processing

3.2.1. Consumption of Energies and Costs of Building

In the processing of all types of tannery and shoemaking wastes the greatest energetic item is the heat energy, in the practice the consumption of steam. It results from the fact that nearly always they produce dry products from heavily wet materials or from dry materials which from technological reasons had to be converted into heavily aqueous condition during the processing. Evaporation of water from semi-products or drying the final product requires very much heat energy.

Consumption of steam in the production of some products from tannery and shoemaking wastes are, for example, the following:

Product	Consumption of Steam in kg per 1 kg of the Product
Artificial casings	32
Gelatine and glue	25
Fibrous leather	40
Hydrolysate of glutin	10
Felt	14

Another economically important energy is water. The problem is in suitable and sufficient sources of water near the production site. In some products, such as artificial casings, surgical materials, edible gelatine, great amounts of drinking water are needed. Both drinking and industrial waters are of a considerable value today which is increased more by further charges for using the canalisation and for the contamination of rivers by effluents. Costs of the consumed water cannot be given because the situation in individual countries is quite different. However, the items of costs for water must be taken very carefully in consideration when planning the plants for the processing of wastes. Consumption of water in lt per kg of the product are approximately the following:

Product	Consumption of Water in lt per 1 kg of the Product
Artificial casings	500 to 600
Gelatine and glue	1,000 to 3,000
Fibrous leather	150 to 500
Hydrolysate of glutin	90
Felt	40

Consumption of electric current for driving the machinery and equipment are of less importance. In the basic products they are, for example, the following:

Product	Consumption of kW per 1 kg of the Product
Artificial casings	3.1
Gelatine and glue	1.0
Fibrous leather	1.0
Hydrolysate of glutin	0.3
Felt	0.4

As the costs for the construction of buildings and for the equipment are concerned, they can be roughly arranged in the approximate following sequence (the data were obtained from the equipment for waste processing having a great capacity. In smaller plants the data can heavily vary:

Product	Cost of Production Equipment in Relative Units	Yearly Output in Tons	Value of the Produced Goods in Relative Units	Yearly Depreciations of Equipment per 1 kg of the Product	Ratio of Costs for Equipment to the Value of the Product
Glue	50	2,500	18.5	20	2.7
Hydrolysate of glutin	7.5	1,300	4.1	5.8	1.8
Fibrous leather	40	2,000	22.3	20	1.8
Artificial casings	130	2,600	136.5	50	0.9

The need of manpower in the processing of wastes is not so difficult when compared with the need of manpower in the overall leather and shoe production, especially in the shoe production, because the technologies of waste processing are organised relatively well and to a considerable extent they are automatised. This higher degree of mechanisation and automation has been enabled by the fact that the wastes are relatively more homogenous than raw hides.

Last but not least problem in the economy of waste processing which must be taken in consideration is the range of production capacity. The higher is the production capacity, the lower are the production costs. Production costs can be substantially reduced if the capacity of waste processing is built inside the existing larger industrial factory. Thus, the investment is lower, e.g. saving on the installation of electric current distribution, installation of steam sources, water distribution piping, canalisation, roads, administrative, guarding service, railway siding, etc. As the minimum content of the production is concerned in waste processing, we cannot give exact data because these problems are influenced by the situation in individual countries, by the possibility of building the processing plant inside a larger production unit, and by other circumstances. However, the practice shows that we can expect the rentability in units producing up to several hundred tons of finished product every year. This factor is the most important impule for the mentioned centralisation of tannery and shoemaking waste processing.

3.2.2. Coefficient of Evaluation

Illustrative data on the convenience of processing individual types of waste for accessible products were obtained by comparing the price ratios between raw materials and products in Czechoslovakia in the approximate following sequence[1]:

Waste	Product	Relative Price of Used Waste	Relative Price of 1 kg of Product	Coefficient: Product Price / Waste Price
Chrome tanned shavings + vegetable tanned clicking waste	Fibrous leather	0.03 0.06	11.15	124.2
Split glue stock	Photographic gelatine	1.41	70.00	49.8
Split glue stock	Edible gelatine	1.41	35.40	25.1
Chrome tanned clicking waste	Hydrolysate of glutin	0.42	3.90	9.3
Split glue stock Ia	Artificial casings (ø 50 mm)	8.57	52.50	6.1
Hand glue stock	Glue Ia	2.02	7.40	3.7
Machine glue stock	Hide fat	2.42	6.00	2.5
Vegetable tanned clicking waste	Used instead of coal	0.11	0.12	1.1

It is comprehensible that in other countries the sequence of coefficients will be another owing to other price dependences. However, in every case it is necessary to study the relations concerning the problems of utilizing tannery and shoemaking wastes.

3.3. Incidence of Waste Utilization in the National Economy

The given data explain the advantages of plant economy in waste processing because it is clear that every plant will process the wastes only in that case if it is effective for it either in the increased profit or in the savings on eventual charges for unsuitable methods of waste liquidation.

However, from wider respect, we must realize that in the future years the processing of wastes will be necessary also from the viewpoint of making the living conditions more healthy. Canalising the effluents into rivers, free putrefying or combustion of wastes will lead to ever increasing charges imposed by sanitary authorities for the contamination of rivers and air.

Last but not least effect from waste processing will have also the national economy, namely in the improved economy in proteins. The majority of countries, especially inland countries, is deficient in the economy with animal proteins and imports the hides and skins from abroad. In such cases it is impossible for the national economy to be satisfied with the utilisation of raw hides for the production of leather only in which they utilise only 40 to 20% of the imported raw material and the remainder is wasted without any profit.

To the economically important production of edible products from untanned tannery wastes they add in the last years also the possibility to feed lower-grade wastes after having developed suitable technologies of fodder preparation. In this evaluation of wastes the national economy has double profit: it fully utilizes the originally bought or produced protein, and moreover, it saves money for eliminating the increased import of digestible or feedable proteins.

L i t e r a t u r e :

1) Halámek, Červený: Zpracování kolagenního odpadu. (Processing of Collagen Waste.), Lecture at the International Conference on Tannery and Shoemaking Wastes, Gottwaldov, 1967, Czechoslovakia.

2) Pektor, Šmika: Bilance kožní hmoty při kožedělné výrobě. (Balance of Hide Substance in Leather and Shoe Production.), Lecture at the International Conference on Raw Hides, Gottwaldov, 1969, Czechoslovakia.

3) Bose et.al., according to Musil, Adam, Houba: Vysokomolekulární složky pojiva. (High-Molecular Components of the Binder.), Academia, Praha, 1966, p.80.

4) Henning A., Grühn K., Schwebe M.: Tierzucht 18, (1964), 2, 104.

5) Steigmann A.: Leder 11, (1960), 1, 12.

6) Halámek C.: Výroba krmiv z manipulačních usňových odpadů. (Production of Fodder from Leather Clicking Wastes.), Lecture at the International Conference on Raw Hides, Gottwaldov, 1969, Czechoslovakia.

7) Selle H.D.: Chem.Techn. 10, (1958), 12, 679.

8) Mládek M.: Technologia spracovania kožolužských odpadov. (Technology of Processing Tannery Wastes.), SVŠT, Bratislava, 1962.

9) Beneš A. and col.: Informátor kožedělného průmyslu. (Informative Data on Leather and Shoe Industry.), SNTL, Praha, 1970.

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CHAPTER II : PRODUCTION OF FIBROUS LEATHER FROM LEATHER WASTES

Production of Fibrous Leather from Leather Wastes

C O N T E N T S

1. Sources and Quantity of Leather Wastes

In shoemaking plants considerable quantity of leather wastes is produced both from sole leather and from upper leather. Wastes occur mainly in clicking out individual shoe parts, such as soles, insoles, etc. These parts have an irregular shape and therefore they cannot be clicked out of leather in such a way to eliminate the clicking waste. The leather itself has also an irregular, and therefore, in its marginal portions a considerable quantity of waste is produced. Though the shoe parts are clicked out with the greatest possible care, a considerable quantity of waste arises in the form of cuttings having various shape and size. For example, in the processing of sole leather approximately 29% of clicking waste is produced and in the processing of upper leather it is 14 to 16% of clicking waste(1, 2, 3).

Table I - Waste in the Processing of Leather

Type of Leather	Type of Waste	% of Processed Weight of Leather
Vegetable tanned	Sole clicking waste	29
	Upper clicking waste	14 - 16

Another considerable quantity of waste is produced in the production of leather, i.e. in tanneries. Mainly chrome tanned shavings from these wastes are imported for the production of fibrous leather. Owing to the fact that the raw hide is ununiformly thick, it is evened by splitting and after tanning it is evened by shaving. Thus, another waste is produced in the form of chrome tanned shavings. The quantity of chrome tanned shavings varies according to the type of leather. In the average we can consider approximately 10% (calculated in dry substance) of shavings waste from the dry weight of hide substance put in production(3).

Moreover, in tanneries a great number of other wastes is produced, such as hair, glue stock, etc. which are utilized in other branches of the industry, e.g. for the production of felt, glue, etc.

In the production of leather and footwear more than one half of raw hides is wasted[1, 2, 3] in the form of various wastes, and therefore, with respect to high prices of raw hides, which for many countries are the imported raw material, in the whole world an effort exists to process the raw hides as rentabil as possible.

Table II - Utilization of Hide Substance in Leather and Shoe Production

	The Used Raw Material in dkg		
	Sole Leather 100	For Russet Upper Leather 100	Calf Leather 100
Dry matter of hide substance in %	41	41	46
Soaked weight in dkg	115	115	115
Waste in processing the pelt in %	25	40	50
Pelt weight in dkg	86	69	59
Weight of the produced leather in dkg	64	37	21
Losses in clicking in %	25	16	14
Weight of leather used for footwear in dkg	48	31	18
Content of hide substance in %	48	35	66
Utilised dry matter in dkg of hide substance	23	11	12
% of utilizing the hide substance from the original raw hide	56	27	26

According to our opinion, one of the most effective methods of waste processing is to use them for the production of materials substituting genuine leather, i.e. for the production of fibrous leather, which can be used again for the production of footwear. This Chapter deals with this method, i.e. with using the wastes from vegetable tanned sole leather and chrome tanned shavings for the production of fibrous leather.

2. Processing of Leather Wastes to Fibrous Leather

2.1. Characteristics of Fibrous Leather

Under the term fibrous leather we mean fibrous sheet materials produced from defibred leather wastes and bound together by proper binders based on latices and aqueous dispersions of polymer substances. As a fibrous raw material we use the clicking waste from vegetable tanned sole leather, i.e. butts, shoulders, bellies, and at second, chrome tanned shavings. These fibrous raw materials are mutually combined in certain ratios.

Fibrous leather are not considered for inferior leather substitutes but for new shoemaking materials which are fully convenient for the given purpose and from certain standpoints they are even more convenient than natural leather because by proper composing the ingredients we can regulate the properties of the product and adjust the latter for the needed use. For example, counters should have a very good mouldability and shape retention, but the margin of counters should not be stiff in order not to rub the skin of the foot[4, 5].

Fibrous leather is used mainly for counters, midsoles, insoles for some types of footwear, and soles for house slippers.

Fibrous leather has been practically proven and its production in the worls has had always increasing trend. The production of finrous leather, compared with leather production and footwear production, is a young branch of the industry which is in a great development. The original nearly hand production was changed to discontinual method of production and in the latest time a continual method of production is being spread in the world using a high degree of automation.

2.2. Production of Fibrous Leather

The proper production can be divided in the following sections:

1. Defibring of leather wastes
2. Preparation of fibrous pulp
3. Dewatering and forming sheets
4. Pressing
5. Drying
6. Finishing

2.2.1. Defibring of Leather Wastes

The most usual and the most suitable raw material for the production of fibrous leather are clicking wastes from vegetable tanned sole leather and chrome tanned shavings. With both these basic raw materials it is necessary to carry out sorting and defibring.

Shoemaking wastes are sorted partly in the shoemaking plants where the care must be taken to store individual types of leather wastes separately, partly directly in the production of fibrous leather. The purpose of the second sorting is to remove the undesirable foreign substances which would be harmful in the technological process or which would deteriorate the appearance and quality of products. Mainly there are metal bodies and rubber.

Sole leather waste is usually sorted manually on a conveyor and metal bodies are removed by means of electromagnet.

Chrome tanned shavings can be sorted mechanically on various sorting means. For example, it is possible to mix them with water and let the heavier bodies sediment on cascade partition walls.

Well sorted fibrous raw material is a good pre-condition for obtaining first-grade fibrous leather.

Then, both mentioned raw materials must be defibred to be possible to bind the fibres and form homogenous sheets of certain size in the following stages of the production. Defibring of chrome tanned shavings, which are in wet condition (they have approx. 35% of dry substance) and have small dimensions, is quite easy. Defibring of stiff sole leather waste is more difficult and the most difficult is the defibring of the clicking wastes of upper leather which has not yet been solved to a full satisfaction. Therefore, this type of waste is used for the production of fibrous leather only in a small extent. In our country the waste from upper leather is used for the production of proteinous fodder.

The defibring of leather wastes is difficult because the organisation of fibres in leather is very complicated. According to Prof. Kubelka[6] the fibres in leather are inter-woven in a perfectly closed unit and unless we artificially destroy the continuity of this unit, we cannot find a free end of any fibre.

Fibres are led in the most different directions through the whole thickness of leather, they are thinned up to fine fibrils which are situated in the grain side and from it they again return back towards the flesh side and increase in their thickness. The more diverse is the course of fibres, the more perfect is their labyrinth and the higher is the strength of leather, but on the other hand, the more difficult is also the defibring of leather.

Defibring is carried out in various milling machines either in dry or in wet condition. For defibring in dry condition they use various types of hammer, cross or disc mills. The disadvantage of defibring (milling) in dry condition is relatively intensive heating of the milled material, and further, the fact that the obtained fibrous material contains a considerable amount of undefibred pieces and dust. From these reasons the other method of defibring in wet condition has become considerably spread. It means that the defibring is carried out under continuous inflow of water into the milling equipment, or it is done directly in aqueous suspension of fibres in a hollander, i.e. the milling equipment used in the paper industry, but properly modified for this purpose.

For the method of defibring in wet condition several types of mills have been developed. In the last years the use of CONDUX mills has become very spread (Fig. 1). There are mills with horizontally positioned milling discs. The discs are provided with teeth the size of which gradually descreases in the direction from the centre of the disc to its edge. The upper and lower jaws engage one to the other and the fineness of milling depends on the mutual approaching of these jaws[7]. Three-stage milling is used. In the first stage the waste pieces are made smaller in the mill provided with coarse toothing or on a rotary knife cutter (it is done in dry condition). In the second stage the proper defibring is carried out in wet condition in a mill provided with metal discs having fine toothing. In the third stage the defibring is finished in a mill provided with stone discs. Usually the individual mills form a line which can have various arrangement according to the capacity of production. The milling line produces aqueous fibrous suspension with the concentration of about 2 to 4%.

For defibring of chrome tanned shavings usually machines of the paper hollander type are used (Fig. 3) in which the aqueous suspension of shavings circulates in a tub provided with the milling equipment the main part of which is a milling roller provided with milling blades, and an insertion provided with milling blades which is located under the roller.

It is also possible to carry out the defibring of chrome tanned shavings in the CONDUX mill provided with fine toothing, or in other machines having similar effect. Both types of machines can be also combined.

2.2.2. Preparation of Fibrous Pulp

The defibred wastes in the form of aqueous fibrous suspension are transferred into the storage tub provided with a proper stirring means. Walls of tubs are covered with a smooth ceramic material or they are provided with a smooth protective coating. Important is the method of stirring which must be of a sufficient intensity throughout the whole space of the tank in order to produce a homogenous fibre suspension and to prevent sedimentation or flotation of the fibrous material. It is necessary because in these tubs various adjustments of the fibrous material are carried out and the tubs are used as the storage and homogenizing spaces.

In the following production process various adjustments of the fibrous material are carried out according to the need, such as the adjustment of concentration, adjustment of pH value, greasing, glueing, dyeing. The purpose of greasing is to obtain more supple and more flexible product. Similar greasing agents are used in this operation like in the production of leather. There are the compounds of sulphated animal and vegetable fats and oils.

The purpose of glueing is to give the fibrous leather, in cases where it is required, lower absorption capacity, lower plumpness and an improved area stability in wet medium. Further, this process also improves the smoothness of cut edges. For glueing various hydrophobic agents are used. These agents are transformed to tthe condition of water dispersion by means of chemical emulsifiers and emulsifying means.

In order to get the needed shade of the fibrous leather, some types of leather are dyed.

Another, and one of the most important operations, is binding. The pure fibrous material after felting would not give a high-grade product. Therefore, it is necessary to perform the so-called binding. To a certain extent the binder must replace the perfect and purposeful interweaving of fibres in the genuine leather. Besides binding the fibres, the binder has still another purpose, i.e. it acts also as hydrophobic agent.

In the production of fibrous leather we can use various elastomer or plastomer agents as a binder, but with respect to the production system of agglomeration in wet condition it is necessary that also the type of this agent would be in the form of aqueous dispersion[8].

The choice of binder type is very important from the viewpoint of the suitability of products for the intended purpose of use, further from the viewpoint of mixing the fibrous base from individual types of leather wastes (vegetable tanned wastes, chrome tanned shavings - their mutual ratio). Also the price of the binder plays an important role.

From elastomer materials there are for example copolymers of butadiene with styrene, acrylonitrile, polychloroprene, etc.

From plastomer materials it is for example plasticised polyvinyl acetate. Natural latex is an often used binder both from economic reasons and also with respect to a good binding effect.

Nearly every from the used binders requires various admixtures with respect to its feature. For example, in order to obtain a good course of binding, some binders use special stabilisers, i.e. precipitation regulators[9]. These agents prevent the occurence of undesirable block coagulation of binders after the coagulating agent has been added, but on the other hand they enable its fine precipitation and distribution of the particles in the fibrous material what will result in a uniform binding of fibres and obtaining a compact and flexible product. A correct choice of the kind, amount and method of application depends on the kind of binder and on the composition of the fibrous material.

In some kinds of binders it is necessary to use various vulcanising admixtures and agents preventing ageing.

From binders and admixtures a latex is prepared which is then applied into the fibrous suspension in tanks for the purpose of binding. The tube should be provided with smooth walls and with an equipment for effective but slight stirring.

The precipitation of the binder on to the fibre is performed by various coagulating agents, e.g. by aluminium sulphate[4, 9]

In the precipitating process the emulsion form of the binding ingredient is destroyed by the influence of coagulating agent solution,and flocculation of solid binder on to the fiber occurs. At the same time pH value of the fibrous compound falls to the acidic range.

The process of precipitation is one of the most important technological operations which, to some extent, is decisive for the quality of the final product.

2.2.3. Dewatering and Forming Sheets

After the fibres are bound, it is necessary to form sheets from the fibrous material in the desired size and thickness. This is done during the so-called dewatering the purpose of which is partly to remove the dispersing water, partly to form a continuous layer of fibrous material under certain felting the fibres, what is very important for obtaining good mechanical and physical properties of the final product. The course and method of dewatering process influence the location of felted fibres in the fibrous material, and thus, to a considerable extent they influence the properties of the product. Here, the basic principle is that dewatering should be slight, at least in the first stage. However, there are also other factors which must be considered, such as the productivity of labour and the connected economic results what is more or less contradictory and it is necessary to compromise between them.

For dewatering the fibrous material it is possible to use several types of dewatering equipment(10, 11, 12, 13, 14):

1) Dewatering presses
2) Vacuum suction tables
3) Continual dewatering machines with flat sieve
4) Dewatering centrifuges
5) Dewatering machines with cylindrical sieve

Each from the given dewatering systems has its advantages and drawback both with respect to the properties of the produced material and its use, and with respect to the cost value. There is also a difference as to the productivity of labour. For example, as the cost value is concerned, the suction tables are the cheapest equipment and the continual dewatering machines are the most expensive equipment. However, in case of labour productivity the situation is contrary.

The method of dewatering influences also the quality because it influences the deposition of individual fibres in dewatering. In the continuous machines mostly one-direction depositiong of fibres occurs which coincides with the direction of machine run and the material has different strength and flexibility in the longitudinal and transverse directions. It is convenient if the production plant is equipped with several dewatering systems because then it is possible better to meet the requirements for a wider assortment of the produced materials, both from the viewpoint of thickness and also from the viewpoint of quality of these materials and the purpose of use.

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2 OF 3

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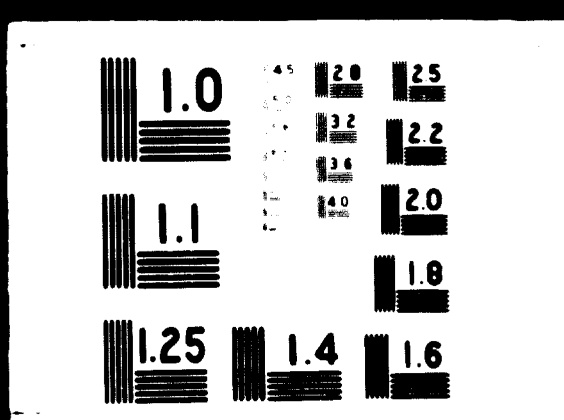

2.2.3.1. Dewatering Presses

Dewatering presses (Fig. 5) belong to the discontinual dewatering machines. Dewatering process is speeded up by pressure. The fibrous material, positioned in a pressure carriage with movable perforated bottom provided with a sieve, is gradually pressed, and thus, it is dewatered. This method can be combined with the suction process.

2.2.3.2. Vacuum Suction Tables

Vacuum suction tables (Fig. 7) belong also to the discontinual dewatering equipment. Dewatering process is speeded up by vacuum action. It is the simplest dewatering equipment with low demands for investment and maintenance. In fact, it is a suction filter of rectangular shape connected with a pump.

2.2.3.3. Continual Dewatering Machines with Flat Sieve

The continual dewatering machine (Fig. 8) enables to produce the material in a flow line which combines all operations beginning from the dewatering process up to the drying. The equipment is similar to through-feed paper machine. The fibrous compound is poured on to a movable flat sieve on which it is gradually dewatered, first spontaneously under the influence of gravity and then by vacuum action. Then, the material is pressed and dried in the through-feed method. The advantage of these machines is in a high productivity of labour, uniform thickness and the possibility to produce thin sheets which can be used,for example, to socks or in the production of fancy goods. As it was mentioned, the disadvantage is in a high cost value and in a difficult maintenance.

2.2.3.4. Dewatering Centrifuges

Centrifuges (Fig. 2) belong to discontinually working dewatering machines and the dewatering process is speeded up by centrifugal force. Centrifugal drums are used with horisontally positioned axis. The productivity of labour of these dewatering machines is approximately the same as that of dewatering presses, i.e. it is higher when compared with suction tables and lower when compared with continual working machines. The advantage is in a relatively good uniformity of the thickness, the disadvantage is in a worse appearance and quality. This dewatering method is relatively little used.

2.2.3.5. Dewatering Machines with Cylindrical Sieve (Fig. 4)

This machine is used for the production of cardboard from wood fibres. It is also used for the production of fibrous leatherboard from the combination of wood and leather binres. It is rarely used for the production of fibrous leather. Dewatering is performed on the cylindrical sieve from which the continuously formed thin layer is picked up by a felt and is transferred to a metal forming cylinder on which one layer after another are gradually wound up to reaching the needed thickness of material. Thus, in this case, the produced material is laminated what is a disadvantage because there is a greater risk of delamination of the finished product.

2.2.4. Pressing

The dewatered sheets from discontinual dewatering machines contain about 60 to 80% of water, therefore, their pressing is carried out the purpose of which is to remove further proportion of water and to compact the obtained sheets. The pressing is carried out in sets by approximately 100 pieces. In placing the sheets they are separated by filtration inserts which enable the removal of water released by pressing. The whole set is pressed in a hydraulic press (Fig. 6). Pressing in continual pressure machines has the same purpose. It is carried out in through-feed presses which are usually combined in several pieces in a line what prevents the severe pressing out of water, and thus, also eventual destruction of the material structure. By pressing, the content of water is reduced to about 50%. The remainder of water is removed by drying.

2.2.5. Drying

Drying can be carried out in various driers in which the sheets of fibrous leather are positioned either horizontally or they are hung in vertical position. Horizontal position of sheets is usual in the case of single or multi-stage driers. Method of drying and its course have an influence on the quality of the finished product, but also on the appearance and flat surfaces of sheets. The regime of drying depends on the composition of the fibrous leather. In the fibrous leather based mostly on vegetable tanned fibrous material it is necessary to choose slower drying than in the fibrous leather with a higher content of chrome tanned leather fibres.

Drying in continual machines is similar to the drying of paper or cardboard. With respect to the used raw materials, i.e. leather fibre, this drying must proceed at lower temperatures and at correct relative humidity in order not to destroy the fibrous structure of the product. The disadvantage of this drying method is a high investment cost. The advantage is in the productivity of labour and in the possibility to supply the finished products in sheets or in longer rolls.

2.2.6. Finishing

The purpose of finishing is to improve the appearance, to make the surface flat and smooth, and partially, to even the thickness. It consists mainly of smoothing or calendering the sheets. Further, the sheets can be buffed. Another possibility of finishing is dyeing by pigments. It is carried out in the similar way as in leathers. It is an advantage that the material has exact standard shapes. After trimming the edges, the sheets of the fibrous leather are sorted according to thickness and quality and are piled for storing.

3. Use of Fibrous Leather

Fibrous leathers are used mainly in the shoe industry. At the present time they are not considered to be substitutes used as emergency materials, but there are new shoemaking materials without which the shoemaking production would hardly do. In fact, these products do not reach in all respects the mechanical, physical and hygienical values of genuine leather, but on the other hand they have some properties which are more convenient, such as volume weight, flexibility, elasticity, content of extractible matters, shaping ability. A great advantage for the shoe industry is also the fact that the sheets are produced in regular shapes what enables to reach a greater productivity of labour in the shoemaking production in clicking out shoe parts. A greater use in fibrous leather was also caused by new developments in the shoe production, e.g. the fact that tack or staple lasting has been replaced by cement lasting. As the processability is concerned, in the majority of cases the fibrous leather can be processed by identical methods as genuine leather. A favourable point is that the fibrous leather is a product which contains a major proportion of leather fibrous material.

A great proportion of fibrous leather is used for counters. They are suitable practically for all types of shoes because they meet the basic demand on this part, i.e. a good shape retention of the shoe and its elasticity which occurs mainly on counter margins and contributes to comfortable wear.

The possibility of using fibrous leather for the production of insoles is not so wide as in the case of counters. It is used only in some types of footwear, mainly in open designs. In the last time the insoles are very often produced from cellulose insole materials which are lighter and more suitable from the hygienical viewpoint and appearance.

Further, the fibrous leather is used for midsoles, rands and sole pieces. It is also used for some types of house slippers. For standard footwear it is not used because the material has not the needed resistance to wet rubbing.

Thin types of fibrous leather are used in the fancy goods industry.

4. Physical and Mechanical Properties of Fibrous Leather

For evaluation of quality the fibrous leather are subjected to laboratory tests in which the physical and mechanical properties are determined which are important for their use in the production and wear of footwear. For every purpose of use a little other properties are needed. In standard inspection for example the following properties are determined: thickness, volume weight, tensile strength in dry and wet conditions, elongation in dry condition, stitch tear strength, number of double flexures (resistance to repeated flexure), absorptivity, swelling ability, area increase under the influence of water, water vapour permeability, artificial ageing at higher temperatures. Of course, all mentioned determinations are not carried out in all types of fibrous leather but they are chosen according to the purpose of use.

5. Economic Viewpoint of the Utilization of Leather Wastes for Fibrous Leather

Shoemaking wastes from vegetable tanned leather and chrome tanned shavings wasted in the tannery had no economical use in the last time. Combusting leather wastes was an emergency solution and economically it was not advantageous. Processing these wastes for fibrous leather which can be used in the shoemaking industry for the purpose for which previously genuine leather had to be used means their maximum economical evaluation. It is supported by the fact that in countries which have introduced this production a deficiency of these wastes exists instead of the previous excess.

Their processing for the fibrous leather has enlarged the material base for the production of footwear what is another economical effect because the production of footwear, with respect to over increasing population and increasing consumption of footwear per capita, is economically very interesting and its increasing trend is quite necessary. Even from this viewpoint the processing of leather wastes for the fibrous leather is their best evaluation.

Literature

1. Cyril Halámek, Michael Radil, Jaroslav Lačňák: K otázce zpracování odpadu kožedělného průmyslu. (To the Problem of Processing the Tannery and Shoemaking Wastes.), Kožařství VII, No.10, p.275-278.
2. Claude H.Spiers: Economics of Leather Wastage, The Leather Trade Review 1955, 117, 3516, 135-137.
3. Vladimír Červený, Josef Nádvorník: Ekonomická studie. (Economic Study.), SVÚK, Gottwaldov.
4. A.S.Barkan, L.J.Kostrjukova: Primenenije koževěnnogo volokna v proizvodstve obuvnych kartonov. (Utilising the Hide Fibre in the Production of Shoemaking Cardboards.), Gizlegprom, Moskva.
5. Arthur Jameson: The Advantage of Fibre Counters, American Shoemaking, 1959, 251, 7, 88.
6. Václav Kubelka: Kolagenové vazivo v kůži. (Collagen Bonds in Hide.), Vydavatelstvo slovenskej akademie vied, Bratislava, 1961.
7. Milan Mládek: Technológia spracovania koželužských odpadov. (Technology of Processing Tannery Wastes.), SVŠT, Bratislava.
8. Adolf Suchomel, Miroslav Mazánek: Suroviny potřebné pro výrobu umělé vláknité kůže na kodeřve pro domácí obuv. (Raw Materials Needed for the Production of Artificial Fibrous Leather for Soles of House Slippers.), Kožařství VI, No.11, p.193-194.
9. K.Craemer: Kunstleder, seine Herstellung und Eigenschaften. (Artificial Leather, its Production and Properties.), Grasmann: Handb.r.Gerbereich.u.Lederf., B.III, 2.T., 639-766.
10. Ľuboslav Hasner: Výměnné hmoty za usně. (Leather Substitutes.), Technická hlídka koželužská, 1944.

11. I.I.Tugov: Technologija zaměnitělej koži i techničeskich tkaněj. (Technology of Leather Substitutes and Technical Fabrics.), Gizlegprom, Moskva.
12. R.Pielka: Stuczna skora z odpadkow skor jako polnowartościowy surowiec. (Fibrous Leather from Leather Wastes as a Full Valuable Material.), Przemysl skórzany, 1960, 15, 3, 62-64.
13. Anonym: Expansion in Leather Board Production, Foowear 1958, II/89.
14. M.Souček: Exkurse do papírny. (Excursion in Paper Producing Plant.), SNTL, Praha.

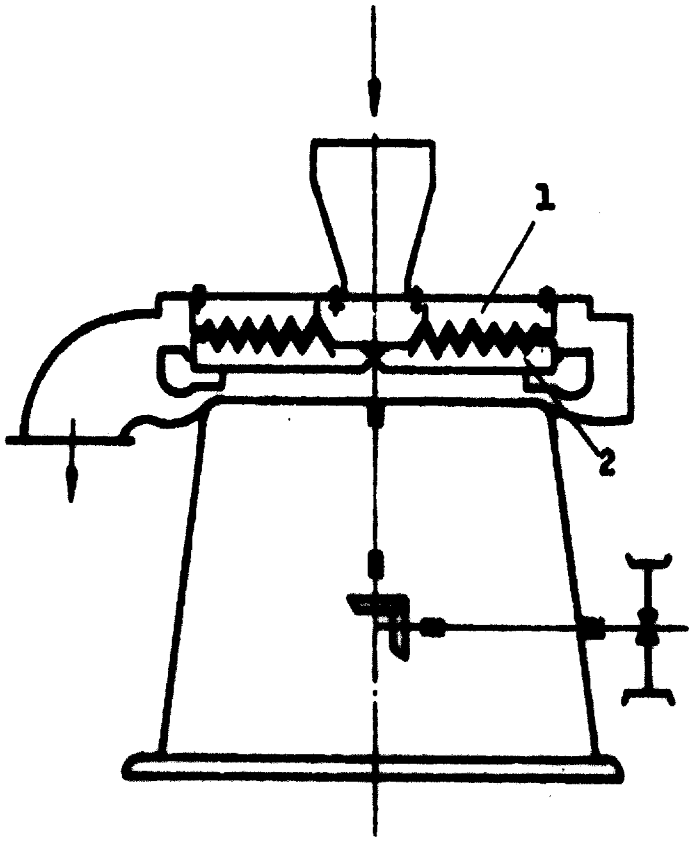

Fig. 1 : Chart of CONDUX Mill

1. Upper milling disc
2. Lower milling disc

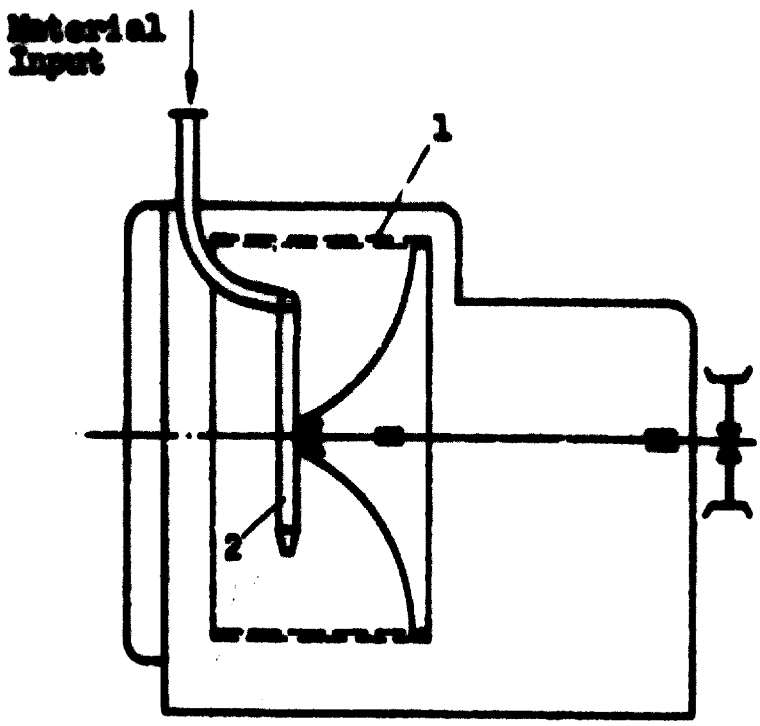

Fig. 2 : Chart of Dewatering Centrifuge

1. Centrifugal drum
2. Dosing means

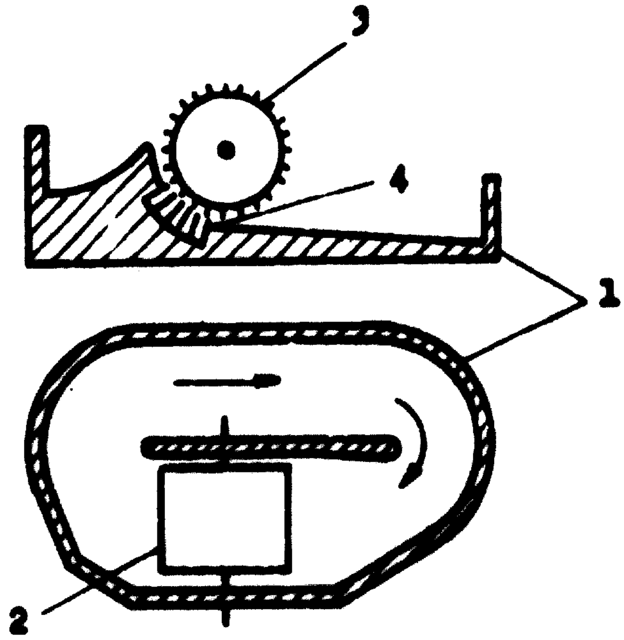

Fig. 3 : Chart of Hollander

1. Tub 2. Milling roller
3. Blades 4. Lower blades

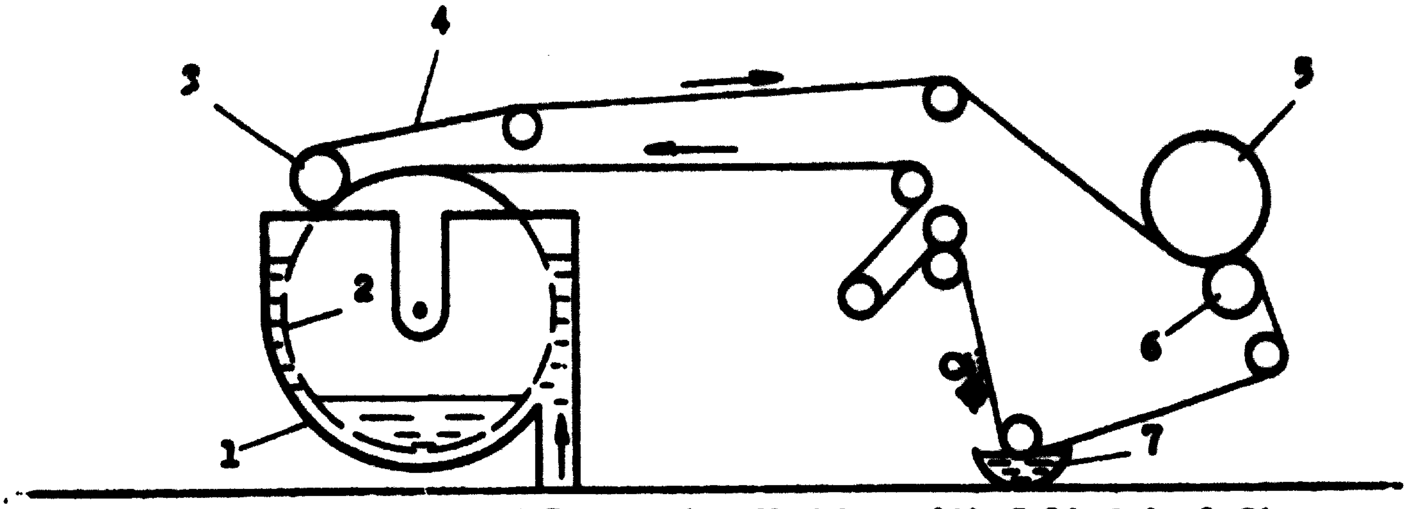

Fig. 4 : Chart of Dewatering Machine with Cylindrical Sieve

1. Inlet tub 2. Cylindrical sieve 3. Squeezing roller
4. Felt 5. Sizing roller 6. Lower pressure roller
7. Felt washer

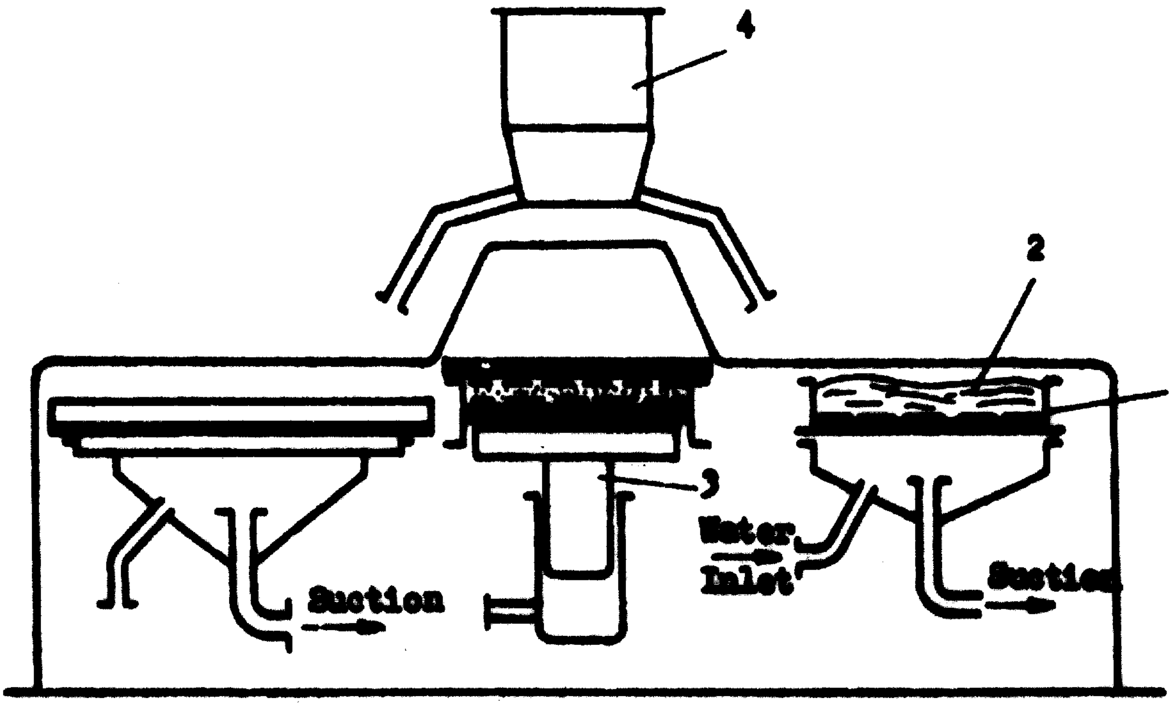

Fig. 5 : Chart of Dewatering Press

1. Pre-dewatering carriage 2. Fibrous leathers
3. Piston of the press 4. Measuring tank

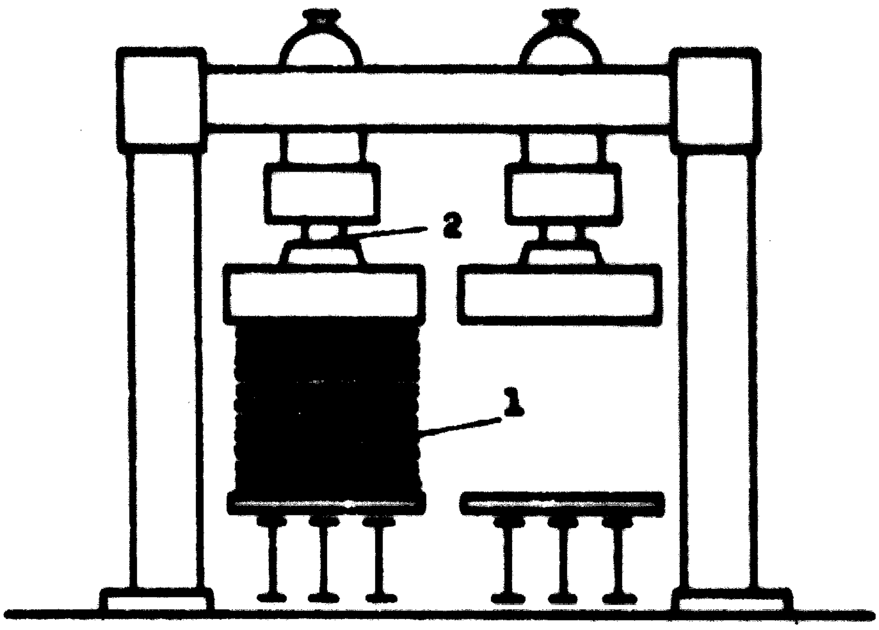

Fig. 6 : Chart of Hydraulic Press for Re-Pressing Sheets

1. Sheets with filtration inserts
2. Piston of the press

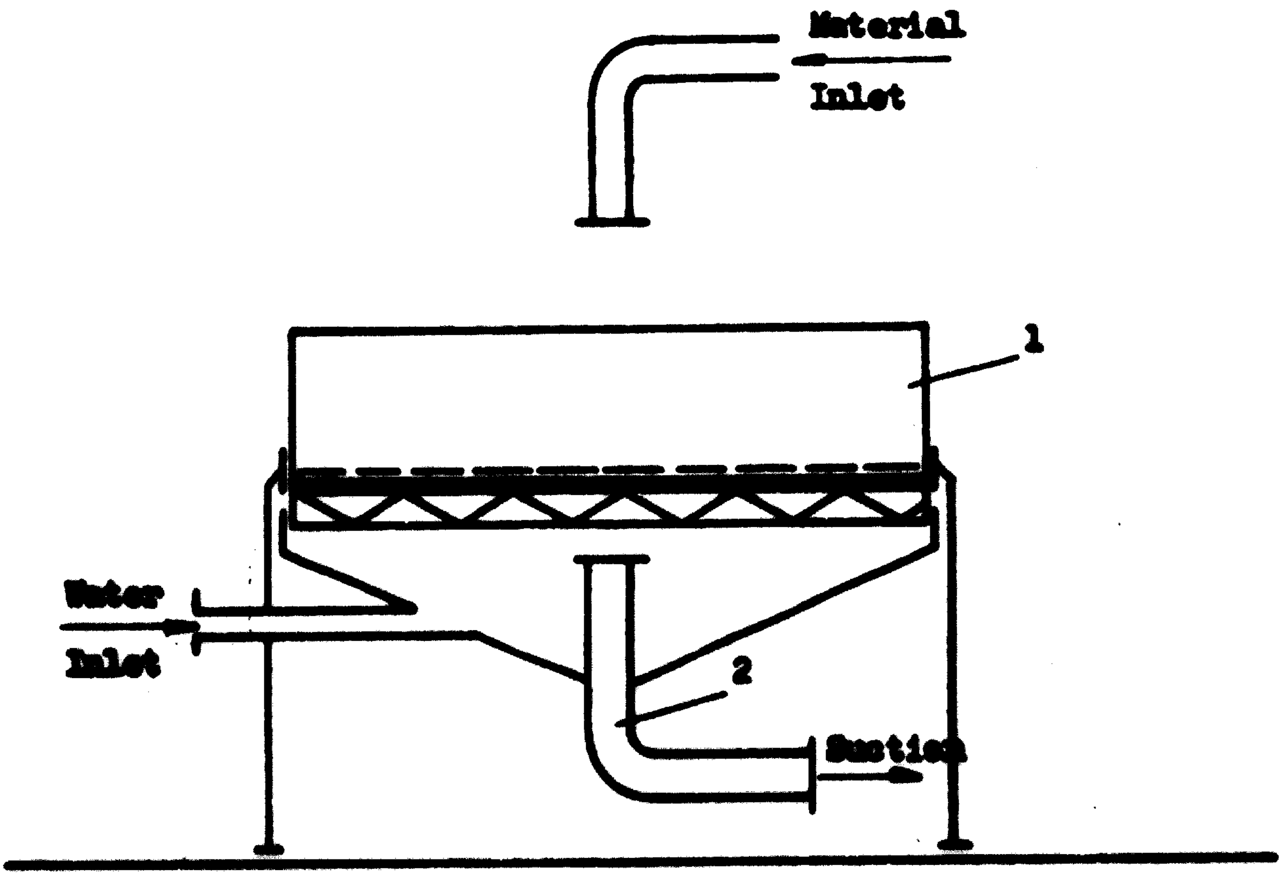

Fig. 7 : Chart of Suction Table

1. Suction filter
2. Branch line to the pump

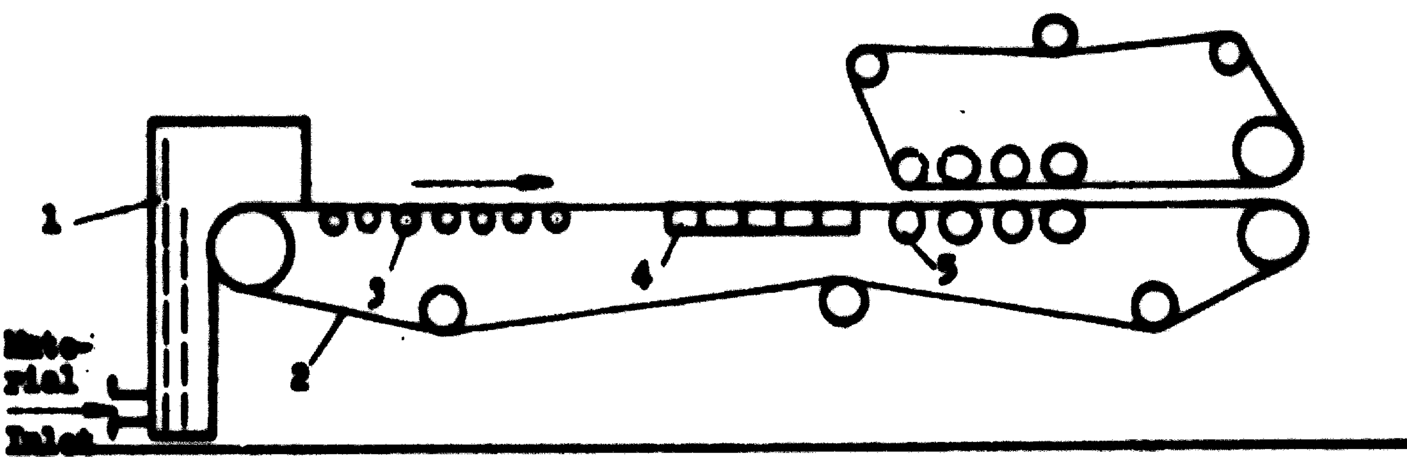

Fig. 8 : Chart of Continual Dewatering Machine

1. Input box 2. Sieve 3. Register rollers
4. Suction boxes 5. Squeezing presses

NATIONAL RESEARCH INSTITUTE FOR SHOE,

LEATHER AND ALLIED INDUSTRIES GOTTWALDOV - CSSR

Ing. Vladimír PEKTOR :

CHAPTER III : USING THE TANNERY WASTES FOR THE PRODUCTION OF SEMI-SYNTHETIC POROMERIC UPPER LEATHER

Using the Tannery Wastes for the Production of Semi-Synthetic Poromeric Upper Leather

CONTENTS

1. Introduction

Perspective development of raw material basis for leather industry does not meet the needs of production of final articles, especially the needs of shoemaking industry. According to the statistical report by United States Department of Agriculture, Foreign Agricultural Service, 1967, the herd in the world amounted 1,140 million pieces. Production of raw hides in the countries which are the members of the world commercial organisation "International Hide and Skin Sellers Association (EEC and EFTA countries, Europe, Greece, Ireland, Spain, USA, Argentine, Uruquay, Australia, New Zealand, South Africa) amounted in 1967 475,900 tons of cattle hides and 100,800 tons of calf skins in Europe, 806,400 tons of cattle hides and 27,000 tons of calf skins in the USA, 79,300 tons of cattle hides and 5,000 tons of calf skins in Canada. For the production of leather they consumed in 1967 739,700 tons of cattle hides and 126,800 tons of calf skins in Europe, 564,000 tons of cattle hides and 29,700 tons of calf skins in the USA, and 59,500 tons of cattle hides and 2,500 tons of calf skins in Canada.

From this data it is obvious that, especially in Europe, there is a deficiency in raw hides at the present time. The deficit in the consumption of raw hides is covered by imports from non-European countries. New development of leather industry in developing countries and increasing the production of leather in developed countries will, of course, result in a deficiency in raw hide deliveries.

Production of footwear after the World War period has considerably spread both in developed countries and especially in developing countries. At the present time the production of footwear amounts in the average 0.8 pairs per capita in the world, what represents about 2,646.5 million pairs of shoes. At the same time the consumtion of leather in relation to one pair of footwear descreases. For example in 1950 the consumption of leather to 1 pair of shoes was 1.50 kg of hide green weight, in 1965 it was only 1.19 kg. According to the statistics of United Nations Organisation the consumption will further decrease, namely to 1.02 kg in 1975 and 0.96 kg in 1980. The prognosis of the development supposes the consumption 0.76 kg in 2000 only.

During this period a considerable increase in the total footwear production is expected, namely 3,800 million pairs in 1975, 4,429 million pairs in 1980 and 8,400 million pairs in 2000.

According to the mentioned perspective of the development of footwear production, the computers have said that in 1983 the demands for genuine leather will be able to be covered only to about two thirds.

The deficiency in the basic material for footwear production is solved in individual countries by the development of new substituting materials. At the present time the majority of shoe bottom materials is substituted by non-leather materials. According to the statistics, the proportion of non-leather soles in the USA was 73% in 1963, in Germany it was 71.2% in 1962 and in Czechoslovakia it was 66% in 1965. It can be supposed that this proportion will increase to about 80% to 85% in the near future. There is a certain delay in substituting shoe upper parts. The proportion in 1963 was 18.9% in the USA and only 5.5% in Czechoslovakia.

From this numerical data it follows that the main development of substituting materials will be performed in upper leathers. In this respect we can see that in the last time a considerable progress has been made. In order to illustrate this development I want to mention the main characteristics of the most important types of the produced synthetic shoe upper materials.

In September 1962 the E.I. du Pont de Nemours Inc. introduced a term "POROMERICS" for synthetic upper materials which should express the breathability of synthetic upper materials.

The Shoe and Allied Trades Research Association (SATRA) defines the poromeric material as follows:
"Artificial shoemaking upper material comparable with its feature, apparance and water permeability with natural leather".

According the the Czechoslovak experience the definition of poromerics should be supplemented in that the name "poromerics" should characterize the shoemaking, fancy, garment, upholstery and other sheet materials having above all the following features:

a) Laminated structure resembling the basic layers of leather (corium, grain layer, finished layer).
b) The basic laydr is formed by non-adjusted, highly interwoven volume net of fibres mutually bound by various adhesive systems.
c) Microporous structure of bearing as well as grain layers must enable the transport of water and water vapours above all in the direction flesh-grain, and at the same time, it must meet the defined requirements for hygiene and comfort of wearing or use.
d) Physical and mechanical parameters of porometic materials, values of static and dynamic tests, as well as their changes due to ageing and wearing must meet the requirements of the use and processing and some basic values must be near the values of natural leather. Also the appearance, feel and character of the grain side should correspond with various types of equivalent leather.

From the standpoint of basic materials and methods of production the poromerics can be divided into synthetic and semi-synthetic materials. Synthetic poromerics contain exclusively synthetic fibres. The needed properties of the final product are obtained by a proper choice of synthetic fibres, by a proper type of polymer for binding and formation of the grain layer, together with a proper technology in the final product.

On the other hand semi-synthetic porometics are characterized by a certain content of natural fibres, especially collagenous fibres, which favourably influence the needed properties, so that the choice of polymers and the proper technology have not a decisive influence on the important properties of the poromeric material.

Both groups of poromerics can be further divided into multi-layer bound materials and into single-layer ones.

The most known multi-layer materials with polyurethane grain layer are:

AZTRAN	manufacturer :	B.F.Goodrich, USA
BAREX	"	Research Institute of Rubber and Plastics Technology, Gottwaldov, Czechoslovakia
COLATEN	"	National Research Institute for Shoe, Leather and Allied Industries, Gottwaldov, Czechoslovakia
CORFAM	"	E.I. du Pont de Nemours Co., Inc.USA
CLARINO	"	Kurashiki Rayon Co., Japan
HI-TELAC	"	Toray Industries, Japan
JENTRA - 3	"	Genner Corporation (Tenneco Co.),USA
PATORA	"	Toyo Rubber Co., Ltd., Japan
SKAILEN	"	K.Hornschuh A.G., Germany
XYLEE	"	Sterebound, Glanzstoff Co.,Germany

The most known single-layer materials are:

CLARINO (various types)	"	Kurashiki Rayon Co., Japan
PORVAIR	"	Porvair, Ltd., Kingslyon, England

2. Tannery and Shoemaking Wastes

The characteristic feature of leather and shoe production is a considerable occurence of wastes. These wastes occur both in the production of leather and in the production of footwear.

2.1. Wastes from Leather Production

According to the histological structure of raw hide and the technology of leather production it can be considered that in converting the hide into leather a great amount of wastes is produced. Consequently, the amount ant type of wastes can considerably affect the rentability of leather production. Therefore, such technological principles are used with which it is possible to reduce the occurence of wastes and to a maximum extent to utilise the wastes for further leather production.

In leather production the wastes are produced in machine processing of hides and skins and in trimming the margins of hides. Before being processed, the raw hide is cleaned from all undesirable portion which would make troubles in machine processing and do not guarantee that the leather would be handled well. The produced wastes is commonly called trimmings.

After machine unhairing we get hair. Its quantity and quality depend on the process of chemical or microbial unhairing.

By machine fleshing the machine glue stock is produced. According to the condition of leather in fleshing the machine glue stock can be obtained from fresh or unlimed soaked cured hide, or from limed hide.

In hand trimming of edges and hand re-fleshing of the fleshed pelt the hand glue stock is produced.

Split glue stock is produced after splitting the hide in the pelt condition. It is formed by the flesh side of the hide which is not suitable for further processing to leather. The above mentioned wastes belong to the group of untanned wastes.

If splitting is done after tanning and if the split cannot be used for leather, we obtain the tanned split wastes.

Further, in machine processing the dried leather, e.g. after staking, the trimmings are obtained if the edges of leather are trimmed. These wastes belong to the group of tanned wastes.

2.1.1. Commercial Values of Wastes

Individual wastes in the tannery are checked by weighing. From the results obtained we cannot compile the balance of hide substance utilization because the condition of individual wastes is not identical from the viewpoint of dry matter. Therefore, the balance of wastes can be made by converting the results either to absolute dry matter or to pure N. When expressing the results in dry matter they are affected by the content of anorganic matters and auxiliary agents used in curing and chemical processing of the hide. These agents remain in the hide and increase the dry matter. By converting the results to pure N we can relatively easily ascertain the balance of utilising the proteinous matter.

In the balance of proteinous material loss it is further necessary to include the loss occuring in chemical treatment of hides during the production of leather.

The loss in wastes of upper cattle hide expressed in dry matter of N is given in the Table No. 1.

Table No. 2 shows the loss during chemical treatment of upper cattle hide, i.e. in the determination of non-returnable losses.

On the basis of ascertained values of losses of N, it is possible to calculate the balance of N in the processing of upper cattle hide. This balance is given in the Table No. 3.

From the results of the Table No. 3 we can compile the final balance of N in the processing of upper cattle hide. This balance is the following:

Machine glue stock	2.7 %
Hand glue stock	1.4 %
Split glue stock	6.8 %
Shavings	5.5 %
Soaking - liming	6.6 %
Deliming - bating	21.4 %
Tanning - pre-finishing	7.8 %
Tannery split	13.0 %
Leather	23.4 %

The balance of proteinous material in leather production can be divided into five items. Above all, it is hide substance contained in the final product - in leather. It makes only about one third of original proteinous material of the hide. To this item we can add 13 % proportion of proteinous material of split leather (in upper cattle hide). Thus, the percentage of proteinous material in leather increases to 44.1 %.

Another very important item of the balance are non-returnable wastes in chemical treatment of the hide. There are non-fibrous proportions of proteinous material which are soluble in water are modified by a chemical process of leather production to such an extent that they can be washed out by water. They come to waste liquors and then they come to tannery effluents. Therefore, there are non-returnable wastes. Their proportion is relatively high and is approximately as high as hide substance in leather.

Wastes from leather production which can be industrially utilisable are another balance item. There are returnable wastes. From them the most important are split glue stock and shavings produced from upper cattle hides.

Finally, the balance contains the item designated as other wastes. It was calculated from the difference of the total of registered items from 100. For example, there are torn off pieces, cuttings, other wastes occured in the processing of pelt and leather, etc. Their proportion is low and varies around 4 %.

From the total recapitulation of balance items it clearly follows that the utilizability of proteinous material of the hide in the final product is very low and varies in area-measured leather around 25 %. The increase of this proportion can be reached by the following provisions:

1) Reducing the returnable wastes and their transferring into leather.
2) Proper choice of the technological process in leather production with respect to the increasing of area or weight yield.
3) Trimming the hide pattern in order to increase the utilisability in the production of leather goods and in order to reduce t' clicking waste.

The transfer of returnable wastes into leather is above all possible in case of shavings. The decrease of shavings by 1 kg represents the increase in area by 45 dm^2. An exact splitting with respect to the thickness is a pre-condition of such a process. It depends on the type of splitting machine, on the condition and pattern of the hide. Practical experience shows that it is quite real to reduce the shavings by about 30 %. Another reduction of returnable waste can be obtained by the introduction of more perfect processing of raw hides. In this respect a great experience was gained in the USA. The processing of hides consists in the fleshing and trimming the edges. By fleshing the weight of cattle hides is reduced in the average by 16 % and by trimming edges by 4 %. Practically it means that from the balance in the item of returnable wastes the machine glue stock is eliminated and the occurence of hand glue stock is considerably limited. Then, it is obvious that the percentage of proteinous material in leather increases.

Compared with the price of raw hide (cattle hides) with respect to the occurence of individual wastes, their value is the following (value of the waste is expressed in % of the value of raw hides):

Raw cattle hide	100 %
Hair	0.51 %
Machine glue stock	0.13 %
Hand glue stock	0.05 %
Split glue stock	0.39 %
Shavings	0.08 %

From this respect the hair and split glue stock is the most valuable material.

Another viewpoint for economical comparison of wastes are the prices of final products. In comparison to the proce of the finished leather - full grain box side - considering the yields from 1.0 kg of green weight in leather and in wastes and considering the yields of final products from wastes, the comparison is the following:

Full grain side box	100 %
Machine glue stock for common glue	8.0 %
Hand glue stock for technical galatine	4.0 %
Shavings for common glue	3.4 %
Shavings for fibrous leather	8.2 %

From this viewpoint the processing of shavings for fibrous leather is the most effective utilisation.

However, it is necessary to note that in no case the waste is used for a product the qualitative features and utilisability of which will approach or equal natural leather.

It is also possible to compare individual wastes in such a sense that the waste is evaluated with respect to its basic price and how many times this proce is evaluated in the final product. For a better comparison we give also the values of natural box sides:

Box side	1.4 times
Machine glue stock for common glue	3.0 times
Hand glue stock for technical gelatine	11.4 times
Shavings for hide glue	6.7 times
Shavings for fibrous leather	163.6 times
Split glue stock for Colaten	1,115.0 times

From this it clearly follows that the most economic evaluation of tannery wastes is if they are converted to sheet materials, especially, if these materials possess great values of utilisability and if their properties approach the properties of genuine leather. It is for example semi-synthetic collagen leather Colaten.

2.1.2. Qualitative Features

Glue Stock

According to the raw material from which it was obtained, the glue stock is divided in the following way:

a) from cattle hides
b) from calf skins and grassers' skins
c) from horse hides
d) from sheepskins, goat skins, dog skins and buck skins
e) from pigskins

According to the method of processing hides we know the following types of glue stock:

a) hand flesh, i.e. small trimmings produced in hand fleshing of hides and pelts
b) machine flesh from first fleshing obtained in machine fleshing of hides with hair
c) machine flesh from the second fleshing obtained in machine fleshing of unhaired hides (pelts)

d) cuttings of split and various torn off or trimmed off portions of hides and pelts which are not suitable for the production of leather, including the parchment waste
e) chrome tanned and pickled shavings
f) waste from alum dressing of skins
g) cuttings of dried skins which are not suitable for the production of leather (heads, shanks, etc.)
h) cattle split glue stock which is not suitable for the production of artificial casings
i) remainders of skins from hat production.

According to the method of curing we know the following types of glue stock:

a) limed
b) salted by crystalline salt
c) salted and dried (the so-called dry-salted)
d) dried
e) pickled.

Delivery of uncured glue stock is permitted only if it can be delivered to the plant of the customer at least 36 hours after having been obtained.

In other cases the glue stock must be cured by any of above mentioned methods.

The delivered glue stock must be homogenous (according to the raw material from which it was obtained, according to the method of hide processing and method of glue stock curing).

Glue stock must not contain mechanical impurities and similar foreign materials, e.g. wood, iron, rubber, plastics or other admixtures, and must not be contaminated by tanning materials and dyestuffs.

Dried glue stock can contain at most 0.5 % of naphtaline.

Limed glue stock, salted by crystalline salt and pickled must be thoroughly and uniformly drained.

Glue stock must not be heated, it must not show any sign of putrefaction, i.e. it must not have ammonia or putrefactive smell, it must not be over-rippen and must not be attacked by insec., larvae or moths.

Cattle split glue stock can be delivered in pieces of the maximum length of 70 cm.

Glue stock obtained from limed hides with the use of arsenic trisulphide must be properly marked. It is not permitted to mix this glue stock with a glue stock obtained from hides by other methods.

Cattle, Calf and Horse Hair

Cattle, calf and horse hair are obtained in processing cattle hides, calf skins and horse hides in tanneries by help of:

a) older lime liquors

b) combined liquors in liming pits

c) sulphide painting (sodium sulphide is used).

Cattle, calf and horse hair is an important raw material especially for the products of consumption goods industry and technical articles.

Hair is partially destroyed by chemicals by help of which it was released from hides.

Cattle, calf and horse hair must meet the requirements of the customer - it must not be excessively destroyed. For a destroyed hair we must consider such hair which has lost the basic properties, i.e. elasticity (hair excessively breaks, its surface is excessively attacked by chemicals).

Cattle, calf and horse hair must have following binding values:

a) moisture content	max. 14 %
b) content of foreign admixtures (pieces of hides, paper, strings, lime dust, etc.)	max. 1 %
c) pH value of water extract	max. 7-9 %

d) hair must not be felted . felting of
fiber tufts is permitted max. 1 %
e) hair must meet the agreed reference sample

Goat and Kid Hair

Goat and kid hair is an important raw material, especially for the products of consumption goods industry and technical articles. This hair is divided according to the length into:

a) long
b) semi-long
c) short

According to the colour the hair is divided into:

a) white
b) light grey
c) coloured and grey
d) black.

Note: All types of hair are sorted according to the length. For long is consider goat and kid hair with the average length of 50 mm and more, for semi-long one is considered hair with the average length of min. [illegible] mm and for short one is considered hair with the average length of 30 mm and less.

Goat and kid hair is partially destroyed by chemicals by help of which it is released.

Goat and kid hair must meet the requirements of the customer - it must not be excessively destroyed. For a destroyed hair is considored such hair which looses the basic properties, i.e. elasticity (hair excessively breaks, its surface is excessively destroyed by chemicals).

Goat and kid hair must have the following binding values:

a) moisture content	max. 14 %
b) content of foreign admixtures (pieces of skins, paper, strings, lime dust, etc.)	max. 1 %
c) pH value of water extract	max. 7-9 %

d) hair designated as white can include coloured hair — max. 1 %

e) hair must not be felted - felting of fiber tuft is permitted — max. 1 %

f) hair must not be attacked by insect, larvae or moths

g) hair must meet the agreed reference sample

<u>Pigskin Bristles</u>

Pigskin bristles are the raw material for the production of brush and stuffing semi-products.

Pigskin bristles must meet the requirements of the customer - they must not be destroyed. For destroyed bristles are considered such bristless which loose the basic properties, i.e. elasticity (bristles break excessively, their surface is destroyed by chemicals). Bristles must be free of fat, animal smell, they must have a smooth feel, they must be dry and must not be sticky. Immediately after the bristles are separated from the skin, they must be thoroughly washed in order to degresse them and remove the remainders of sodium sulphide or lime. Pigskin bristles must have the following binding values:

a) moisture content	max.	12 %
b) contdnt of foreign admixtures (lime, epidermis, pieces of skin, paper, strings, etc.)	max..	0.8 %
c) bristles must not be felted - felting of bristle tufts is permitted	max.	2 %
d) colour		natural
e) average content of matters extractible by CCl_4	max.	4 %

f) bristles can be partially destroyed by liming in lime liquors

g) bristles obtained by two or more technological processes must not be mutually mixed.

Shavings

Shavings are divided:

a) according to the method of tanning

b) according to the type of the processed raw material from which they were obtained.

According to the method of tanning the shavings are divided into:

a) chrome tanned

b) vegetable tanned

c) chrome-vegetable tanned

According to the type of the processed raw material from which they were obtained, the shavings are divided into shavings from:

a) cattle hides

b) calf skins

c) sheepskins

d) goat skins

e) pigskins

f) horse hides

Shavings must meet the following requirements:

a) moisture content max. 65 %

b) they must not contain shaving dust in the amount greater than 40 %

c) they must not contain foreign admixtures (sand, metal of wooden chips, or strings, cloth, coal, rubber, etc.)

d) they must not be contaminated with machine oil, vaseline, etc. or other lubricants

e) they must not contain torn off parts or trimmings of hides or leathers

f) they must not be heated or rotted, etc.

g) shavings of different methods of tanning and from different types of raw material must not be mutually mixed.

2.2. Wastes from Shoe Production

Wastes are produced also in the manufacture of footwear. Above all there are clicking wastes.

Loss in the processing of upper side leather to footwear is given in the Table No. 4.

The balance of hide substance would not be complete if we consider leather production only. Leather is further processed for final articles, and also here the wastes are produced. In common designs of footwear it is about 25 % of hide substance. Of course, this waste further decreases the proportion in the utilisation of hide substance.

3. Semi-Synthetic Leather Based on Collagen

Special hydrophylic properties of collagen fibres of the hide and leather impressed the chemists who tried to utilize these fibres for the production of reconstituted leather-like sheet materials. For many years the wastes of leather were defibred and reconstituted to sheets in such a way that the fibres were bound together, sometimes with the combination of cellulose fibres, with the use of rubber of other elastomer binders, and thus, the usable shoemaking materials were produced. Strength of these materials in flexure, as well as their tensile strength are insufficient for the purpose of using them for shoe uppers. The distribution of desintegrated leather fibres through wet processes, resembling the processes used in the production of paper, resulted in the production of material which can be used for shoe linings.

The most known types of foreign collagen poromeric materials are the following:

Pedura

It is produced by Armstrong Cork Co., USA. It is supposed that it is produced by defibring of leather, its partial dissolving, and then, by re-depositing of fibres and regeneration of fibrous collagen together with a proportion of synthetic fibres and synthetic binder, probably polyurethane. It is produced with several finishes of the grain, such as box calf, embossed calf leather, imitation of tortoise and ostrich. It is said that it is sold in "economic" prices. Pedura is well suitable for standard shoemaking operations and it is said that it is very sensitive to removing folds from lasting, etc. by using temperatures normally applied like with natural leather. Wide wearing trials showed a great comfort of footwear with Pedura uppers, excellent durability and easy care of footwear. A factory with the capacity of 5 million sq.ft. in a year will be soon finished in Fulten, New York. First, mainly ladies' shoes will be produced at popular prices. Pedura (like Corfam) will be finished by other companies. Since to now, two firms have been chosen for this purpose: Hermann Lewenstein, New York and Beggs & Cobb, Boston.

Armstrong Cork Co. produces also Durvel - material for shoe linings which is also based on the utilisation of leather, i.e. collagen fibres.

Elboyan

It is produced by Fuji Spinning Co., Japan. It is said that Elboyan consists of non-woven web produced from collagen fibres bound by polyurethan elastomer, with microporous polyurethane grain layer. It is said that absorbency is 90 % (natural leather has probably 100 %), air permeability is 2.0 cc/cm^2/sel., tensile strength 1.5 kg/mm^2 and tearing strength 6.0 kg/mm. Production capacity of the firm is more than 5 million sq.ft. yearly and a proportion of the output is already exported to the USA.

Other Collagen Poromeric Materials

Armour Chemical Co. in cooperation with United Shoe Machinery Corp., USA developed a process based on the utilization of untanned collagen dispersed in water and applied on non-woven nylon fabric. Then, the wet web is tanned and needled what produces a substrate for breathable poromeric material. The United Shoe Machinery Corp., who buys Clarino, offers a license for this collagenous process.

In Japan several firms offer plants for the production of leather-like and collagenous sheet materials.

Colaten

This material was developed by the National Research Institute for Shoe, Leather and Allied Industries in Gottwaldov, Czechoslovakia in cooperation with the state production organisations.

Absorbency and permeability of this material, which is also called PKK, approach the values of natural leather more than it is in any other poromeric material reinforced with synthetic fibres. Modul and elongation which also affect the comfort of feet approach more the properties of shoe uppers made of genuine leather. Colaten shall be produced in a large scale and, at present, it is used for the shoe production in Czechoslovakia. The details on available types, weights, grain finish and price have not yet been announced.

Technological and pilot research has been substantially finished. At the present time a production plant is being built which shall be put in full production in 1973.

3.1. Raw Material Basis

The basic raw material for obtaining collagen fibres are tannery wastes of non-grain type in the pelt condition or after chrome tanning. So, there are split glue stock and chrome splits which, otherwise, are unsuitable for further processing in the tannery. To this group we can include also machine glue stock. The most convenient raw material is split glue stock from bellies and shoulders. In these portions of hide, the hide fibre can be chemically and mechanically sufficiently desintegrated, and thus, it is possible to obtain first-grade fibre with relatively high yield. Quite unsuitable are shanks because in these portions the fibres are strongly bound together and cannot be sufficiently released. Then, hide fibres are brittle, short and can be badly separated.

Also bend splits are of less convenience. Their fibres are plumped and can be chemically and mechanically desintegrated with difficulties. The resultant fibres are shorter, less flexible and the yield is low.

More detailed results in pelt split occurence in the main types of hides are given in the Table No. 5.

From this Table it is obvious that glue stock from bellies and shoulders, suitable for the production, amounts about 55 % from the total split glue stock occurence.

For example, according to the Table No. 5 and the occurence of raw cattle hides in Europe (475,000 tons) the occurence of split glue stock, suitable for the production of upper leather, is about 48,000 tons.

It represents the production of about 37 million m^2 of material. Considoting that the yield coefficient is 1.4 from the green weight of cattle hides per the area of finished leather, this occurence represents about 70 million m^2 of leather. By using all glue stock from bellies and shoulders for split materials the occurence in the area value can be increased by one half of the existing production. From this brief explanation we can clearly see the importance of solving this task.

For the processing of split glue stock for collagen fibres is very important the degree of pelt liming. Usually, two methods of liming are used: rapid liming, i.e. liming with strong short lime liquors in the drum, usually containing sodium sulphide of a higher concentration, and liming in pits lasting a longer period with a low concentration. The period and intensity of liming considerably influences the degree of removal non-fibrous proteins and the degree of desintegration of the structure. According to Tabara, about 58 % of albumins, 63 % of globulins and 37 % of mucoids are removed in time of soaking and liming. At the same time the denaturation of these proteins takes place which are then more easily removed in the following chemical operations. Next "cleaning" of the pelt follows especially in bating process where about 20 % of proteinous material is lost. Mainly non-fibrous proteins are removed, however, also a slight degradation of fibrous proportion (collagen) occurs.

The degree of pelt plumpness considerably affects the longitudinal releasing of hide fibres, i.e. fibrils and subfibrils. Of course, this degree must be controlled in such a way that the collagen fibres should have the needed properties especially the strength and length of the fibre.

Another raw material that is interesting above all for the countries in which the hides are split even after chrome tanning, is the preparation of collagenous raw material from wet blue splits. Laboratory and pilot tests revealed that with the Czechoslovak technology of collagen fibrous material preparation it is possible to process even this raw material without a great adjustment. After de-tanning the chromed leather, which was developed on the basis of original works by Lollar and Okamura, we obtain only a little shorter fibres than from split pelt glue stock. Also the consumption of splits in the original production weight compared with the production pelt weight of the split is only by about 15 % higher.

In Czechoslovakia we are investigating the possibility how to use other raw materials for the preparation of collagen fibres. Laboratory trials show that in principles it is possible to use also machine glue stock for the preparation of collagen fibrous material. Of course, here the problem of yield is the principle problem. On the basis of a great set of determinations we can suppose that machine glue stock has in the average only 19.6 % of dry substance. This dry substance consists of 37.3 % of fat, 15.9 % of ash and 40.6 % of proteins (calculated from the content of N). If we consider that a proportion of protein content is of non-collagen origin, and that in mechanical treatment of finer fibres which are obtained from machine glue stock, higher losses occur, we can expect an increased consumption of machine glue stock compared with split glue stock. Practically, in machine glue stock we found about 6.5 times higher consumption compared with split glue stock, calculated per the weight of raw materials in that condition in which they are wasted in tanneries. Despite this, the problem of processing machine glue stock is very interesting because fat obtained in pre-adjustment of the glue stock makes the machine glue stock cheaper than is the split glue stock. Thus, the degreasing of machine glue stock for the purpose of preparing collagen fibrous material is one of the main problems in the adjustment of machine glue stock. Up to the present this provlem has not yet been satisfactorily solved. The problem consists in that glue stock must be heated in degreasing to a higher temperature (80 to 90°C) what results in the denaturation of fibrous proteins. Therefore, the problem of degreasing machine glue stock is being intensively investigated at the present time.

Another raw material which could be considered for the preparation of collagen fibres are hide wastes with the grain layer. As we know, up to the present the research in this field has not yet been started. It is because of the fact that in the preparation of collagen fibrous material simpler and easier methods are used. In grained wastes there is a problem of removing the grain layer what is not a simple task. We cannot consider the application of mechanical method, i.e. splitting, because the process would require a greater number of manpower. On the other hand chemical method is considerably more difficult. Nevertheless, we suppose that in the future it will be necessary to apply this method, namely from two reasons:

a) deficiency of classic raw materials for the production of collagen fibrous material
b) introduction of segmentating hides (separation of bellies and shoulders) what will result in a problem how to utilise these cut off portions for the production of first-grade shoe upper material.

3.2. Technological Aspects

At present the application of fibrilary collagen proteins for the production of semi-synthetic shoe upper materials is oriented to three fields the mutual limitation of which is, however, considerably problematic.

At the present time it was found that the classic reconstitution of collagen, based on converting at least a proportion of procollagen to a soluble form and creating the conditions for the development of microscopic collagen fibrils, is very difficult from technical point of view and the utilisability of the produced materials in the shoemaking production was not satisfactory. From these reasons the interest in this working process has slid on a therapeutic field and partially also on a alimentary field where considerable successes were reached in the preparation and use of collagen threads, foams, supporting and reinforcing foils, veins and artificial casings of a thin walls. A number of Institutes makes investigations in this very interesting field in Czechoslovakia as well as in abroad (also CTC, Lyon, France)

From leather and shoemaking standpoint, a greater importance have research works concentrated to the utilization of short collagen fibres or collagen proteins as binder or filling agents for semi-synthetic shoe upper materials.

It can be supposed that the technological model for these processes was the production of artificial fibrous leather of LEFA type which was based on crushing the leather waste and shavings and their bonding by elastomeric impregnation binders.

These known products have a high rigidity and low elasticity and are used only for inner parts of footwear or for some fancy purposes.

In order to reach a greater flexibility, elasticity and other features of the shoe upper material, the basic skeleton is usually formed by a supporting net of synthetic fibres which are arranged in the form of non-woven fleece and filled with short collagen fibres and fibrils, and impregnated by various elastomer systems (e.g. polyurethanes, polyacrylates, etc.) and then mutually bonded. The basic type of these semi-synthetic collagen leathers are materials developed by Shu-Tung-Tu within the so-called Armour-United Collagen Project.

For an important trend in the production of semi.synthetic collagen poromerics we consider the orientation to the use of relatively long collagen fibres for the production of non-woven webs in which these fibres, either alone or in combination with synthetic fibres, form a bearing, highly inter-woven net.

In the last period a great number of informative data appeared in the literature dealing with the development of these types of semi-synthetic shoe upper materials in Japan, USA, France, USSR, Germany and in other countries. However, usually the given data are insufficient for making an exact imagination on the technology used.

The National Research Institute for Shoe, Leather and Allied Industries in Gottwaldov, Czechoslovakia has developed a semi-synthetic leather which in the first stage of development was called FKK and nowadays it is put on the market with its Trade Mark "COLATEN". This name is supplemented with various numerals which characterise the type of Colaten.

At the present time the production of Colaten is being proved in a pilot plant scale with the use of production equipment. Moreover, invensive investigations are carried out how to improve the quality of Colaten, as well as in order to develope new types of Colaten. It is necessary to develope new types of Colaten in order to meet the fashion demands of customers. Technological processes of the production of Colaten are covered by many patents.

The production process is about the following:

3.2.1. Preparation of the collagen fibrous material

3.2.2. Textile processing of the fibrous material for obtaining a web

3.2.3. Binding the web

3.2.4. Preparation of a grain layer

3.2.5. Binding the web with the grain layer

3.2.6. Finishing of the grain layer

3.2.1. Preparation of the Collagen Fibrous Material

The raw material for the production of collagen fibrous material are split glue stock, wasted chrome tanned splits or machine glue stock. Only splits from bellies or shoulders are used. Split in a certain stage of swelling and in a regulated stage of pre-tanning is mechanically defibred in special crushing machines. After the next chemical treatment and after dewatering it is defibred again and the produced fibrous material is separated. The result of these operations is the separated collagen fibre with a low content of non-fibrous proportions, knops and conglomerates. The length of collagen fibres varies within the range of 16 to 21 mm.

The quanlitative factors of collagen fibrous material produced in Czechoslovakia are given in the Table No. 6.

3.2.2. Textile Processing of the Fibrous Material for Obtaining a Web

Collagen fibres are mixed in a proper proportion with synthetic fibres, e.g. polypropylene, polyester, polyamide, viscous, in order to obtain two- or multi-component mixture which is perfectly homogenized. The mixture of fibres passes through a set of machines arranged in a flow lime in which a web is prepared using the technique of non-woven textile production. A great proportion of collagen fibres in the web increases the hygienic properties, and thus, the quality of Colaten. Square weight of the collagen web varies within the range 0.320 to 0.480 kg/m^2 and considerably depends on the thickness of the product. Important operations in the production line for the preparation of collagen web are needling and precipitation.

3.2.3. Binding the Web

The collagen web prepared in the mentioned process has not suitable properties due to its non-bound structure. Therefore, it is necessary to subject it to further operations in which its structure is sufficiently reinforced and obtains the needed physical and mechanical properties. One of the most important operations in this process is binding the collagen web by solutions or dispersions of polymer materials. By a proper choice of the binding system it is possible substantially to affect both physical and mechanical properties, as well as the appearance of the final product.

Binding with the solutions of polyurethanes is carried out by immersing the web in the solution of polyurethane in dimethyl formamide. After the web is saturated and the excessive amount of binder is removed, polyurethane coagulates on the fibres in a set of baths containing water in which the content of dimethyl formamide gradually decreases. In the end the solvent is washed out from the saturated web with clean water. Thus, a microporous structure is formed in the web. After squeezing and the following drying the web is buffed on both sides and is prepared for next operations. Binding by the solutions of polyurethanes is quite difficult technology owing to the necessity to use special machinery and owing to the complications connected with the regeneration of the solvent.

Another process of binding utilizes synthetic latices. The needed equipment for binding the collagen web by this method is relatively simple. The production line consists of a re-winding machine of collagen web, of a binding equipment, of a jet drier and a winding machine.

The whole production line is properly synchronized. The saturated and dried collagen web is then buffed from both sides to the needed thickness.

3.2.4. Preparation of a Grain Layer

The bound and buffed web is provided with a grain layer. After proper finishing the grain layer, the combination web-grain layer obtains the appearance of natural leather and the respective physical properties. The bound web alone has usually not suitable mechanical properties. The same is with the grain layer alone. Therefore, in the majority of cases a reinforcing fabric is put between these two layers. Similar lamination has the majority of synthetic leathers. The reinforcing fabric is stuck to the web either independently or it is embedded in the grain layer. The majority of grain microporous layers is prepared from linear polyurethanes, dissolved in dimethyl formamide or in dimethyl sulphoxide, or in other suitable solvents. The used polyurethanes can be filled with suitable organic matters, and thus, it is possible to affect both certain properties of the grain layer and also the price of the final pproduct.

Grain layers can be prepared from solventless systems. For the preparation of these grain layers they use water dispersions of elastomers to which they add suitable materials which give the grain layer not only the required strength, stretch, resistance to repeated flexure, but they also form form the microporous structure of the layer.

These grain layers are produced by spraying water dispersion on to a proper smooth or embossed material and the reinforcing fabric is embedded in the applied layer. After drying, the applied grain layer is removed and is prepared for the next operation.

9.2.5. Binding the Web with the Grain Layer

Binding the web with the grain layer is very important operation in the production of synthetic leather. It is important that the applied adhesive would form such a film which would not substantially reduce the properties of moisture absorbency, water vapour permeability and would provide a perfect sticking of the grain layer to the web. It is also the most difficult operation from the viewpoint of machinery and working process.

9.2.6. Finishing the Grain Layer

In the majority of synthetic leathers the finishing of the grain layer is performed by applying thin polyurethane or other layers which, however, do not give the synthetic leather a perfect character of natural leather. Therefore, such methods are investigated which would imitate in a maximum extent the appearance and character of natural leather. In this respect the development is ever changing. It can be said that the last methods developed are successful to a much greater extent.

It was found that it is possible perfectly to imitate natural meather, and in some properties even to reach better results (uniformity of appearance, colour fastness, elasticity in grain break).

er, finishing remains a domain of specialists who not only a great practical experience but also a aesthetics, a sense for inventiveness and a certain alent. Therefore, it is not curious that in world a of poromeric materials the grain finishing is t by special very experienced plants.

tative Factors

cal and mechanical properties of Colaten depend on a er of factors, especially on the processes of binding, he grain layer to the web and grain finishing. In the me we have two basic types which have been reliably

binding and sticking the grain layer by polyurethane agents

binding and sticking the grain layer by elastomers.

esults of analytical evaluation of these basic types in the Table No. 7. This Table includes the basic of the semi-synthetic leather Colaten and the diffe- pared with natural leather. These differences are in ecific weight, in a lower strengths, in a little r vapour permeability and in a lower resistance to

e semi-synthetic leather Colaten it is further nece- otice the so-called hygienic properties. According to Mitton, Herfeld and Blažej the hygienic properties ydrophylness, permeability, thermal conductivity and wearing.

at hydrophylness of Colaten results in a relatively vapour permeability, in a great moisture absorbency re desorbency. These are obtained by including the ibres in the web which is best obvious from the 8. This Table clearly shows a high sorption of ibres.

According to Blažej the comparison of hygienic properties of poromeric leathers with box side is the following (see the Table No. 9). According to these results Colaten possesses the best values from the investigated poromeric leathers and is nearest natural leather.

Blažej and Borovský determined the volume and distribution of pores in poromeric leathers. Results of their determinations are showed in the Table No. 10.

Among poromeric leathers the greatest volume of pores has Patora, the least has the material Xylee. Colaten belongs to materials with a great volume of pores. Thermal properties of poromeric leathers depends on porosity. In this respect the poromeric materials have an advantage against natural leather (they have a greater volume of pores).

Among other poromeric leathers Colaten has the most favourable comfort properties in wearing footwear. It is because Colaten contains collagen fibres the behaviour of which is similar to natural leather considering the properties from the viewpoint of volume changes.

This analysis clearly shows that semi-synthetic leather Colaten, compared with the known poromeric leathers, has the most favourable hygienic properties.

9.4. <u>Range of Products</u>

Up to the present time we have developed a great number of semi-synthetic leathers of the type Colaten. Their characteristic properties are denominated numerically.
There are the following types:

Colaten 1111 - Shoemaking semi-synthetic leather based on a collagen web which is bound by polyurethanes together with polyurethane grain layer reinforced by fabric. It is produced with smooth grain or with embossed grain. All colour shades can be produced except white one, in one colour or multi-colour execution. With advantage it is possible to apply a technique of printing or re-pringing from pre-printed foils (imitation of snake skins, etc.). Also the application of metal foils is possible.

Colaten 017 - Shoemaking semi-synthetic leather based on a collagen web which is bound by synthetic latices. Grain layer is made of elastomers. The possibilities of grain finishing are similar to Colaten 1111.

Colaten 007 - Shoemaking semi-synthetic leather based on a collagen web which is bound by synthetic latices. Grain layer is formed directly in the collagen web and has suede appearance. It is possible to produce it in all colour shades except white one.

Colaten 1220 - Garment semi-synthetic leather based on a collágen web which is bound by synthetic latices. Grain layer is made by a thin polyurethane foil. It is supplied in all colour shades, in patent, semi-patent and matt execution. It can be single-colour, multi-colour, or printed.

3.5. Processing in Footwear Production

The basic specifications for individual production processes in shoe manufacture are the following:

Clicking

At the beginning we recommend to click out the material in two layers which are folded grain to grain. Clicking is done in longitudinal direction.

Splitting

We do not recommend to split Colaten. If this requirement arises, e.g. in heel covering, it is possible to split from the flesh side to one third of the thickness at the maximum.

Skiving

Skiving can be carried out without troubles on all types of the known machines.

Cementing

Cementing is more difficult. The collagen web absorbs more adhesive, therefore, it is necessary to use thickened and adjusted latices.

Folding

Folding with latex makes no troubles. It is necessary only to consider a greater absorbency and a little longer process of drying.

Stitching

Stitching with lock stitch and chain stitch seams makes no troubles. Stitches have better appearance. Number of stitches per 1 cm can be chosen in the same way like with natural side leather. Threads are of polyester type, needles with rounded point.

Assembling of upper parts by other methods than by stitching is very modern at the present time, and often, it is discussed by shoe stylists, designers, technologists and above all by the manufacturers of machinery and equipment.

We know very well that in many of these materials it is possible to use a modern and progressive technique. Above all there are the application of high frequency, ultrasound, new types of adhesives, etc. By a proper application of these methods it is possible to obtain a higher strength of semas compared with stitching.

Lasting

Lasting belongs to the most important operations. It is performed on standard lasting machines.

Mulling and Setting

In experiments it has been proved that Colaten can be lasted and shaped without previous mulling. However, if a correct setting is to be obtained, it is necessary for the leather to be slightly mulled.

Roughing

Roughing the lasting margin is recommended to be carried out on standard roughing machines. Forepart of the shoe should be roughed by emery cloth, the waist portion by a wire roughing wheel.

Washing and Cleaning the Shoe Upper

The shoe upper is sometimes soiled by adhesive, dye, fats, etc. Before dressing it is necessary to remove all these dirts in order to obtain:

a) uniform coat of dressing agent

b) uniform gloss throughout the whole shoe upper.

The purpose of washing is also to prepare the grain layer of leather for a good anchoring of the dressing agent.

Solid dirts, such as adhesives, are removed by crepe. The shoe upper is washed by 1 % aqueous solution of some saponates or soap. In case of more intensive soiling by fats it is necessary to use bensine. Solvents, such as acetone or spirit, are not recommended to be used because they are harmful for Colaten finish. If it is in some cases necessary, you can use spirit diluted in water 1 : 1.

The shoe upper is washed by a sponge or by a fine cloth. Washing must be slight and careful. The sponge or cloth is regularly and in short intervals washed in clean water and is squeezed in order to remove dirts caught on the shoe upper. Washing solution is to be regularly changed.

Washing and cleaning is made in footwear with the last in. The number of labourers needed for cleaning and washing uppers is the same like in footwear with side leather upper.

Repairing

The purpose of repairing is to remove the damages occured in the shoe upper in time of mechanical processing (rubbed off dye, scoured grain layer, scratches, etc.).

For the repair of surface damages (rubbed off dye) we use a special repairing dye which, in the contrary to existing repairing dyes, becomes insoluble in water after having been dried and conditioned for several days (it is not necessary to fix it or protect by a solvent spray of nitrocellulose or another synthetic resin) and is flexible (it does not crack when being bent). Before repairing the dye must be thoroughly stirred. Small rubbings-off or cracks are repaired by a brush. More intensively damaged spots are scoured by emery paper No. 150 and the dust is removed. Then, the repairing dye is applied which evens the surface of the damaged spot. Finally, the damaged spot is sprayed with the repairing dye by help of spraying gun.

For the repair of a damage which is deeper we have developed a new repairing material. Deeper damages are removed above all in the reinforced portions of the shoe (toe, heel). First, the damaged spot is scoured by emery paper. Then, the melted repairing material having a proper colour shade is applied by a small spatula, the applied material is smoothed, polished, coated and spryed with repairing dye.

The repairing material is flexible and has a good adherence to the material. It is suitable for repairing damaged spots also in portions of the shoe upper which are flexed.

Dressing

By dressing the shoe upper (together with the sole edge and heel) we obtain the final and required appearance of footwear.

Dressing is performed by a proper solvent dressing spray which has a short time of drying.

Before dressing it is important thoroughly to clean the shoe upper, above all in case of light-colour shades. If it is not done, the soiled spot would be visible under the coat of dressing agent. It is also necessary to take care of a thorough drying the shoe upper after washing and after repairing the damaged spots. Moisture can cause the creation of matt up to white stains. Therefore, it is recommended for the shoe to pass through a short infra-red drier before being dressed. Dressing agent is applied on to the shoe upper in one coat. One spray is sufficient for reaching the required appearance.

After the dressing agent has been sprayed, the shoe passes through a tunnel infra-red drier in which the dressing agent is dried.

3.6. Economic Factors

According to the existing situation in the price policy for poromeric leathers it is obvious that poromeric materials cannot compete with low prices of coated fabrics and will not be able to compete with them probably even in the future.

However, they can compete with first-quality natural leather on the basis of their overall properties and appearance, i.e. in those fields where coated fabrics do not meet the requirements.

Poromeric leathers have already overdone the drawbacks which were a sign of the first synthetic materials, and thus, natural leather is exposed to a very real competition.

Prominent manufacturers of ladies' and men's footwear, who use poromeric leathers Corfam, Clarino, Skailon and some other poromeric materials, stated that "As far as the substituting shoe upper materials are more expensive or of the same price as natural leather, the production of footwear from substituting materials will have little hope to be successful. The material should be sold at most for a half price of genuine leather. Then the special types of cheap footwear should have a good chance to win the market".

This is considered for typically conservative approach of shoemaking firms in Europe and Great Britain in the starting period of the introduction of poromeric leathers and it illustrates some of troubles which the manufacturers and distributors of these materials had to overdo.

At the beginning of 1967 Corfam was sold in England for 55d to 97d per sq.ft. depending on the thickness. In smooth-grain types (calf) it was about an equal price for genuine calf leather of a good quality, if we consider also the percentage of waste in clicking leather.

In 1968 to 1970 the prices of the most important poromeric leathers were considerably cut down.

Price level of individual types of poromeric leather was the following (1970):

	d/sq.ft.
Corfam	
box calf	47 - 45
patent	80
Clarino	
box calf	50
patent	75
Xylee	
box calf	58 - 53
patent	76

Eikas

smooth finish	38
crushed patent	40

At the seminar of the British Boot and Shoe Institution (SATRA) in London, October 1967, one of the manufacturers, who was experienced in the production of footwear with leather, PVC and poromeric upper, said that poromeric materials were hardly to be distinguished from leather, but if an economic potency was utilized the shoe with poromeric upper could be sold by 10s per pair cheaper that comparable leather shoes. Another manufacturer said that poromeric material priced 100d per sq.ft. was comparable with leather priced 80d (the price after clicking). Just another manufacturer said that poromoric materials priced 72d per sq.ft. were clicked more economically than leather priced 60d per sq.ft. and that the quality was better than that of leather.

In February 1969 the British Shoe Corporation used its whole plant Berlington Works in Leicester for the production of footwear from Corfam. The firm G.B.Britton announced recently that it has introduced Corfam in its Tuf footwear, i.e. footwear of a cheaper price group than was the Gluv footwear. Another interesting development of the firm G.B.Britton is the introduction of a new type of Gluv footwear from Corfam in suede execution, in three styles, which is sold per 89s, 6d and can compete with natural pigskin suede. Marks & Spencer Ltd. sells ladies' footwear "Poromar" with poromeric uppers at the price of 39s, 11d, but it is not clear what type of poromeric material is used here.

From the above mentioned it is obvious that poromeric leathers are a good shoemaking material and all signs exist that this trend will continue. Several years ago these materials were limited only to footwear of a high-priced group. Now they are used for the production of middle-priced groups and it can be expected that they will be successful even in low-priced groups.

If we consider the forecasts on a deficiency in hides with the perspective of a deficiency in natural leather and an increased demand for shoes with leather upper, we can expect that the price of raw hides will be increased. It is supposed that the production costs of leather will decrease supposing the introduction of automation and mechanisation of tanning and finishing processes. This decrease in costs will be, however, only of a slight character because the workers, despite a lower number of them, will be paid more.

On the other hand, in poromeric materials the trend of prices is ever decreasing since the time of their introduction. Together with synthetic materials also the costs of raw materials and production costs are being decreased because the volume of production is ever increasing. Moreover, we can suppose that the improvement of production processes will further contribute to the decrease in production costs. It is also within the framwork of our possibilities to develop new poromeric materials for a lower price.

4. Conclusion

The leather industry stands in front of a problem how to utilize the wastes in an economic way. It is important because about 70 % of the proteinous substance of raw hide is wasted. Only a smaller proportion of these wastes is used for the production of split leather. A great proportion of wastes is a basic raw material for the production of other proteinous products which are not used in the leather and shoe industry.

The National Research Institute for Shoe, Leather and Allied Industries in Gottwaldov, Czechoslovakia has developed a new method of utilizing split glue stock, machine glue stock and pre-tanned split glue stock for the production of semi-synthetic poromeric leather Colaten. This method is, in the meantime, the most economical utilization of the mentioned wastes because it returns the proteinous wastes back to the leather and shoe industry in the form of upper leather.

Semi-synthetic poromeric leather Colaten belongs to the known synthetic poromeric leathers. However, it differes from them by more convenient hygienic properties, such as better hydrophylic property, porosity, sufficient thermal insulating ability and comfort in wearing. These properties are obtained because the web contains collagen fibres.

Further, Colaten has very favourable mechanical and physical properties. In the production of footwear it is used like natural leather.

From the technological standpoint the production of Colaten can be divided into the following sections:

- preparation of collagen fibrous material
- preparation of a web
- binding of the web
- binding the web with the grain layer
- finishing the grain layer.

The production is considerebly complicated and requires a close connection of individual sections.

From the price viewpoint it can be supposed that poromeric materials will find their application in the production of footwear and that they can compete in their price with natural leather.

L i t e r a t u r e

Apley: Poromeric Materials for Footwear, A study, Tenterden-Kent, England, 1970.

Beneš: Informátor kožedělného průmyslu, (Informative Data on Leather and Shoe Industry), SNTL, Praha, 1970.

Blažej, Borovský: Studium specifických povrchů, objem a distribuce pórů obuvnických materiálů, (A Study of Specific Surfaces, Volume and Distribution of Pores in Shoemaking Materials), Lecture at the Conference on Poromeric Leathers, Nový Smokovec, CSSR. 1970.

Hlaváček: Druhy záměnných materiálů v kožedělném průmyslu a jejich cenové relace ve světě, (Types of Substituting Materials in the Shoe and Leather Industry and Their Price Relations in the World), Lecture at the Conference on Poromeric Leathers, Gottwaldov, CSSR, 1970.

Kotásek: Některé problémy výroby semi-syntetických usní z kolagenových odpadů, (Some Problems in the Production of Semi-Synthetic Leathers from Collagenous Wastes), Lecture at the Shoe and Leather Symposium, Gottwaldov, CSSR, 1969.

Pektor, Šmika: Bilance kožní hmoty při kožedělné výrobě, (The Balance of Hide Substance in the Leather and Shoe Production), Lecture at the Conference on Raw Hides, Gottwaldov, CSSR, 1969.

Strachota, Svoboda, Štangl: Výroba, vlastnosti a zpracování Colatenu, (Production, Properties and Processing of Colaten), Lecture at the Conference on Poromeric Leathers, Gottwaldov, CSSR, 1970.

Table 1

Quantity of Wastes in Tannery Processing of Upper Sides Expressed in Dry Matter of N

Green hides	100 % of N
Machine glue stock	2.7 % of N
Hand glue stock	1.4 % of N
Split glue stock	6.8 % of N
Shavings	5.5 % of N

Table 2

Non-Returnable Loss in Tannery Processing of Upper Sides Expressed in Dry Matter of N

Cured salted cattle hides	100 % of N
Wastage in the section soaking to liming	6.6 % of N
Wastage in the section deliming to bating	21.4 % of N
Wastage in the section tanning to pre-finishing	7.8 % of N

Table 3

Balance of N in Tannery Processing of Upper Sides

(Expressed in % of Dry Matter)

Fresh hide	100 % of N	
Machine glue stock	2.7 % of N	
Hand glue stock	1.4 % of N	
Split glue stock	6.8 % of N	
Shavings	5.5 % of N	
Returnable wastes total	16.4 % of N	16.4 % of N
Soaking to liming	6.6 % of N	
Deliming to bating	21.4 % of N	
Tanning to pre-finishing	7.8 % of N	
Non-returnable wastes total	35.8 % of N	35.8 % of N
Split for further processing		13.0 % of N
Leather		31.1 % of N
Total		96.3 % of N
Other loss		3.7 % of N

Table 4

Loss in the Processing of Upper Leather for Footwear
(Expressed in Dry Matter of N)

Leather for clicking	100 % of N	
Clicking waste	24.7 % of N	
Dry matter of leather	87.4 % of N	
N in leather dry matter	13.1	
10 dm^2 of leather	=	11.6 g
10 dm^2 of clicking waste	=	14.0 g

26. 5. 72

3 OF 3

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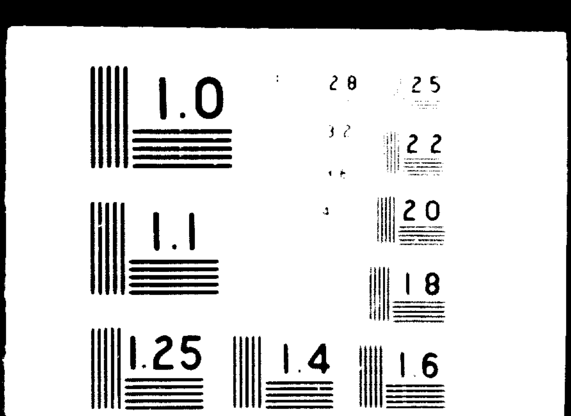

Table 5

Split Glue Stock in Main Types of Raw Hides
(from Pelt Weight)

Raw Hide	Split Glue Stock Total %	Proportion per: Bend % rel.	Shoulder % rel.	Belly % rel.	Proportion of Split Glue Stock from Bellies and Shoulders %
Home Bulls 34/39 kg (green weight per piece)	24.4	42.8	34.3	22.9	14.0
Big Packer 50/60 lbs	19.6	44.5	32.2	23.3	10.9
Swedish Hides from Castrated Heifers 17/24 kg	24.8	46.0	32.0	22.0	13.4
Frigorifico Standard 19/23 kg	22.5	45.5	31.0	23.5	12.3
Average	22.8	44.7	32.4	22.9	12.6

Table 6

Properties of Collagenous and Synthetic Fibrous Material

Determination	Unit	PE	PP	KV (St V/4)	KV (St V/13)
Weight for length unit	day	0.8	4.0	25.7	43.0
Breaking length	km	49.3	50.8	23.3	16.4
Elongation	%	41.0	87.9	25.3	24.9
Tensile strength	p/day	5.54	5.64	2.6	1.8
Shortened fibres after thermal treatment (100°C, 15 min.)					
a) by hot air	%	28.3	8.6	1.6	1.6
b) hydrothermically	%	24.5	7.0	64.0	71.6

Abbreviations: PE - polyester CSSR

PP - polypropylene CSSR

KV - collagen fibrous material CSSR

Table 7

Physical and Mechanical Properties of Colaten

Value		Type I	Type II	Box Side
Thickness	mm	1.5	1.43	1.52
Square specific weight	kg/m^2	0.7	0.873	1.194
Tensile strength	kp/mm^2	A 1.30	A 1.48	A 2.25
		B 0.90	B 1.00	B 1.65
Elongation	%	A 24	A 51	A 51
		B 56	B 34	B 60
Slot tear strength	kp/mm	A 4.9	A 3.8	A 7.8
		B 5.2	B 4.1	B 8.5
Torsional rigidity	kp/cm	A 0.8	A 1.0	A 0.6-2.1
		B 0.8	B 0.9	B 0.6-1.8
Tensile rigidity at 10 % elongation	kp/cm	A 120	A 45	A 31
		B 18	B 58	B 35
Water vapour permeability	mg H_2O/cm^2/ /24 hours	65	69	67
Moisture absorbency	%	13.5	14.9	2.3 (water repelent finish)
Moisture desorbency	%	- 10.6	- 12.7	- 30.0
Resistance to repeated flexure		A 3	A 3	A 5
(Bally Flexometer)		B 3	B 3	B 5

Resistance degree

Degree 3 = slight destruction of the layer

Degree 5 = without any change

Table 8

Balanced Condition of Water Vapour Absorption at 20°C and 100% Relative Humidity (According to Chabert)

Fibre Type	Water Vapour Absorption %
Collagen fibrous material (SVÚK)	36 - 39
Wool	33.6
Cotton	22.4
Viscous fibres	48.7
Polyvinyl alcohol fibres	15.9
Polyamide fibres	13.2
Polyester fibres	2.7

Table 9

Comparison of Hygienic Properties of Poromeric Leathers with Box Side (According to Blažej)

Product	Sorption of Water Vapour %	Relation to Box Side %	Water Vapour Permeability mg/cm/ /hour 25°C	Relation to Box Side %	Thermal Conductivity 1.10^{2} kcal/m/ /hour	Relation to Box Side %
Corrected grain box side	29.7	100	4.2	100	7.91	100
Colsten	16.0	59	3.4	80.9	7.86	101
Corfam	2.3	7.7	3.6	85.7	7.41	107
Clarino 1000	3.64	12.2	3.2	76.2	8.29	94

Table 10

Total Volume of Pores in Poromeric Leathers

Product	Total Volume of Pores ($cm^3\ g^{-1}$)
Corfam	1.208
Clarino	1.142
Patora	1.308
Xylee	0.969
Colaten	1.250
Unfinished box side	1.022
Finished box side	0.692
Corrected grain box side	0.608

26. 5. 72