(REFEREED RESEARCH)

# DYEING PROPERTIES OF SIMPLE ACID AND METAL-COMPLEX DYESTUFFS ON THE LEATHERS TANNED WITH VARIOUS TANNING MATERIALS

# BASİT ASİT VE METAL KOMPLEKS BOYARMADDELERİN ÇEŞİTLİ TABAKLAMA MADDELERİ İLE TABAKLANMIŞ DERİLER ÜZERİNE BOYAMA ÖZELLİKLERİ

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**ABSTRACT**

Tanning materials used for production of leathers may vary according to the properties required and the field of use. Since different tanning materials react with different reactive groups of the collagen, this results changes in the reactive groups available for the chemicals that will be used in further processes. Simple acid dyes are the most common used dyestuffs in the leather industry, generally without considering the type of tanning. Starting from this point, it has been investigated the consumption and fastness properties of the simple acid dyes on the leathers tanned with various tanning materials. Chromium and aluminium from mineral tanning materials; tara, gambier and valonea from vegetable ones were selected for the trials. Simple acid dyes gave good consumption and fastness values for dyeing of mineral tanned leathers however the values for vegetable tanned leathers were relatively bad. 1:1 metal complex dyes were tried as an alternative, and the results of the trials were rather good for both the mineral and vegetable tanned leathers.

**Key Words:** Acid dyes, Metal-complex dyes, Leather dyeing, Tanning.

**ÖZET**

Deri üretiminde kullanılan tabaklama maddeleri, derinin kullanım alanına ve deriden beklenen özelliklere göre değişebilmektedir. Farklı türdeki tabaklama maddeleri kollagenin farklı grupları ile reaksiyona girdiğinden, bu ileriki işlem basamaklarında kullanılacak kimyasal maddeler için mevcut reaktif gruplarda değişime sebep olur. Basit asit boyarmaddeler, genellikle tabaklama türü gözönüne alınmaksızın, deri endüstrisinde en yaygın kullanılan boyarmaddelerdir. Bu noktadan hareketle, farklı tabaklama maddeleri ile tabaklanmış derilerin basit asit boyarmaddelerle boyandıklarında verdikleri tüketim ve haslık özellikleri araştırılmıştır. Denemeler için, mineral tabaklama maddelerinden krom ve alüminyum, bitkisel tabaklama maddelerinden ise tara, gambir ve valeks seçilmiştir. Basit asit boyarmaddeler, mineral tabaklanmış derilerin boyanmasında iyi tüketim ve haslık değerleri verirlerken bitkisel tabaklanmış derilerde değerler daha düşük bulunmuştur. Alternatif olarak 1:1 metal kompleks boyarmaddeler ile çalışılmış ve denemeler sonucunda hem mineral hem de bitkisel tabaklanmış derilerde oldukça iyi tüketim ve haslık değerleri elde edilmiştir.

**Anahtar Kelimeler:** Asit boyarmaddeler, Metal kompleks boyarmaddeler, Deri boyama, Tabaklama.

Received: 26.03.2009 Accepted: 13.09.2009

## 1. INTRODUCTION

During conversion of hides/skins to leather; non-fibrous proteins, carbohydrates and lipids, etc. are removed and only the fibrillar proteins remain. Amongst these fibrillar proteins, collagen is the major one with 98% amount (1). For this reason, leather can be defined as a protein based fibrillar network.

Collagen is a three-dimensional structure of the protein and consists of polypeptide chains which are made up of structural units (amino acids) that are linked to one another by peptide linkages. These structural units also have side chains, which often contain reactive groups such as carboxyl, amino, imino or hydroxyl.

As the hides/skins are protein based, they are putrescible by bacterial activity in wet-form until tanning process. The tanning process is the stabilization of the collagen matrix to retain a separated fiber structure and to increase the hydrothermal stability. This is the stage at which the pelt becomes 'leather' and is then resistant to putrefaction or rotting. Organic or inorganic based materials which are able to crosslink with reactive groups of the collagen are used in the tanning process. The reactive group used in fixation/binding differs depending on the type of the tanning material. For example; while mineral tanning materials (chromium, aluminum, and zirconium) react with carboxyl groups of the collagen; vegetable tannins,

aldehydes, and syntans react with amino groups. These reactions change the number of the reactive groups available, and charge balance of the collagen for further processes and chemicals.

The rate of fixation between the collagen structure and pre- tanning / tanning/retanning agents, dyes, and many polymeric resins and fatliquors is determined by the charge of the collagen and the charge of the product (2).

Chromium is the most common used tanning material in leather industry. As it reacts with carboxyl groups of the collagen, the ratio of available anionic/ cationic side-chains change, which makes the leather cationic (Isoelectric Point (IEP) change from 5.2 to 6.0). In this case, the most suitable dyestuffs for fixation to leathers are anionic dyes.

A dyestuff consists of two main groups: chromophore and auxochrome groups. Chromophore groups are one or more unsaturated bonds or groups giving the color of the dye molecule (3). Auxochrome is a functional group of atoms with nonbonded electrons which, when attached to a chromophore, modifies the ability of that chromophore to absorb light, and also determines solubility and charge of the dye molecule. Anionic dyes, amongst them simple acid dyes, are the most used dyestuffs in leather industry.

Acid dyes are salts of complex organic acids and they form an important group of leather dyes. According to the Colour Index, approximately 1000 leather dyestuffs are in use, and 70% of them are the acid dyes (4). Simple acid dyes are mainly low-molecular dyes. Their advantage consists in their low price and good dyeing and penetrating capacity, and in most cases they give clear, brilliant shades (5).

In recent years, the use of vegetable originated tannins as tanning materials has been increasing due to the interest and demand towards natural products. However, if the simple acid dyes are used for dyeing of these vegetable tanned leathers, which are anionic charged, the producers will possibly observe difficulties in fixation and fastness properties, since vegetable and synthetic tannins are aromatic substances which resemble dyestuff molecules in many respects (6) and react with the same groups of the collagen. For this reason we wanted to compare dyeing ability of the simple acid dyes on the leathers tanned with different types of tanning materials, as leather consists of protein fibers, and its reactivity toward dye is changed by the action of tannins (6). For this purpose, consumption rates and fastness properties of the simple acid dyestuffs were examined, since wet or dry dye migration to textile materials may cause big problems in leather product's use. Upon the problems observed on dyeing of vegetable tanned leathers, 1:1 metal complex dyes which are one of the subgroups of acid dyestuffs were tested to figure out if these dyes would be a solution to consumption and fastness problems.

**Table 2.** Tanning materials used in trials

| **Tanning Material Type** | | | **Commercial Name** |
|---|---|---|---|
| **Mineral** | Chromium | | Tankrom AB |
| | Aluminium | | Lutan B |
| **Vegetable** | Hydrolysable | Gallotannin | Tara |
| | | Ellagitannin | Valonea |
| | Condensed | | Gambier |

**Table 2.** Chromium tanning

| **%** | **Chemical** | **Time** | |
|---|---|---|---|
| 80 | Water + NaCl 7-8 $^0$Be' | | 25 $^0$C |
| 4 | Chromium | 20 min. | |
| 4 | Chromium | 5 h. | overnight |
| 2 | NaHCOO | 20 min. | |
| 0.*8* | $NaHCO_3$ | 75 min. | pH= 4.0 |
| | | | washing |

**Table 3.** Aluminium tanning

| **%** | **Chemical** | **Time** | |
|---|---|---|---|
| *80* | Water + NaCl 7-8 $^0$Be' | | 25 $^0$C |
| *7* | Aluminium | 20 min. | |
| *5* | Aluminium | 5 h. | overnight |
| *2* | NaHCOO | 20 min. | |
| *0.2* | $NaHCO_3$ | 75 min. | pH= 4.0 |
| | | | washing |

## 2. MATERIALS AND METHODS

### 2.1 Materials

South African originated 20 pickled sheep skins were used as materials. 5 different type of tanning materials were used in tanning of these skins. Chromium and aluminium from mineral tanning agents, and tara, valonea and gambier representing 3 different chemical subgroups of vegetable tannins were used in tanning (Table 1). After tanning, each leather was divided into 4 pieces, totally 80 samples were obtained. 2 pieces of leather samples were used for each dyeing. Each dyeing experiment was performed with two repetitions.

1 red and 1 black colored dyestuff both from acid dyes (*CI Acid Black 210, CI Acid Red 88*) and 1:1 metal complex dyes (*CI Acid Black 172, CI Acid Red 423*) were selected for dyeing of leather samples tanned with various tanning materials.

### 2.2 Methods

The pickled pelts for the conservation purposes, were depickled first (approx. pH=4.5). Then, acidic bate was applied to remove globular proteins and open up fibrous structure. Later, pelts were degreased to remove the natural fats. The samples that would be used for vegetable tanning were separated for tanning process, and the rest of the samples which would be used for mineral tanning were pickled and their pH values were adjusted to 3.0 for tanning.

The tanning recipes are given in Table 2, 3, and 4.

**Table 4.** Vegetable tanning

| % | Chemical | Time | |
|---|---|---|---|
| *80* | Water | | 25 $^0$C |
| *5* | Veg. Tannin | 10 min. | |
| *5* | Veg. Tannin | 10 min. | |
| *10* | Veg. Tannin | 8 h. | overnight |
| *x* | HCOOH | 30 min. | pH= 3.5 washing |

**Table 5.** Neutralization and Dyeing

| % | Chemical | Time | |
|---|---|---|---|
| 250 | Water | | 35 $^0$C |
| 1.5 | NaHCOO | 20 min. | |
| X | $NaHCO_3$ | | |
| 1 | Synthetic Fatliquor | 60 min. | pH 5.0 washing |
| 200 | Water | | 35 $^0$C |
| 3 | Dyestuff | 30 min. | |
| 5 | Combination of Fatliquors | 60 min. | 45 $^0$C |
| | HCOOH | 20 min. | |
| x | HCOOH | 20 min. | pH 3.5 washing |
| x | | | |

**Table 6.** Mean concentrations of dyestuffs remaining in dyeing baths (mg/l).

| Tanning material | Simple Acid Dyes | | Metal Complex Dyes | |
|---|---|---|---|---|
| | Acid Black 210 (mg/l) | Acid Red 88 (mg/l) | Acid Black 172 (mg/l) | Acid Red 423 (mg/l) |
| Chromium | 4.5 | 12.5 | 0 | 0 |
| Aluminium | 16.4 | 59.0 | 0 | 0.0011 |
| Tara | 70.4 | 58.8 | 0.018 | 0.019 |
| Valonea | 218.3 | 74.5 | 0.019 | 0.028 |
| Gambier | 75.3 | 92.4 | 0.123 | 0.255 |

**Table 7.** Mean values of wet and dry rubbing fastness of dyed leather samples.

| Tanning material | Acid Dyes | | | | Metal Complex Dyes | | | |
|---|---|---|---|---|---|---|---|---|
| | Acid Black 210 | | Acid Red 88 | | Acid Black 172 | | Acid Red 423 | |
| | Dry | Wet | Dry | Wet | Dry | Wet | Dry | Wet |
| Chromium | 3/4 | 2/3 | 2 | 1/2 | 4/5 | 3 | 3/4 | 3 |
| Aluminium | 2/3 | 1/2 | 2 | 1/2 | 3 | 1/2 | 3 | 1/2 |
| Tara | 3/4 | 1/2 | 2/3 | 1/2 | 4 | 4 | 4/5 | 3/4 |
| Valonea | 3 | 1/2 | 2/3 | 1/2 | 4 | 2 | 4 | 2 |
| Gambier | 3/4 | 2 | 2/3 | 1/2 | 4 | 2 | 4/5 | 2 |

The tanned leather samples were neutralized and dyed according to the recipe given in Table 5.

Samples were taken from the exhausted dyeing baths at the end of the dyeing process, and the amounts of remaining dyestuffs were measured by Shimadzu UV-1601 spectro-photometer.

The wet and dry rubbing fastness of dyed leathers were tested by using the ASTM Test Method D5053 “Color-fastness of Crocking of Leather” (7).

## 3. RESULTS AND DISCUSSION

Consumptions of the simple acid dyestuffs when used in dyeing of mineral tanned leathers have been found rather good, as expected and explained in the introduction.

Strong interactions of various types occur between mineral tannins and organic dyes. Mineral tanning agents in the form of soluble salts are capable of forming coordinate bounds with suitable residues of dyes in the inner sphere of the metal atom. Highly basic insoluble compounds of mineral tanning agents also react with both anionic and cationic dyes (6).

However, it was seen that, consumptions were worse, when simple acid dyestuffs were used in dyeing of vegetable tanned leathers. The reason for this is thought to be that: most of the functional groups that would react with the dyestuffs were reserved previously by the vegetable tannins in tanning process.

Vegetable and synthetic tannins are aromatic substances which resemble dyestuff molecules in many respects, thus they have nonionic coordination valencies. It is to be expected; therefore that dyestuffs and vegetable tannins can form addition compounds. This assumption is quite correct, but the degree of aggregation depends largely on the ionic groups present. If ionic groups of the same charge are present in both of the substances taking part in the aggregation, then the addition compounds are restricted to only a few molecules and these compounds are readily soluble(6).

When we look at the values of metal complex dyes, we see that they have excellent consumptions for all types of leathers tanned with tanning materials used. We think the reason for that is the great affinity of 1:1 metal complex dyes to protein fibers and complex forming ability of metals with vegetable tannins.

A concentration of 10 to 0.1 ppm dyes in the waste water comes out for an average tannery. Such a concentration is well below any level for concern for ecotoxicity and would hardly be visible in a well-mixed effluent. However, it should not be forgotten that low concentrations, that is more than 10 ppm of colorant in receiving waters,

can cause visible coloration and may raise public concern, although the low concentrations involved do not normally pose any significant environmental hazard (8).

Considering the wet and dry rubbing fastness values of the dyed leather samples, it is seen that the fastness properties of the leather samples are in accordance with consumption results: better for the samples dyed with metal-complex dyes than the samples dyed with simple acid dyes.

**4. CONCLUSIONS**

As the type of tanning material change, the sites available for reaction with dyestuffs may also vary, resulting different dyeing properties for the same dyestuff. While acid dyestuffs are very suitable for dyeing of mineral tanned leathers with their advantages of low price, brilliant shades, good dyeing and penetrating properties, they have consumption and fastness problems in dyeing of vegetable tanned leathers. For better dyeing properties in vegetable tanned leathers, it is advisable to use 1:1 metal complex dyes which are known with their good light fastness, washing properties and good levelling capacities (5). Additionally, use of 1:1 metal complex dyes in vegetable tanned leathers is also helpful with their high consumption values, for reducing the amount of dyestuff discharged to environment or needed to be treated.

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*Bu araştırma, Bilim Kurulumuz tarafından incelendikten sonra, oylama ile saptanan iki hakemin görüşüne sunulmuştur. Her iki hakem yaptıkları incelemeler sonucunda araştırmanın bilimselliği ve sunumu olarak **"Hakem Onaylı Araştırma"** vasfıyla yayımlanabileceğine karar vermişlerdir.*


Fiona Fairhurst, ünlü deniz modası ve spor markası Speedo firmasının Fastskin Mayosu ve bu teknolojideki gelişmeler, gözleri profesyonel yüzmede dünya rekorları ve olimpiyat madalyaları kazanan yeni "gümüş kurşunlara" çevirdi.

Çığır açan "Fastskin" mayosu Speedo'da bir tekstil uzmanı olarak çalışan ve ar-ge ekibinin başına geçen Fiona Fairhurst ve ekibi tarafından tasarlandı. Mayoyu, insan vücudunu daha "hidrodinamik" hale getirmek yani suyun içerisinde süzülmesi esnasında en küçük su direncine maruz kalabileceği biçimde tasarladılar.,

Fairhust'un takimi köpek balıkları üzerine odaklandı. Vücutları su altında yoğun türbülansa neden olmasına rağmen oldukça çevik yüzücülerdi. Speedo'nun öğrendiği sır, köpek balıklarının derisine dayanıyordu. Dişçikler (denticle) içeren küçük sırtlardan oluşan bir desene sahipti. Bu yapı, köpek balığı yüzeyken ona temas eden su miktarını azaltıyordu.