# An investigation about the effect of oxazolidine on modified valonea extract tanning

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## Abstract

In this research it is aimed to combine usage of valonia or modified valonia with oxazolidine to obtain an increase in hydrothermal stability, thus to devolope tanning efficiency and to produce leathers that have better properties then the ones tanned with valonea only. On the other hand, oak trees, which produce tannins of valonea, grow in the western parts of Turkey and its extract is known as valex. So, an increase in valonea consumption was also expected.

Experiments conducted with 94 halfs of pickled kid skins that have same properties as a uniform party. Natural and three modified valonia extracts and oxazolidine were used as tanning materials. Skin samples were divided into two main groups according to the tannage system. In first group which was called A, valonia extracts were used as tanning materials in a fix ratio of 20% and oxazolidines as retanning ones. Group A was divided into 4 subgroups according to the used extracts types. And each subgroup was also seperated into four lots according to the oxozolidine percentages used (e.g. 0-2-4 and 6 which use as retanning materials). In group B, oxazolidines were used as pretanning agents and extracts as tanning materials. It has also three subgroups with 2-4 and 6% of used oxazolidine. Each subgroup had four lots according to the used extracts, e.g. natural and tree modified ones. Pelts were processed according to the design of research and their thickness and thermal stabilities were measured. Related official standarts were used in the research. General mean of Shrinkage Temperature (Ts) for group A was found as 78.62 $^{o}$C. For group B, in which primarly oxazolidines were used as pretanning materials, had an avarage mean Ts value of 83.42 $^{o}$C. General mean of shrinkage temperature for group B was found superior than group A and that means oxazolidine pretanning followed valonia retanning had beter tanning efficiency. On the base of uniqe experiment, 4% oxazolidine and 20% modified vegetable tannin combination has given the best result among others.

## Introduction

Vegetable tannins and tanning have kept their importance since a thousands year ago. Up to present, many researches on vegetable tannins have been realized on both single and combined use of them with other vegetable ones such as, aldehides, syntans and various metal salts. Although the vegetable tannins are thought as alternatives of chrome but superiority of the leather properties and tanning systems of second one has not reached a perfection yet. But new attemps are being made continously. On the other hand, oak trees which produce tannin of valonea, are grown in the western parts of Turkiye and its extract is known as valex. In this research it was aimed to combine usage of valonia, modified valonia and oxazolidine to obtain an increase in hydrothermal stability, thus to have beter tanning efficiency and to produce leathers that have better properties then single valonea tanned ones. So, an increase of valonea consumption was also expected.

On the other hand, chrome is still a problem for the leather industry. For example, chrome (III) turnes into chrome (VI) both in waste and leather with the effect of various factors. Discharge of chrome containing wastes have been restricted by environmentalists and laws due to chrome (VI) which has allergenic, toxsic, mutogenic and so carsinogenic influences. Because of these handicaps, many researches have been carried out which aim to find alternatives to chrome tanning by making use of new tanning materials and methods. [1] Vegetable tanning have always been one of the most important alternative as an environment friendly system and for that reason, researches on vegetable tannin combinations with oxazolidines, syntans, metal salts and others have been on focused.

Vegetable tannins with high molecular weights include lots of pheonolic OH groups and complicated organic materials. They are colloidal and soluble in alcohol, alcohol ether mixture and partly in acetic acid. They are not soluble in waterless ether, pethroleum ether and cloroform. But they can easily change their structures through oxidative, reductive and enzymatic effects. When they are heated they don’t dissolve but turn into coal. They generate sediment with gelatine, adhesive solutions, alcoholoids, amines and metal salts. Also they give characteristic colour reactions with iron salts. Vegetable tannins are adstrigenst and hydroscobic. In increasing temperatures their viscosity rise. They are polyphenolic compounds able to associate and combine with protein by different modes of interactions such as; hydrogen bonding, hydrophobic interactions and ionic interactions.

Vegetable tannins are classified in to two groups as hydrolysable tannins (pyrogallol) and condensed tannins (pyrocatechin). Hydrolysable tannins which are liable to decomposition by hydrolysis. They include gallotannins, derivatives of gallic acid and ellagitannins and derivatives of ellagic acid. Their phenolic aromatic compounds out of oxygen atom combined with glucose molecule by ester bonds. Hydrolysable tannins are investigated in three sub-groups as depsides, gallotannins and ellagitannins. We can give myrobalan, chesnut, valonia, sumac, tara and divi divi as a samples of hydrolysable tannins. [3,4,7,8,14,18,19]

Condansed tannins are not decomposed by hydrolysis but liable to oxidation and polymerisation to form insoluble products. Their principal molecules are flavan-3-ol and flavan- 3,4 diol. Condansed tannins have more stabil composition than hydrolysable tannins which cause phenolic aromatic compounds to combine with carbon atoms. Mimosa, quebracho, hemlock, willow and gambir are few samples of condansed tannins. [4,7,8,14,18,19]

Cross-linkage is effected by phenolic OH groups of vegetable tannins with carbonamid groups of collagen through hydrogen bridges. In other word, the cross-linking between leather and vegetable tannins are based on hydrogen briges. Hydrogen atoms of OH groups react with oxygen atoms of peptid groups in collagen (Figure I). Hydrogen bridges are optimal in acid region. [2,5,7]

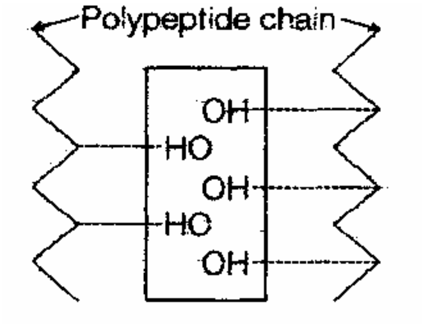
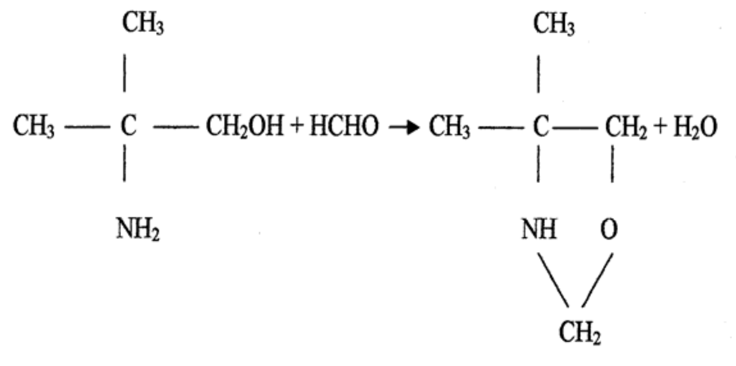



Figure 1 Cross-linkage of vegetable tannins with polypeptid chain

The other main chemical compound which was used in the research was oxazolidine. Oxazolidines are heterocyclic derivatives prepared from various amino alcohols and formaldehyde and although they possess some of the properties of aldehydes. Oxazolidines which are multifunctional agents do crosslinks with phenols and proteins. They can be use as pretanning or retanning agents. Tanning with oxazolidines increases the shrinkage temperature of the leather (Ts) . Oxazolidines are industrially important due to their ability to react with Novalac phenolic resines. These are large molecules obtained from condensation of phenols and cresols with formaldehyde. They also react with resorcinol, epoxies and proteins. [6,9,10,12,14]

The three most commonly encountered oxozolidines are oxazolidine A(I), E(II) and T. Oxazolidine A and E are yellow liquids . T is an off-white solid. [9] The chemical formulations of the three products are shown below in Figure 2,3 and 4:




Oksazolidin (I) A : 4,4-Dymethyl-1,3-oxazolidine

Figure 2 Oksazolidin (I) A 4,4-Dymethyl-1,3-oxazolidine

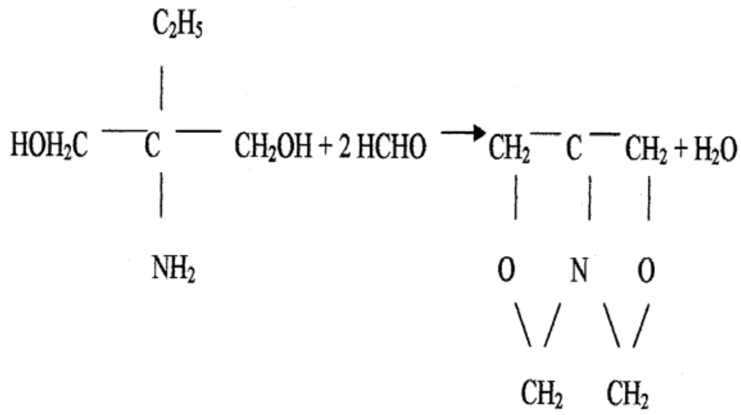



Figure 3 Oksazolidin (II) E : 1-Azo –3.7dioxabcyclo-5ethyl (3,3,0) octane

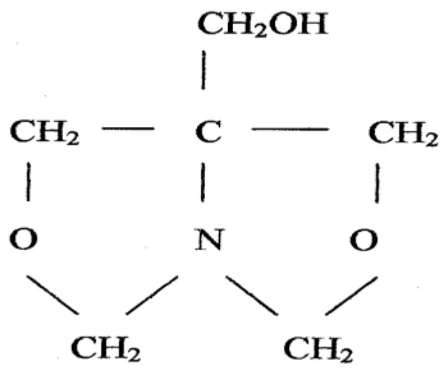



Figure 4 OksazolidinT: Hydroxymethyl-1-azo-3.7-dioxabcyclo(3,3,0) octane

Oxazolidine A (I) reacts too rapidly with protein and suggested as pretanning agent to increase the shrinkage temperature of pickled pelts for aqueous degreasing at higher temperatures thus leading more efficient degreasing. [9,12, 13, 14]

Although offered no theory as to the reaction of oxazolidines with hide protein, a reasonable explanation seems to be that cross-linkage may occur through the openning up of the heterocyclic rings by hydrolysis, followed by cross-linkage with amino groups in the protein chain. [9,12, 13, 14]

Oxazolidine II gives good results with chrome and vegetable tanin agents. It is suitable quiete different. When 20 % condensed tanins based on pickled pelt were used, Ts of leathers easily reached up to 100°C after retannage with 4-6 % oxazolidine E (II), even higher up to to be used in all types of leathers; especially in the tanning of wool-on leathers and this gives positive results on wool colour. [12,13,16,17]

In the event of tanning leather which is pretannned with Oxazolidine II we can see an increase in tanning rate, float exhaustion, Ts and even in less 50% float rates, exhaustion and decomposition. Oxazolidine usage in chrome tanning increases bath exhaustion so it’s important for environment control. Furthermore, leathers with high hydrotermal stability could be produced when vegetable tanned leathers are retanned by oxazolidine E (II) while their tensile strength, tear strength and perspiration resistance were also improved.

The shrinkage temperatures (Ts) of leathers produced by combination tannages of condensed tannins + oxazolidine E (II) and hydrolysable tannins + oxazolidine E (II) were 110°C when mimosa was used. On the other hand, when hydolysable tannins were used, the increase of Ts after retanning with oxazolidine E (II) was only a few degree. [9, 10,12,13,14]

The mechanism of condensed tannins – oxazolidine E (II) combination tannage can be described as the following: Vegetable tannins penetrate into pelt and are fixed with collagen fibers by hydrogen bonds. Then the fixations are enhanced through crosslinkages of oxazolidine E (II) during retanning. The crosslinkages are mainly contributed by electrophilic reaction between C-4 methylene of oxazolidine E (II) and C-6 and C-8 of condensed tannins. The interactions happens at ambient temperature and are enhanced when temperature is raised. Hydrolysable tannins are not as effective as condensed tannins in the combination tannage because they do not contain phloroglucinol structure responsible for crosslinkage of oxazolidine E (II). [9, 14,15] Oxazolidine T has not proved a usage like others yet.

The advantages of oxazolidine usuage are:

- Assistance in the production of soft leathers with improved uptake of chrome, considerably beter than using gluteraldehyde and without risk of staining the leather.
- Quicker chrome tannage with beter exhaustion.
- Wool-on skins can be tanned with the additional advantage of no wool staining or tipping.
- In vegetable leather tanning higher shrinkage temperatures may be achieved with improved degree of tannage and lower water solubles.
- Improved tensile, tear strengths, moist, heat and perspiration resistance.
- With chrome tannage a greater surface area of finished leather is obtained.

However there are some disadvantages :

- The price for 100 % oxazolidine E (II) is in excess of €2000 per metric tonne.
- Although non-toxic, its vapour is very irritating to the eyes.
- It has a pungent smell, harmless, but intolerable to many. [7,9,14]

## Materials and Methods:

### Materials:

Experiments conducted with 94 halfs of pickled kid skins that have same properties as an uniform party. Natural and three modified valonia extracts and oxazolidine were used as tanning materials. Commercial grade of chemicals were used in processing of the skins. Oxazolidine II* was used in an activity of 100% and sodium hydrogen sulphite** was at analytical reagent grade. Valone*** was purchased by the producer firm.

### Methods:

Previously, valonia extracts were modified. For this aim, the extracts were offered based on the pickled weight, dissolved by warm distilled water and heated up to 65 $^{o}C \pm 2$.

For the three types of modifications, sodium hydrogen sulphites were prepared as 5-10 and 15 % of valonia weights and added to each valonea solution drop by drop which stand at fixed temperature and the reactions were carried on for one more hour. Therefore, Modified Valonea Extracts of I, II and III were prepared in accordance with the sulphites respectively.

According to the experimental design, skin samples were divided into two main groups according to the tanning systems which would be applied. Three skins were used in each experiment. In the first group called A, valonia extracts were used as tanning materials in a fixed ratio of 20% and oxazolidines as retannings. Group A was divided into 4 subgroups according to the used extracts types. And all subgroups were also seperated into four lots according to the used oxozolidine percentages e.g. 0, 2, 4 and 6 % as retanning materials.

In group B, oxazolidines were used as pretanning materials and extracts as tanning agents. It had also three subgroups as 2, 4, 6 % of used oxazolidine. Each subgroup had four lots according to the used extracts, e.g. natural and three modified ones. The distributions of groups A and B are given in Table 1 and 2.

**Table 1. Distrubution of Subgroubs Related Group A**

| | |
|---|---|
| **NV :** Natural Valonia Extract | $\mathbf{A_1}$ |
| $\mathbf{MV_I}$ **:** Modified Valonia Extract I | $\mathbf{A_2}$ |
| $\mathbf{MV_{II}}$**:** Modified Valonia Extract II | $\mathbf{A_3}$ |
| $\mathbf{MV_{III}}$ **:** Modified Valonia Extract III | $\mathbf{A_4}$ |
| 0% Oxazolidine | $\mathbf{a_1}$ |
| 2% Oxazolidine | $\mathbf{a_2}$ |
| 4% Oxazolidine | $\mathbf{a_3}$ |
| 6% Oxazolidine | $\mathbf{a_4}$ |
| **Vegetable Tanning and Oxazolidine Retanning:** | |
| $\mathbf{A_1\ a_1}$ | 20% NV + 0% Oxazolidine |
| $\mathbf{A_1\ a_2}$ | 20% NV + 2% Oxazolidine |
| $\mathbf{A_1\ a_3}$ | 20% NV + 4% Oxazolidine |
| $\mathbf{A_1\ a_4}$ | 20% NV + 6% Oxazolidine |
| $\mathbf{A_2\ a_1}$ | 20 %$MV_I$ + 0% Oxazolidine |
| $\mathbf{A_2\ a_2}$ | 20% $MV_I$ + 2% Oxazolidine |
| $\mathbf{A_2\ a_3}$ | 20% $MV_I$ + 4% Oxazolidine |
| $\mathbf{A_2\ a_4}$ | 20% $MV_I$ + 6% Oxazolidine |
| $\mathbf{A_3\ a_1}$ | 20% $MV_{II}$ + 0% Oxazolidine |
| $\mathbf{A_3\ a_2}$ | 20% $MV_{II}$ + 2% Oxazolidine |
| $\mathbf{A_3\ a_3}$ | 20% $MV_{II}$ + 4% Oxazolidine |
| $\mathbf{A_3\ a_4}$ | 20% $MV_{II}$ + 6% Oxazolidine |
| $\mathbf{A_4\ a_1}$ | 20 %$MV_{III}$+ 0% Oxazolidine |
| $\mathbf{A_4\ a_2}$ | 20% $MV_{III}$+ 2% Oxazolidine |
| $\mathbf{A_4\ a_3}$ | 20% $MV_{III}$+ 4% Oxazolidine |
| $\mathbf{A_4\ a_4}$ | 20% $MV_{III}$+ 6% Oxazolidine |

**Table 2. Distrubution of subgroubs related Group B**

| | |
|---|---|
| 2% Oxazolidine | **$B_1$** |
| 4% Oxazolidine | **$B_2$** |
| 6% Oxazolidine | **$B_3$** |
| **NV :** Natural Valonia Extract | **$b_1$** |
| **$MV_I$:**ModifiedValoniaExtract | **$b_2$** |
| **$MV_{II}$:** Modified Valonia Extract II | **$b_3$** |
| **$MV_{III}$ :** Modified Valonia Extract III | **$b_4$** |
| **Oxazolidine Pretanning and Vegetable Tanning** | |
| **$B_1$ $b_1$** | 2% Oxazolidine + 20% NV |
| **$B_1$ $b_2$** | 2% Oxazolidine + 20% $MV_I$ |
| **$B_1$ $b_3$** | 2% Oxazolidine + 20% $MV_{II}$ |
| **$B_1$ $b_4$** | 2% Oxazolidine + 20% $MV_{III}$ |
| **$B_2$ $b_1$** | 4% Oxazolidine + 20% NV |
| **$B_2$ $b_2$** | 4% Oxazolidine + 20% $MV_I$ |
| **$B_2$ $b_3$** | 4% Oxazolidine + 20% $MV_{II}$ |
| **$B_2$ $b_4$** | 4% Oxazolidine + 20% $MV_{III}$ |
| **$B_3$ $b_1$** | 6% Oxazolidine + 20% NV |
| **$B_3$ $b_2$** | 6% Oxazolidine + 20% $MV_I$ |
| **$B_3$ $b_3$** | 6% Oxazolidine + 20% $MV_{II}$ |
| **$B_3$ $b_4$** | 6% Oxazolidine + 20% $MV_{III}$ |

Pickled pelts were processed according to the recepies shown in Table 3 and 4.

**Table 3. Process Recipe of Group A**

**Weight:** Pickled Weight + 50 %

| Process | Product | Amount (%) | Temperature | Duration | Notes and pH |
|---|---|---|---|---|---|
| Depickle | Water | 150 | 20-25 $^{o}$C | 10 min | 10 $^{o}$Be |
| | Sodiumformate | 1 | | 40 min | pH : 4.0 |
| | Sodium bicarbonate | 1.5 | | 40 min | pH : 6.6; drain |
| Tanning | Water | 100 | 20 $^{o}$C | | |
| | Valonia | 10 | | 90 min | |
| | Valonia | 10 | | 120 min | Over night in the float |
| | | | | | Morning 60 min run |
| | Water | | 20 $^{o}$C | 90 min | |
| | HCOOH | 0.25 | | 90 min | Horse |
| Retanning | Water | 200 | 20 $^{o}$C | | |
| | Oxazolidine | X | 35 $^{o}$C | 60 min | |
| | | | 40 $^{o}$C | 60 min | |
| | | | 50 $^{o}$C | 60 min | |
| | | | 60 $^{o}$C | 60 min | |
| | | | | | Horse |

**Tablo 4. Process Recipe of Group B**

**Weight:** Pickled Weight + 50 %

| Process | Product | Amount (%) | Temperature | Duration | Notes and pH |
|---|---|---|---|---|---|
| Depickle | Water | 150 | 20-25 $^{o}$C | 10 min | 10 $^{o}$Be |
| | Sodiumformate | 1 | | 40 min | pH : 4.0 |
| | Sodium bicarbonate | 1.5 | | 40 min | pH : 6.6 ; drain |
| Pre-Tanning | Water | 200 | 20 $^{o}$C | | |
| | Oxazolidine | X | 35 $^{o}$C | 60 min | |
| | | | 40 $^{o}$C | 60 min | |
| | | | 50 $^{o}$C | 60 min | |
| | | | 60 $^{o}$C | 60 min | |
| | | | | | Horse |
| Retanning | Water | 100 | 20 $^{o}$C | | |
| | Valonia | 10 | | 60 min | |
| | Valonia | 10 | | 120 min | |
| | | | 35 $^{o}$C | 60 min | |
| | | | 40 $^{o}$C | 60 min | |
| | | | 50 $^{o}$C | 60 min | |
| | | | 60 $^{o}$C | 60 min | |
| | | | | | Horse |

After processing, the thickness and thermal stabilities of leathers were measured. In the tests of the leathers, some related official standards were used such as Institution of Turkish Standards TS-4114 "Taking Samples for the Laboratory", TS-4115 "Conditioning of Samples for Physical Tests", TS-4117 "Measurement of Thickness", TS-4120 "Measurement of Shrinkage Temperature" which are identical with IULTCS and SLTC Test Methods.[20]

**Findings and Discussion:**

General mean of shrinkage temperature (Ts) for group A was found as 75.38 $^{o}$C. Means of subgroups $\mathbf{A_1}$, $\mathbf{A_2}$, $\mathbf{A_3}$, **and** $\mathbf{A_4}$ were 76.08; 75.50; 75.75; and 74.20 $^{o}$C respectively. All findings related to group A were given in Table 5.

Group B in which primarly oxazolidines were used as pretanning agents had a general mean of shrinkage temperature value as 83.42 $^{o}$C. Means of subgroups $\mathbf{B_1}$, $\mathbf{B_2}$ and $\mathbf{B_3}$ were also found as 83.96; 84.76 and 81.53 $^{o}$C in the given order. The results related to group B were shown in Table 6.

**Tablo 5. Findings Related Shrinkage Temperature (Ts) for Group A**

| **20% Valonia** | **% Oxazolidine** | **$T_s$ Min** | **$T_s$ Max** | **$T_s$ X±Sx** |
|---|---|---|---|---|
| NV | 0 | 65 | 67 | 65.66±1.15 |
| | 2 | 77 | 81 | 79.00±2.00 |
| | 4 | 79 | 82 | 79.66±2.08 |
| | 6 | 79 | 81 | 80.00±1.00 |
| **Mean** | | | | 76.08±6.44 |
| $MV_I$ | 0 | 65 | 67 | 65.66±1.15 |
| | 2 | 76 | 79 | 77.33±1.52 |
| | 4 | 77 | 79 | 78.00±1.00 |
| | 6 | 81 | 81 | 81.00± 0,00 |
| **Mean** | | | | 75.50±6.17 |
| $MV_{II}$ | 0 | 65 | 67 | 65.66±1.15 |
| | 2 | 76 | 78 | 77.00±1.00 |
| | 4 | 79 | 80 | 79.33±0.57 |
| | 6 | 80 | 82 | 81.00±1.00 |
| **Mean** | | | | 75.75±6.31 |
| $MV_{III}$ | 0 | 65 | 67 | 65.66±1.15 |
| | 2 | 72 | 73 | 72.33±0.57 |
| | 4 | 78.5 | 79 | 78.83±0.28 |
| | 6 | 79 | 81 | 80.00±1.00 |
| **Mean** | | | | 74.20±6.02 |
| **General Mean** | | 74.20 | 76.08 | 75.38±6.08 |

**Tablo 6. Findings Related Shrinkage Temperature (Ts) for Group A**

| % Oxazolidine | % Valonia | $T_s$ Min | $T_s$ Max | $T_s$ X±Sx |
|---|---|---|---|---|
| 2 | 20 NV | 84 | 86 | 85.33±1.15 |
| 2 | 20 $MV_I$ | 82.5 | 83.5 | 83.00±050 |
| 2 | 20 $MV_{II}$ | 81 | 81.5 | 81.16±0.28 |
| 2 | 20 $MV_{III}$ | 80 | 81.5 | 80.33±0.76 |
| **Mean** | | | | 83.96±3.36 |
| 4 | 20 NV | 84 | 85 | 84.66±0.57 |
| 4 | 20 $MV_I$ | 85 | 85 | 85.00±0.00 |
| 4 | 20 $MV_{II}$ | 83.5 | 85 | 84.16±0.76 |
| 4 | 20 $MV_{III}$ | 81 | 81.5 | 81.16±0.28 |
| **Mean** | | | | 84.76±2.56 |
| 6 | 20 NV | 80 | 81 | 80.33±0.57 |
| 6 | 20 $MV_I$ | 80 | 81 | 80.66±0.57 |
| 6 | 20 $MV_{II}$ | 80 | 81 | 80.33±0.57 |
| 6 | 20 $MV_{III}$ | 79 | 81 | 80.00±1.00 |
| **Mean** | | | | 81.53±2.56 |
| **General Mean** | | 81.53 | 84.76 | 83.42±3.11 |

When the results of group A were taken into consideration, it was clearly determined that shrinkage temperatures were increased along with increasing of oxazolidine offer. Subgroup of $A_1a_{1..}a_4$ had a minimum 65.66$^o$C and maximum 80.00$^o$C of shrinkage temperatures with a mean of 76.08 $^o$C**.** As for $A_2$ $a_{1..}a_{4,}$ min, max and mean were 65.66; 81.00 and 75.50 $^o$C respectively.The subgroup of $A_3a_{1..}a_4$ had the same parameters as min.and max. but mean was 75.75 $^o$C. In the last subgroup named $A_4$ $a_{1..}a_{4,}$ the three mentioned values were 65.66; 80.00 and 74.20 $^o$C in the given order. The general mean was 75.38 $^o$C.

When the group B was inspected, as for $B_1b_{1..}b_4$ min, max and mean were 80.33; 85.33 and 83.96 $^o$C.respectively. Subgroup of $B_2b_{1..}b_4$ had a minimum 81.16 $^o$C and maximum 85.00 $^o$C with a mean 84.76 $^o$C. In the last subgroub of $B_3b_{1..}b_4$ three mentioned values were 80.00; 80.66 and 81.53 $^o$C in the given order. The general mean was 83.42 $^o$C.

General mean of shrinkage temperature for group B was found superior than group A and that means oxazolidine pretanning followed by valonia tanning had beter tanning efficiency. On the base of uniqe experiment, 4% oxazolidine and 20% modified vegetable tannin combination has given the best result among others.

**Chemicals applied**

* Oxazolidine II (Munzig Chemie (%100))
** Sodium hydrogen sulphite (Merck )
***Valonia Extract (Balaban)

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