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Recovery of waste from Algerian raw hides and their development in paper industry based on Alfa

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ABSTRACT/RESUME

Abstract: *The aim of this present work is the valorization of a by-product from the hides and leather industry, Given the nature of these highly polluting wastes and their very large volume, it would be judicious to subtract these wastes from the overall polluting load of environment, to proceed with the recovery the products extracted from this waste and finally perform their recycling in the form of useful products representing commercial value, since they can advantageously replace imported products. Among the numerous possible applications of collagen in the industrial sector, we have opted for its use as a substitute for vegetable resin (imported product), currently used as a binder in paper Industry, especially Alfa-based writing paper. A consequent increase in physico-mechanical characteristics of the Alfa pulps formets in which we have incorporated collagen of* ***1*** *and* ***2%*** *as a gel. Otherwise, it is just possible to use less refined pulps and to obtain the same characteristics of resistance for papers obtained with more refined pulps.*

I. Introduction

In Algeria, leather industry, which has developed gradually since independence, has an honorable place given, on one hand, the growing need for leather of population and on the other hand, the availability of raw matter (hides) from relatively large local livestock, especially the ovine population.

This national Industry deals mainly with hides of bovine, ovine and caprine. However, it imports large quantities of bovine skins while exporting, in exchange ovine's leathers, especially half-finished. All hides of other domestic or wild animals (alpacas, equines, rabbits, wild boars, etc.) are discarded or buried as such [1].

The aim of this work is, at first, inventory at the national level the solid wastes of untanned raw hides (of ovine, bovine and caprine), as well as the scrap of raw hides has no Commercial value for their treatment into leather. This inventory will also cover all hides currently not processes by industry (equines, alpacas).

Given the nature of these highly polluting wastes and their very large volume, we have shown the value of removing these wastes from the overall polluting load of environment [2, 3, 4and 5], recovering the products extracted from this waste and recycling them in the form of useful products representing commercial value, since they can advantageously replace imported products.

Among the numerous possible applications of collagen in industry [6], we have opted for its use as a substitute for vegetable resin (imported product), currently used as a binder in paper Industry, especially Alfa-based writing paper [7]. During its transformation into leather, the raw hide suffers great losses. Given the richness of these wastes of raw hides in proteins, fats and keratins (especially wool) [8], and their large volume, we have considered their recovery and development [2, 3].

II. Raw Matters

When the hide is transformed into leather, whatever the made efforts, the tannery cannot totally develop it. It will strive to master its technology, its management, in order to obtain better quality leather at the lowest cost possible aiming to obtain an optimum price / quality ratio.

We have noted that a large part of this hide is moved as crude as non-exploitable matters in leather, i.e.: non-usable margins, hair, wool, flesh, dermal substances, etc [1].

Other matters are removed from the following stages of production as tanned waste (scrap, undressed leather waste, stain and finish scraps) [1]. The inventory shows at first the importance of waste thrown out by the Algerian leather industry in all its forms [1, 3, 4 and 5], namely:

- 7 to 10% of the hide weight is discarded as raw.
- 15 to 20% of the hide weight is eliminated as soluble protein in solution or in suspension and as various wastes (hair, droppings, blood, sand)
- 6 to 14% are eliminated as carnivore (protein + fat).
- 5 to 16% are eliminated as dry tanned waste (scraps, dust).

In fact, only 40 to 50% of the gross weight (dry matter) is converted into finished leather. About 2/3 of the hide is thrown out at different stages [1, 9].

Waste in all its forms rejected by tanneries and taweries represent in total [1, 9]:

- 10780 ton / year for bovine.
- 4678 ton / year for ovine and caprine.

Taking all these factors into account and in order to benefit from their development on one hand and to reduce environmental pollution on the other hand, we propose to recover and process the raw waste of untanned hides only and to review all the possibilities of their transformation and their development into products or byproducts which may generate a certain interest and even replace certain ingredients used in Algerian industries such as food, chemical, cellulose or textile industry [6, 10, 11].

III.Materials and Methods

III.1. Waste Processing of ovine and bovine raw hides

In this section, we have recovered separately the main components of waste namely: wool, fat and finally the collagenic substance. That is why; we performed tests on raw waste samples of dry ovine and bovine hides recovered during sampling, on their arrival at Rouiba ENIPEC unit.

In parallel, we have determined the percentage of Humidity, of dry material and fat on ovine and bovine hides' wastes removed by manual razing.

III.2. Determination of Humidity level and dry material rate

NF EN ISO 4684. Place a quantity of 5 g of raw hide in a crystallizer previously tared to 0.0005 g and place it and it content in a ventilated oven, set at 105°C ± 2°C. Let them stay for 6 consecutive hours. At the end, remove them from the oven and cool for half an hour in a desiccator. Weigh the test to about 0.0005 g. Continue desiccation until constant mass, made on three tests of 300 to 500 g.

III.3. Recovery of fat

NF EN ISO 4048. Place a quantity of 10 g of raw hide, in filter paper extraction thimbles, seal with hydrophilic cotton (degreased) and introduce it into the extraction apparatus (soxhlet) whose balloon 250 ml was previously tared at 0.0005 g, pass the solvent on the material at least 30 times. Release the excess solvent by distillation. Dry the residue in an oven set at 105°C ± 2°C for 3 hours. eigh after cooling in desiccator, to 0.0005 g.

III.4. Determination of the fatty acid profile of fat

NF EN ISO 12966-1. fat extracts are analyzed after having been saponified and then methylated. The chromatographic analyzes were carried out by gas chromatography "GC" with electronic pressure regulation type (PerkinElmer Gas Chromatograph Clarus 580). The column used is fused silica capillary, length 30m, diameter 0.25 mm. Gas vector is helium with a flow rate of 1.0 ml/min. The temperature of the column is automatically programmed at 50°C for 10 min, then at 50 to 200°C for 75 min and finally at 200°C for 25 min. The injector and detector temperatures keep a constant value of 200°C. The identification of the components was made by co-injection of authentic reference compounds.

III.5. Use of bovine gelatin as a binder in the manufacture of Alfa-based paper

In paper industry, mechanical strength is an essential characteristic. Thus, any increase in the values of physico-mechanical properties is generally obtained either by a high refining or by incorporation of binding agents, or by a combination of the two. In the main Algerian papermaking units, we use an imported vegetable resin.

Our work at this stage consisted in studying the possibility of substituting this resin for the gelatin made from our hide waste, and more precisely which obtained at the fourth racking between 80 and 100 ° C., and at variable rates.

The tests were carried out at cellulose laboratory of Bou Ismaïl TONIC unit. We have prepared six (06) samples of 16 g each of cellulose pulp of baked Alfa with soda (numbered from 1 to 6) and whitened with sodium hypochlorite (NaClO), which we refined to 20.5 degree Shopper (°SR) in a centrifuge paper refiner [1, 7].

Then, we have carried out the making of six cellulose pulp squares for each test to which we added variable gelatin rates (calculated on dry matter) from 0 to 2% (ie 0, 0.4, 0.8, 1.2, 1.6 & 2). In order to lower the pH of the cellulosic pulp and in accordance with industrial practice, we added 2% alumina sulphate [$Al_2(SO_4)_3$] [1, 7].

- pH of the initial cellulosic pulp: 7.8
- pH of the pulp + alumina sulphate: 5.5
- pH of gelatin: 3.85

III.5.1. Preparation of collagen powder

We have taken off a certain quantity of waste as pickles for the preparation of powdered collagen. This step requires two distinct operations, i.e. the drying of these wastes and then their hashing - grinding.

This open-air waste is cut into small pieces manually with a knife. The latter are then ground very finely. Obtaining a powder of white color hide which will be used later to prepare the dispersion of the collagen.

The dispersion of collagen used was at a concentration of 1% (10 g of dry collagen in one litre of sulfuric acid solution at pH = 3.20) and passed into a disintegrator [1, 7].

III.5.2. Preparation of alfa cellulosic pulp

We worked with alfa pulp from Bou Ismaïl TONIC unit. This pulp was baked in sodium hydroxide and bleached with sodium hypochloride (NaClo) according to the usual industrial process of this unit. A refining of the pulp was carried out in a centrifugal refiner of Jokro type at the laboratory of our institute. The notion of this refiner is based on hypocycloid movement of six bowls arranged on a disc and rotated on them by the rotation of the disc. Each of these bowls can receive a hollow container, hermetically closed and containing a roller free of its movements but that the centrifugal force applies against the wall of the container during its rotation. The roller can thus crush the fibers suspended in water on the walls of the cylinder. The refining procedure was given in **Table 1**. Then we prepared dough samples containing 16 g of dry material (ie 131.58 g of pulp with 87.84% of humidity) which we refined to different degrees [1].

Table 1. *Evolution of refining degrees according to time*

Time (mn)	0	5	10	15	20	25	30	35	40	60
°SR	18	20	22	23	24	26	29	32	35	50

III.5.3. Preparation of collagen dispersion

The collagen, as hide powder and prepared according to the described above method by hashing and grinding, is converted into a 1% and 2% dispersion in a solution of strong acid (sulfuric acid) at pH = 3.00 and in a other lower organic acid solution (chloroacetic acid) at pH = 3.5 – 4. The dispersions were carried out using adisperser (Ultra Turrax T.50) at 8000 rpm for 7 minutes [1, 7].

We made formulas by incorporating the dispersion of collagen prepared in two different modes and rates; we studied then some physico-mechanical properties [1, 7]:

- **Mode 1:** Collagen dispersed in $CH_2ClCOOH$ (marked **Coll.C**).
- **Mode 2:** Collagen dispersed in H_2SO_4 (marked **Coll.S**).

III.5.4. Microbiological tests of gelatin

A sample of 50 g of liquid gelatin, preserved in a sterile box, was taken. Four microbiological analyses were carried out: Micro Organisms Revive at 30°C after 44 hours, Fecal Coliforms, Staphylococcus aureus, Clostridium sulfito-reducer 46°C.

III.5.5. Determination of pH

The determination of the pH value was carried out as follows: The collagen, in the form of pulp powder, is prepared in the form of 1% and 2% dispersion in a solution of strong sulfuric acid and in another solution of lower organic chloracetic acid. Then we determine the pH of the dispersions prepared using pH meter. This apparatus is also used for determining the final pH value of the initial cellulose pulps and after treatment.

III.5.6. Determination of Viscosity

The aim of viscosity measurement is to measure the flow ability of fluids under pressure and gravity. It is determined by a Brookfield LVDVE Viscometer apparatus at 20°C and 100 rpm. Using the disk RV-2 HA/HB-2 allows us to realize this disintegration.

III.5.7. Determination of grammage

NF EN ISO 536. It is expressed in grams per m^2. It represents a mass per unit area of paper. The equipment used is a Gramaje Series electronic scale. The analysis of this characteristic is done by taking samples of size 20 x 25 cm by weighing it on the electronic scale, reading results multiplied by 20 gives the weight of one m^2 of paper.

III.5.8. Determination of thickness

NF EN ISO 534. It is expressed in µ. This is the density of a sheet of paper model or form of a specific grammage. It is determined by a device called Mahr millitast 1082 micrometer. The analysis is carried out by putting a paper sample between the two probes of the micrometer, one is fixed serves as a support and the other upper mobile under a certain pressure, and then we read the reading in micron on the micrometer dial which gives readings in microns.

III.5.9. Determination of breaking length

NF EN ISO 1924-2. This is the length beyond which a 15 mm strip of paper suspended by one of its ends breaks under its own weight. It is expressed in m. It provides information on interfiber bonding in paper (fine particles and elements, internal and external fibrillation).

The breaking length is determined using a dynamometer according to the TAPPI TI 250 technique. It is the most important characteristic; it sets the quality of the paper obtained, from resistance. The break length is calculated:

$$L_R = (1 / 9.81) . (R_f / G) . (10^6/15)$$

Where:

L_R: Average tensile breaking length in m,

R_f: breaking strength at average tensile in N for 15 millimeter,

G: Weight of the sample in g / m²,

15: Width of the test strip in millimeter.

III.5.10. Determination of the tear index

NF EN ISO 1974. It is a dynamic test where the absorbed energy is measured to cause tearing. The test is performed on an Elmendorf Tearmeter. It has two jaws for clamping samples; one is secured to the frame the other of the pendulum, removable. The test of paper measuring 65x75 mm each one, are fixed on the jaws. After having cut a notch, the free movement of the pendulum prolongs the entire tearing of the sample.

Measuring the initial potential energy difference and the kinetic and potential energy difference at the end of the tear test gives the force required to tear the sample. Beforehand, a vacuum test is carried out (in the absence of paper) where the energy released by the pendulum is measured. Long fiber pastes give high tear resistance. Tear resistance values drop with refining. The tear resistance is measured in millinewton. The tear index is given by the following ratio:

$$I_D = \text{tear strength (mN) / grammage (g/m}^2) . 100$$

I_D in mN.m^2/g and usually expressed in %.

III.5.11. Determination of bursting index

NF EN ISO 2758. It is expressed in kPa.m^2/g. The bursting test is performed on a brightness meter. The notion of measurement is to constrain a piece of paper, applied by means of a flange against a flexible membrane, until the surface breaks. The flange is of flat annular shape whose central round space is hollow and the membrane is rubber, set in the tray of the device. The dilation of the membrane is ensured by the pressure of a fluid. As the pressure in the dilatation chamber increases, the membrane swells and causes a gradual spherical deformation and finally the breaking of the paper. The pressure at which the paper sample breaks is called bursting strength and is expressed in KPa in the international system.

Bursting resistance is mainly developed by refining. Generally the resistance to bursting is related to theweight per square meter of the paper, which is called bursting index, I_E.

$$I_E = \text{bursting strength (kPa) / grammage (g/m}^2)$$

$I_E$in kPa.m^2/g and usually expressed in %.

III.5.12. Determination of air permeance

NF ISO 5636-3. It is the ability of the paper to let through the air. The used method in this study is Bendtsen roughness. It is expressed by the volume of air in milliliters that gets through a paper test tube for a specified time under a pressure of 1 bar. More and less it increases, the paper is porous. It is expressed in ml/min.

III.5.13. Determination of the index collage

NF EN ISO 535. The purpose of this operation is to evaluate the ability of a paper to resist the penetration of water and aqueous solutions. Collage index is determined by L&W COBB SIZING TESTER, used for determining the adhesion strength of collage. The paper sample is held in a reservoir ring of 100 cm^2 of surface in which 100 cm^3 of water is poured. After a specified time of contact, the water is quickly emptied; the paper is blotted with a blotter and then weighed. The difference in weight before and after absorption relative to a m^2 of surface area, the Cobb index is the water absorption capacity is a function of various characteristics of the paper, such as collage, porosity, etc.

IV. Results and discussion

IV.1. Humidity and dry material content

Humidity and dry material contents of the raw samples are shown in **Tables 2** and **3** respectively.

Table 2. *Humidity content of waste generated during treatment of 60 raw ovine hides at different stages of production.*

	60 dry raw hides	Woolly Scraps waste	Soaked hides before shearing	Land, sand coast losses	Shearing weight	Wool weight	Innards fleshing weight	Carnivore in fleshing	Bleu weight after scraping	Scrap losses	Finished sampling losses	Finished leather weight
Weight (kg)	102	11.1	299	-	202	68.6	175	27	58.1	5.55	1.27	36.31
Humidity (%)	**12**	12	75	-	80	50	80	45	45	45	15	15
Weight(kg) (dry material)	89.76	9.77	74.75	5.24	40.4	34.3	35	5.4	31.95	3.05	1.08	30.87
% of loss (dry material)	-	10.9	-	5.84	-	38.2	-	6.01	-	3.4	1.2	-

Table 3. *Humidity content of solid waste from bovine hides generated annually at different stages of technological process at the national level*

	Raw waste (in tone)	Carnivore	Innards waste (refente)	Bleu waste	Finished waste	Total
Mass of waste in its state	1336	4718	1064	3333	329	10780
Humidity %	45	70	70	54	13	
Waste mass (dry residues)	735	1415	319	1533	286	4288
Total (dry material)			4288			

The analysis of the tables reveals at first the great waste that the algerian leather industry rejects in all its forms, namely: solid raw materials, hairs, carnivore, solid waste, soluble proteins or suspended in waste water.

- Scrap, tanned waste discarded in solid form.
- Sanding dusts also rejected in solid form.
- Samplers (finished or half-finished leather in solid form).

However, we should indicate, that at present this waste costs or must cost the tanner considerable sums for their transport, their destruction or for the management and treatment of the caused pollution.

On the other hand, specific studies have been carried out all over the world, particularly in France, raising the complexity of the problem given the volume of this waste and its diversity [12,13, 14].

Also, wastewater is treated through processes that have been initiated, but the problem of solid waste remains till present, and it can even be said that it is alarming in our profession and in our country.

IV.2. Fat content

The results are shown in **Tables 4** and **5** respectively.

Table 4. *Fat content in ovine hides waste (on gross weight)*

Tests	Raw Waste weight (in g)	Fat weight (in g)	Extraction by cooking %	Extraction with hexane %
1	250	25.5	10.2	9.50
2	280	24.0	8.57	-
3	230	20.1	8.74	-
4	300	27.0	9.0	-
5	255	23.4	9.17	-
6	285	25.3	8.87	8.70
7	320	26.45	8.26	-
8	320	30.05	9.39	-
9	340	30.55	8.98	-

10	270	29.85	11.05	11.30
Average	**2850**	**262.2**	**9.20**	**9.83**

Table 5. *Fat content in bovine hides waste (on gross weight)*

Fat	Extraction by cooking %	Extraction with hexane %
On pickled hides weight	3.4	3.2
On raw hides weight	**4.93**	**5.25**

The Fat content values obtained for both ovine and bovine tallow by extraction with hexane are slightly higher than those found by cooking; this difference can be attributed to the traces of fat remaining in the gelatin during this cooking. This gives us a slightly soaked gelatin with very special properties.

As regards the quantification of fat to be recovered from these ovine and bovine hides, this will be the first method that will be taken into consideration, since the second method (solvent) is prohibitively expensive, considering the cost of the solvent.

On the other hand, all these amounts of fat would come in less in the polluting flow, in solid form, in suspension or in solution in wastewater.

IV.3. Determination of fatty acid profile of fat

The fatty acid contents of fats are shown in **Tables 6** and **7** respectively.

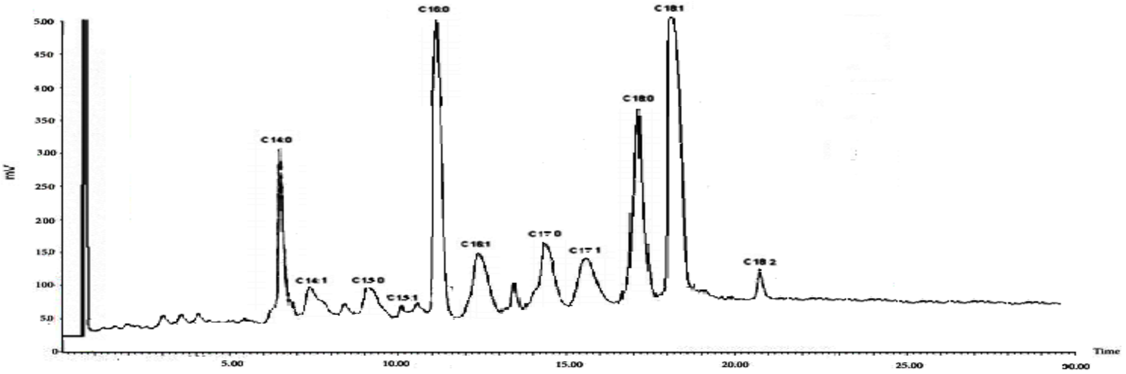

Figure 1. *Chromatogram of ovine tallow.*

Table 6. *Composition of ovine fatty acid tallow*

RT	Fatty acid	Carbone number	Unsaturation Degree	Fatty acid %
6.6	Myristic	14	0	2.77
7.32	Myristoleic	14	1	0.84
8.63	Pentadecanoic	15	0	0.8
9.46	Pentadecanoic	15	1	0.24
11.14	Palmitic	16	0	23.8
12.31	Palmitoleic	16	1	3.14
13.85	Heptadecanoic	17	0	2.24
15.1	Heptadecanoic	17	1	2.15
17	Stearic	18	0	10.61
18.24	Oleic	18	1	**50.88**
20.7	Linoleic	18	2	0.99

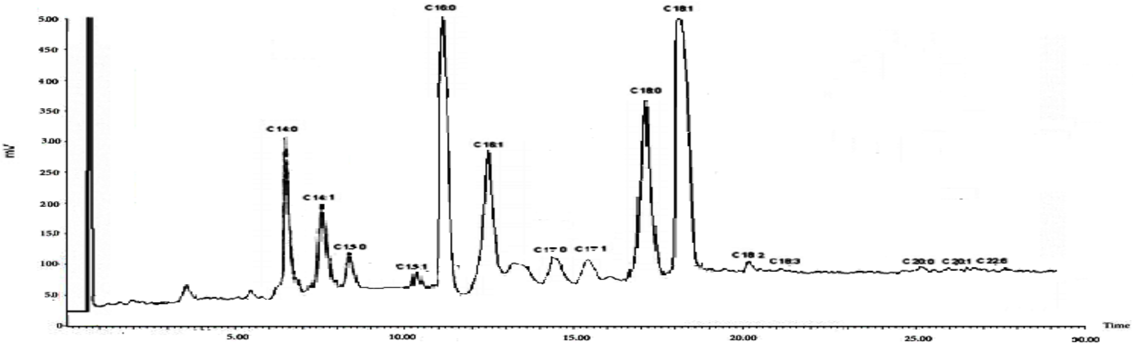

Figure 2. *Chromatogram of bovine tallow.*

Table 7. *Composition of bovine fatty acid tallow*

RT	Fatty acid	Carbone number	Unsaturation Degree	Fatty acid %
6.57	Myristic	14	0	4.77
7.83	Myristoleic	14	1	2.2
8.6	Pentadecanoic	15	0	0.59
9.94	Pentadecanoic	15	1	0.24
11.11	Palmitic	16	0	**25.39**
12.35	Palmitoleic	16	1	5.14
13.81	Heptadecanoic	17	0	0.69
15.11	Heptadecanoic	17	1	0.72
16.94	Stearic	18	0	9.67
18.29	Oleic	18	1	**48.24**
20.63	Linoleic	18	2	0.73
21.7	Linolenic	18	3	0.15
25.09	Arachidic	20	0	0.28
26.92	Gadoleic	20	1	0.05
27.7	Behenic	22	0	0.04

Analysis by gas chromatography show that the fat of bovine and ovine are composed of free fatty acids whose chain length varies between 14 and 22 carbons for the bovine and between 14 and 18 for that of ovine. The majority fatty acids identified for the two types of fats are C18: 1 (oleic acid), C16: 0 (palmitic acid), C18: 0 (stearic acid), C16: 1 (palmitoleic acid) and C14: 0 (myristic acid).

These fats also consist of waxes and cholesterol esters. The saturation rate of fatty acids (C16: 0, C18: 0 and C14: 0) is high, which is characteristic of degraded fats [15].

If we compare the constitution of tallow obtained from algerian ovine and bovine hides to those of other european hides [16], we notice that the results found fall within the average ranges, for the saturated C14 and C16 fatty acids, but Stearic acid (C18) has a noticeable insufficiency and a slight excess of oleic acid, especially for ovine tallow, as well as a slight deficiency of linoleic acid.

However, it is obvious and even proven that the constitution of tallow varies greatly depending on the provenances, breeds, sexes and the mode of farming (climate) of the animals that have generated the hides, that they themselves have produced these fats.

Ovine samples are considered the most used material in Algerian tanneries and widely seen its availability nationwide. Ovine hides that were selected for our study.

IV.4. Microbiological tests of gelatin

The microbiological results of the gelatin are shown in **Table 8**.

Table 8. *The microbiological results of the gelatin*

Analysis	Sample	Analysis method reference
Micro Organisms Revive at 30°C	$9.1*10^2$	**NF T 90 - 401**
Fecalcoliforms	Abs	**NF T 90 - 413**
Staphylococcus aureus	Abs	**ISO 6888-3**
Clostridium sulphito-reducer 46°C	Abs	**ISO 6461-2**

The standard requires the complete absence of fecal coliforms, staphylococcus aureus and clostridium sulfite-reducing 46°C, in gelatin, and the threshold at 10,000 germs/ml for the case of microorganisms revivable at 30°C.

IV.5. Use of ovine gelatin as a binder in the manufacture of alfa-based paper

The results of physico-mechanical characteristics of alfa pulp depending on incorporated gelatin concentration are given in **Table 9**.

Table 9. *Variation in physico-mechanical characteristics of refined alfa pulp at 20°SR depending on gelatin concentration.*

N° Tests	1	2	3	4	5	6
Gelatin (%)	0	0.4	0.8	1.2	1.6	2
°SR	20.5	20.5	20.5	20.5	20.5	20.5
Grammage (g/m^2)	73	77	75	77.8	74.8	75.8
Thickness (µ)	280	220	280	280	260	270
Breaking length (m)	1193	1250	1297	1912	1847	1817
Tear index (%)	65.2	69.6	73.4	77.5	77.5	81.6
Bursting index (%)	12.1	14.1	9.94	12	12	11.1
Air permeance (ml/min)	2000	2000	2800	2900	2800	2800

Compared to control test N°1 (0% gelatin), we notice a slight increase of grammage for paper samples containing gelatin from 2.7 to 6.65%, which is explained by a higher retention of fibers. .

A noticeable increase in breaking length from 4.78% for sample (2) to 60.26% for sample (4) with 1.2% gelatin. It should be noted that beyond 1.2% there is a relative stability of this breaking length.

A fairly significant increase in tear index of:

- 6.75% for sample N° 2 (0.4% gelatin).
- 12.58% for sample N° 3 (0.8% gelatin).
- 18.86% for sample N° 4 and 5 (1.2 and 1.6% gelatin).
- 25.15% for sample N° 6 (2% gelatin).

For bursting index, there is some stability. And concerning air permeance, we notice a significant increase (40 to 45%) with the tests containing 0.8, 1.2, 1.6 and 2% of gelatin

On the whole, these results are positive, since improving certain physico-mechanical properties, in particular the breaking length, tear and air permeance.

However, they are considered insufficient and this is probably due to the too degraded nature of collagen (gelatin = degraded collagen). Since most polypeptides are decomposed at temperatures above 32-35°C. And the gelatin used was withdrawn at 100°C. That is why we continued our tests with another form of the product, that is to say collagen in the form of dispersion.

IV.6. Use of ovine gelatin dispersion as a binder in the manufacture of alfa-based paper

IV.6.1. Determination of the viscosity of the dispersion at 1%

The viscosity results are shown in **Table 10**.

Table 10. *Evolution of the viscosity of the collagen dispersion (1%)*

Viscosity in Centipoises (Cps)	Collagen dispersion at 1% in $CH_2ClCOOH$ (pH = 3.85)	Collagen dispersion at 1% in H_2SO_4 (pH = 3.85)
Viscosity of the initial solution before dispersion	25	25
Viscosity of the solution just after the dispersion	510	125
Viscosity of the solution after 24 hours	1225	1325

There is a very significant evolution of viscosity; it passes in 24 hours, for the gel with sulfuric acid 25 to 1325 centipoise and 25 to 1225 centipoise for the gel with chloroacetic acid.

Both dispersions are in the form of viscous colorless gels, odorless and sticky to fingers. The collagen macromolecule is very complex. Given the very high resistance of its fibers to defibrillation and any form of mechanical destruction, further disintegration at a higher speed (20000 rpm) and for a longer time (about 5 minutes) would have been desirable.

IV.6.2. Determination of the viscosity of the dispersion at 2%

The viscosity results of both 2% dispersions are shown in **Table 11.**

Table 11. *Evolution of the viscosity of the collagen dispersion (2%)*

Time (min)	Before disintegration	0	5	10	15	20	30	45	1440
Viscosity in Cps	25	325	362	-	-	425	462	625	1375

There is a significant evolution of viscosity during treatment time, passing in 24 hours, from 25 Cps to 1375 Cps for both dispersions at 2%. These values are slightly higher than those of 1%.

IV.6.3. Mode 1 "Dispersion Coll.C"

By operating on the refined pulp at 24°SR and using 1% collagen dispersion in monochloroacetic acid at pH 3.85, we reported the results obtained in **Table12**.

Table 12. *Influence of collagen level dispersed in $CH_2ClCOOH$ (Coll.C) on physico-mechanical properties of a pulp from alfa (24°SR)*

Collagen C	0%	1%	2%
Grammage (g/m^2)	94	96	94
Thickness (µ)	220	220	210
Breaking length (m)	2252	3472	3688
Tear index (%)	89.6	130.4	135.6
Bursting index (%)	12.1	23.9	26.5
Air permeance (ml/min)	3000	2700	2300
Collage "COBB" (mg)	500	210	200
pH after collagen add	5.50	4.10	4.00

Examination of these results shows a consequent rise in physico-mechanical characteristics including bursting index, breaking length and tear index. This rise is slightly greaterthan that obtained with the dispersion prepared with sulfuric acid (**Coll.S**).

IV.6.4. Mode 2 "Dispersion Coll.S"

By operating on the refined pulp at 24°SR and using 1% collagen dispersion in sulfuric acid at pH 3.85, we reported the results obtained in **Table13**.

Table 13. *Influence of collagen level dispersed in H_2SO_4 (**Coll.S**) on physico-mechanical properties of a pulp from alfa (24°SR).*

Collagen S	0%	1%	2%
Grammage (g/m^2)	94	100	94
Thickness (µ)	220	220	180
Breaking length (m)	2252	3333	3404
Tear index (%)	89.6	106	130.4
Bursting index (%)	12.1	23	25.5
Air permeance (ml/min)	3000	2700	2200
Collage "COBB" (mg)	>500	229	200
pH after collagen add	5.50	3.85	3.75

We notice consequent increase in physico-mechanical characteristics of alfa pulps in which we have incorporated collagen, in particular breaking length, tear index, and bursting index; however, a decrease in collage index is observed.

We notice that the results of both modes are practically identical that is why we report the results obtained with mode 2.

IV.7. Determination of physico-mechanical characteristics of the pulp according to the degree of refining and the percentage of Coll.S

Table 14. *Variations in physico-mechanical characteristics of pulp according to degree of refining and percentage of collagen*

Refining degree °SR	20.5			29			36			50		
% Coll.S	0	1	2	0	1	2	0	1	2	0	1	2
Grammage (g/m^2)	73	88	82	76.1	82	86	76.1	87	90	79.3	88	92
Thickness (µ)	230	190	188	230	180	160	210	180	170	170	180	188
Breaking length (m)	1193	2510	2720	2502	3517	3820	3042	4660	4750	3520	5900	6123
Tear index (%)	65.2	68.2	73.3	63.5	80.1	82.2	62.1	94	105	61.2	159	168
Bursting index (%)	12.1	20	21.2	23.6	29.5	35	36	42	54	38.2	48	59
Collage "COBB" (mg)	>500	240	205	>500	200	190	<500	210	190	>500	200	185

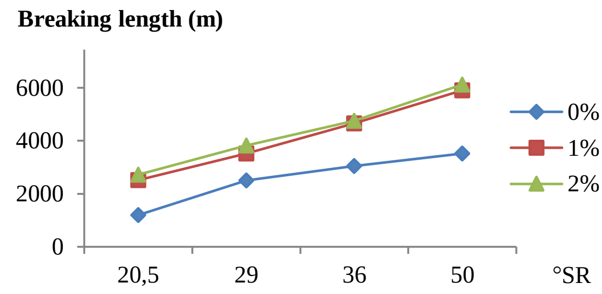

Figure 3. *Breaking length according to refining degree and collagen percentage.*

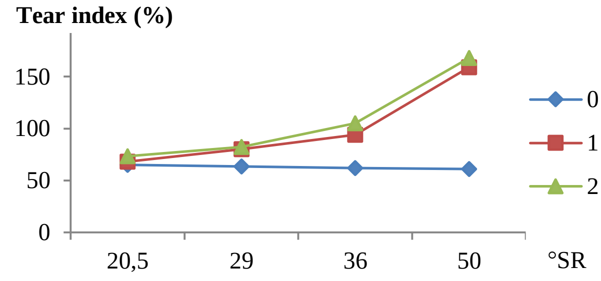

Figure 4. *Tear index according to refining degree and collagen percentage.*

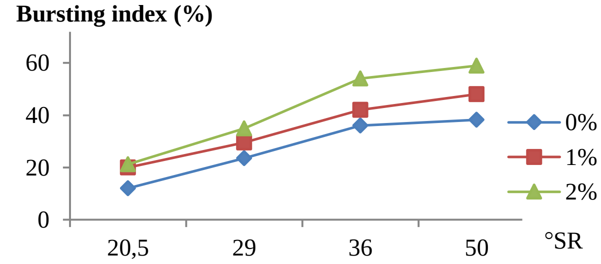

Figure 5. *Bursting index according to refining degree and collagen percentage.*

We notice consequent increase in physico-mechanical characteristics of alfa pulp formet in which we haveincorporated collagen, in particular the breaking length, tear index, and bursting index. In addition, we notice, diminution of collage index.

We also note that the presence of collagen increased breaking length. Indeed, a formet refined at 29°SR with 1% collagen, has the same breaking length (3517 m) as a formet at 50°C sans collagen (3520 m), or a refined pulp to 20.5°SR with 2% collagen has the same characteristics as a 30°SR paper without collagen (**Figure 1**).

All the physico-mechanical characteristics of a pulp refined at 30°SR and containing 2% of collagen are better than those of a 50°SR pulp without collagen.

Thus, we notice that we can obtain pulps having the same mechanical characteristics either by refining a pulp at 50°SR, or by incorporating 1% collagen into a pulp at 29°SR.

Indeed, we notice that the presence of collagen increased breaking length. Thus, a 29°SR refined formet with 1% collagen has the same breaking length (3517) as a 50° SR non-collagen form (3520), or a refined pulp at 20.5°SR with 1% collagen has the same characteristics as 29°SR paper without collagen.

Regarding collage coefficient (COBB), which measures water absorption in milligrams, it decreases sharply from 500 to 200 for the different tests; this is, of course, a sufficient advantage for some writing papers but insufficient for others (particularly high-consistency packaging papers and for which other pulps (eg: kraft) with longer fibers are more recommended because perform well.

IV.8. Comparison of physico-mechanical characteristics of alfa pulp with collagen with an alfa + vegetable resin pulp

At the level of the main Algerian industrial paper units, imported plant resins (for example abietic

acid $C_{19}H_{29}COOH$) are usually used as binder, at a rate of approximately 1%.
The work focused on an alfa pulp produced in a unit in the center of Algiers refined to 22, 32 and 50°SR degrees. A comparative study of physico-mechanical properties of the pulp in the presence of binding agents was carried out. The formets were tested and gave the results in **Table 15**.

Table 15. *Comparison of physicomechanical characteristics of the pulp at different degrees of refining in the presence of binding agents*

Refining time (min)	10				35				60			
Refining degree (°SR)	22				32				50			
Binders %	0%	1% Resin	1% Coll.S	2% Coll.S	0%	1% Resin	1% Coll.S	2% Coll.S	0%	1% Resin	1% Coll.S	2% Coll.S
Breaking length (m)	1400	2077	2700	2900	2700	3504	4000	4200	3520	4890	5900	6123
Tear index (%)	64	70	70	73	62.5	61.5	86	91	61.2	53.1	159	168
Bursting index (%)	14.5	14	22	23	31.5	24	37	44	38.2	32	48	59

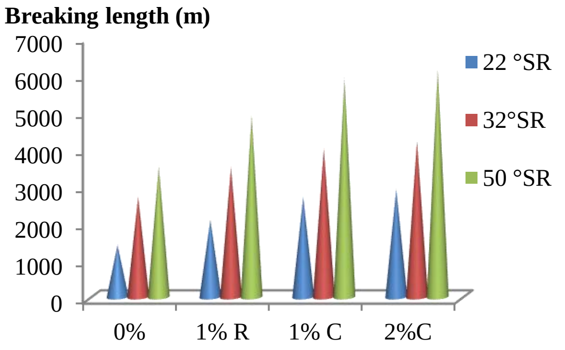

Figure 6.*Variation of breaking index of alfa paper according to the binder and degree of refining °SR.*

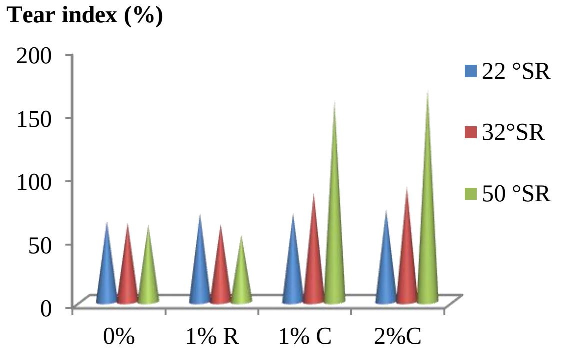

Figure 7. *Variation of tear index of alfa paper according to the binder and degree of refining °SR.*

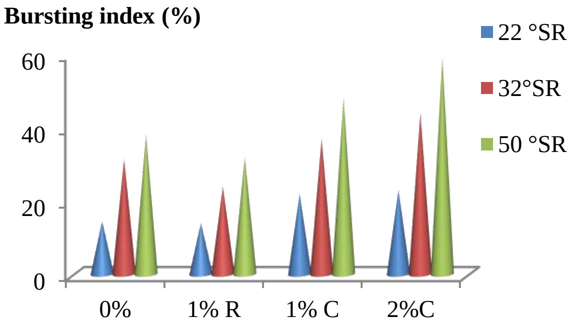

Figure 8. *Variation of bursting index of alfa paper according to the binder and degree of refining °SR.*

For the different tests and for all the values of the tested characteristics, we record substantial increases compared to those of the plant resin used usually (variation from 0 to 216%).

- The breaking length increases from +14.15 to + 39.62%.
- The tear index goes from 0 to + 216.38%.
- The bursting index goes from +50 to + 84.37%.

These increases are summarized in **Table 16** below:

Table 16. *Variation in physico-mechanical characteristics of alfa paper pulp with 1 and 2% collagen compared to those obtained with 1% of plant resin*

Characteristics	22 °SR		32 °SR		50 °SR	
(%) of collagen	1%	2%	1%	2%	1%	2%
Breaking length	+ 29.99	**+ 39.62**	+ 14.15	+ 19.86	+ 22.68	+ 27.32
Tear index	0	+ 4.28	+ 40.52	+ 48.69	+ 199.43	**+ 216.38**
Bursting index	+ 57.14	+ 64.28	+ 54.16	+ 83.33	+ 50.00	**+ 84.37**

V. Conclusion

Taking into account the results of the various previous analyses, it appears that the binder power of collagen incorporated in the form of gel (aqueous dispersion) with percentages of 1 and 2% to alfa pulps causes a significant increase in the values of the physical mechanical characteristics.

Compared with the results obtained with the plant resin usually used in paper industry and in the same proposals, the values are on the whole similar or even better, in particular as regards breaking length, tear and bursting index, which are essential properties for a paper.

On the other hand, we noticed that the mechanical properties of a paper with a lower degree of refining (eg. 30°SR) are comparable to those of another paper refined at 50°SR. This therefore saves time and especially important energy because the refining of cellulosic pulps is done using powerful machines (refiners) consuming a great deal of energy (we note that 25 minutes of additional refining are necessary to go from 35 ° to 50 ° SR).

Finally, it should be noted that the use of this type of collagen, is obtained from waste raw hides (ovine in this case) and which pose many pollution problems, can be substituted perfectly or serves as complementary materials to the plant resin currently being imported by paper industry.

However, before undertaking this type of operation, we should confirm or improve these results obtained in the laboratory, and this by conducting tests on an industrial scale. It is certain that a better control of dispersion conditions (time, pH and rate of collagen disintegration) with specific high-performance equipment, will contribute effectively to the achievement of this target.

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