# Two Stage Leather Dyeing — A Novel Approach to Minimize the Dye Discharge in the Effluent

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## Abstract

Large quantities of synthetic dyes are used in tanneries for coloring leathers. A significant portion of the dyes offered do not fix to the leather and the un-utilized dye is discharged in the effluent, which may be environmentally harmful as it may require a long time for degradation. Depending upon the wastewater treatment methods adopted, sometimes these dyes may generate several highly toxic compounds. These dyes, when discharged into water bodies or land, may also cause severe environmental and health problems. Up to 10% (weight/weight of leather) dye is used in the dyeing process of conventional leather making. There are several physiochemical methods reported for treatment of dyes in effluent, which mainly degrade and remove the dye in effluent and do not aim for recovery and reuse of dye. In the present study an attempt has been made to modify the dyeing process in such a way that minimum dye is discharged in the effluent. Most of the un-utilized dye is recovered and recycled or re-utilized in subsequent dyeing. The visual and instrumental examination of the dyed leathers with this modified dyeing method led to encouraging results. This approach has not only reduced the dye discharge after dyeing but also facilitated substantial reduction in dye input by reuse thereby providing economic benefit to the tanners. The study was carried out for a specific synthetic acid dye and should be also be easily extended to other class of dyes.

## Resumen

Grandes cantidades de colorantes sintéticos se utilizan en las curtiembres para colorear cueros. Una parte significativa de los colorantes que se ofrecen no se fijan al cuero y el colorante no utilizado se descarga en el efluente, lo que puede ser dañino para el ambiente, ya que puede requerir mucho tiempo para su degradación. Dependiendo de los métodos de tratamiento de aguas residuales adoptados, a veces estos colorantes puede generar varios compuestos altamente tóxicos. Estos colorantes, cuando se descargan en los cuerpos de agua o tierra, también puede causar graves problemas ambientales y de salud. Hasta un 10% (peso / peso de cuero) del colorante se utiliza en el proceso de teñido en la fabricación convencional del cuero. Hay varios métodos físico-químicos reportados para el tratamiento de los colorantes en los efluentes, que degradan y eliminan principalmente el colorante en los efluentes y no tienen como objetivo la recuperación y reutilización de colorante. En el presente estudio un intento se ha hecho para modificar el proceso de tintura de tal manera que una mínima cantidad del colorante se descarga en el efluente. La mayoría de los colorantes no utilizados se recupera y se recicla o reutiliza en posteriores tinturas. El examen visual e instrumental de los cueros teñidos con este método de tintura modificada ha dado resultados alentadores. Este enfoque no sólo ha reducido la descarga de colorante después del teñido, sino también facilitó la reducción sustancial de la oferta de colorantes por la reutilización de tal modo que proporciona beneficios económicos a los curtidores. El estudio se llevó a cabo para un colorante ácido sintético específico y debería también extenderse fácilmente a otra clase de colorantes.

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## Introduction

Leather making involves a number of process steps and in most of these process steps water is used as the medium. Generally, 25 to 45 liters of water per kilo of rawhide or skin are being used by tanneries for processing different types of leather and almost the same quantity is discharged as effluent[1] The effluent from the drum yard is often colored mainly because of dyes that are used for coloring the leather. Many of the color bearing compounds from spent dyeing baths are toxic to aquatic, plant and animal species. These compounds exhibit slow degradation kinetics for conventional treatment processes. Acid dyes and direct dyes are some of the most commonly used dyes in the leather and textile industries as they are quite versatile in nature. Approximately half of all known dyes are these classes of dyes, making them the largest group of synthetic colorants'.[2, 3] These dyes are neither totally utilized during the process, nor are they totally recoverable at the end of the process in conventional manufacturing process. In fact, during the process of dyeing in the leather industry, depending upon the shade, dyes up to 5% (wt/wt of skin) and in some cases up to 10% are used for dyeing and often more than 30% of the dye used is discharged in the effluent. Hence, there is a need to remove the residual dye from the large volume effluent in order to overcome environmental concerns. Dye-containing effluents are typically treated by physical (absorption), chemical and biological methods[4]. The drawback with all of these methods is the duration of the treatment, which normally ranges from 24 h to 6 days. Adsorbents suitable for wastewater treatment include charcoals, activated carbons, clays, soils, diatomaceous earth, activated sludge, compost, and plant communities. The biomass such as chitin, chitosan, microbial biomass, unmodified lignocelluloses; chemically modified cellulose and lignocelluloses could also be used for decolorization of dyes containing effluents.[5] The disadvantage of adsorption processes is that the adsorbent needs to be regenerated, which adds to the cost of the process, and is sometimes very time-consuming. Chemical treatments for decolorization of wastewater include reduction, oxidation, complexation reactions, ion exchange and neutralization. The bacterial species capable of removing the color from dye effluent are reported to do so mainly by adsorption into their cell membranes[6]. The degradation of dye chemicals in wastewater by the bacterial species was achieved only by enzymatic reduction/oxidation reactions[7]. There are reports that enzymes, both fungal as well as bacterial, have been employed in dye wastewater treatment.

In the present study an effort has been made to modify the dyeing process in such a way that a very minimum quantity of dye is discharged in the final effluent and the majority of unfixed dye is recovered and recycled in the subsequent batches for leather dyeing thereby gaining economic and environment benefits.

### Leather dyeing

The nature of tanning determines the type of dye to be used for leather dyeing. Acid dyes for example can react with both chrome and vegetable tanned leathers but basic dyes can react or impart color to vegetable and not to chrome tanned leather directly.

### Conventional dyeing

Typically in conventional dyeing system the quantity of dye used is decided based on the target shade required in the leather. The dye along with water is applied to a rotating drum for a specific period of time. After ensuring penetration of the dye, the fixation on the leather is ensured by adjusting to a pH of 3.0 – 3.5 using formic acid. The leathers were then subsequently fatliquored and fixed with an acid.

### Two stage equilibrium dyeing

In the new method the leathers are drummed with the dye for specific period of time. On ensuring penetration of the dye, the used dye liquor is collected separately for reuse and only the leather with the dye that has been penetrated is adjusted to pH 3.0-3.5 in order to fix the dye. The leathers are then fatliquored in the conventional way to impart softness.

### Two stage with 20% excess dyeing to match shade

In the case of two stage dyeing with excess dye, the leathers are treated with dye separately and fixed separately as per the procedure explained in previous section. From the segregated dye bath, 20% (percentage arrived based on separate trials with various percentages for the chosen dye) is used again in fatliquoring in order to achieve the required color intensity.

## Experimental

### Materials and method

The various chemicals and specialty chemicals used in the dyeing procedures includes An acid dye (Colodorm dark brown EFB), Vegetable fatliquor Lipoderm liquor FB20, Synthetic fatliquor Lipoderm liquor SAF, (both the fat liquors were used for fat liquoring), sodium formate and sodium bicarbonate (for neutralization), Formic acid (for fixing), Wet blue bovine leathers.

The following steps were followed before and after dyeing.

- Neutralization
- Dyeing
- Fixing

The steps involved in the process and the amount of various chemicals added are shown in Table 1.

**TABLE 1**
**Process details for making full chrome cow upper leather**

| PROCESS | Water and chemicals added (% based on weight of wet blue shaved skins) |
|---|---|
| The wet blue skins/hides were shaved to 1.0 mm thickness | |
| Washing | Water 200% (10”) |
| Neutralization | Water 200%<br>Sodium formate 1%, --10min<br>Sodium bicarbonate 1%<br>(3*10” + 30”)<br>pH 5.0-6.0 |
| Washing | Water 200% (10”) |
| Dyeing | Water 200% |
| Dye 2% or 4% (40”) | |
| Fat liquoring and fixing | Water 200%<br>Fat liquor 5% (40”)<br>Formic acid 1.0% (3*5” + 20*) |
| Washing | Water 200% (10”) |

**Neutralization**
Wet blue leather was cut to the required size and soaked in water. Sodium formate and sodium bicarbonate were the chemicals used for neutralization. The amount of chemicals and water used were calculated based on the weight of the leather. Around 200% V of water per W of hide was added. 1% W/W of sodium formate and sodium bicarbonate were used and dissolved in 100% V of water. Neutralization was allowed to take place for 40 minutes.

**Dyeing**
Dyeing experiments were conducted with 2% and 4% dye. The required amount of dye was dissolved in water equivalent to 20% float. To the neutralized leather pieces 200% V/W water was added. The prepared dye solution was then added. The dyeing was carried out for 40 minutes.

Three different fixing steps were followed:

- Single stage — (conventional dyeing)
- Two stage — (equilibrium dyeing)
- Two stage with excess dyeing of 20%

In single stage dyeing method (conventional dyeing) the neutralized leather is treated with required amount of dye and subsequently with fat liquor. Finally they are fixed with formic acid. In two stage (equilibrium dyeing) method the neutralized leathers are treated with the equal amount of dye as in conventional dyeing process. After specific duration of drumming, the dye bath was removed and collected separately for reuse. To the drum with dyed leathers fresh water was added, subsequently fat liquor was added and finally fixed with formic acid. In two-stage with excess dyeing of 20% method and similar to equilibrium dyeing, after specific duration of drumming, the dye was quantitatively removed for reuse. Then 20% of the spent dye bath and required amount of water was added to the drum. The leathers were subsequently fat liquored and fixed with formic acid. The schematic representation of this new method in comparison with the conventional single stage method is shown in Figure 1.

**Fatliquoring and fixing**
For conventional dyeing, 5% of fat liquor was added and drummed for specific duration and finally 1% of formic acid was added in parts for fixing. In two-stage or equilibrium dyeing process, water equal to the amount of removed dye solution was used and 5% fat liquor was added, drummed for specific duration and finally 1% of formic acid was added in parts for fixing. In excess dye percentage process, 20% of the spent dye solution along with water equal to the removed dye solution. The amount of fat liquor and formic acid used were similar to the single stage process. Samples were collected at regular intervals during dyeing and fixing steps to obtain the profile of dye uptake by leather at different time intervals. Finally, the leathers were rinsed in water and piled overnight for ageing and next day the leathers were dried and color values were measured.

## RESULTS AND DISCUSSIONS

Experimental trials with acid dye (Coloderm dark brown EFB) 2% and 4% on full chrome bovine upper leathers reveal the following observations. Figure 2 shows the amount of dye present in dye bath at the end of dyeing process. In conventional dyeing for 2% dye offer, at the end of dyeing process 17.8% of total dye used was still present in solution unfixed to the substrate. In the case of 20% excess over equilibrium dyeing, unfixed dye present in water was about 4.0%, slightly higher than the equilibrium dyeing of 3.8%.

Table 2 shows the color values of leather obtained by various dyed leather. Two stage dyed leather lies towards whiter region compared to single stage dyed leather (control) while 20% excess and control leather lie around the same value towards the black region. The dyed piece in conventional and the 20%excess stages are reddish. The color angles of both 20% excess and conventional dyeing lie in the same quadrant. The color intensity of 20% excess matches that of control but color intensity of two stage varies from control. Thus it can be concluded from this table that the color of leathers by conventional dyeing and 20% excess over equilibrium dyeing matches to a large extent matching industry acceptance levels.

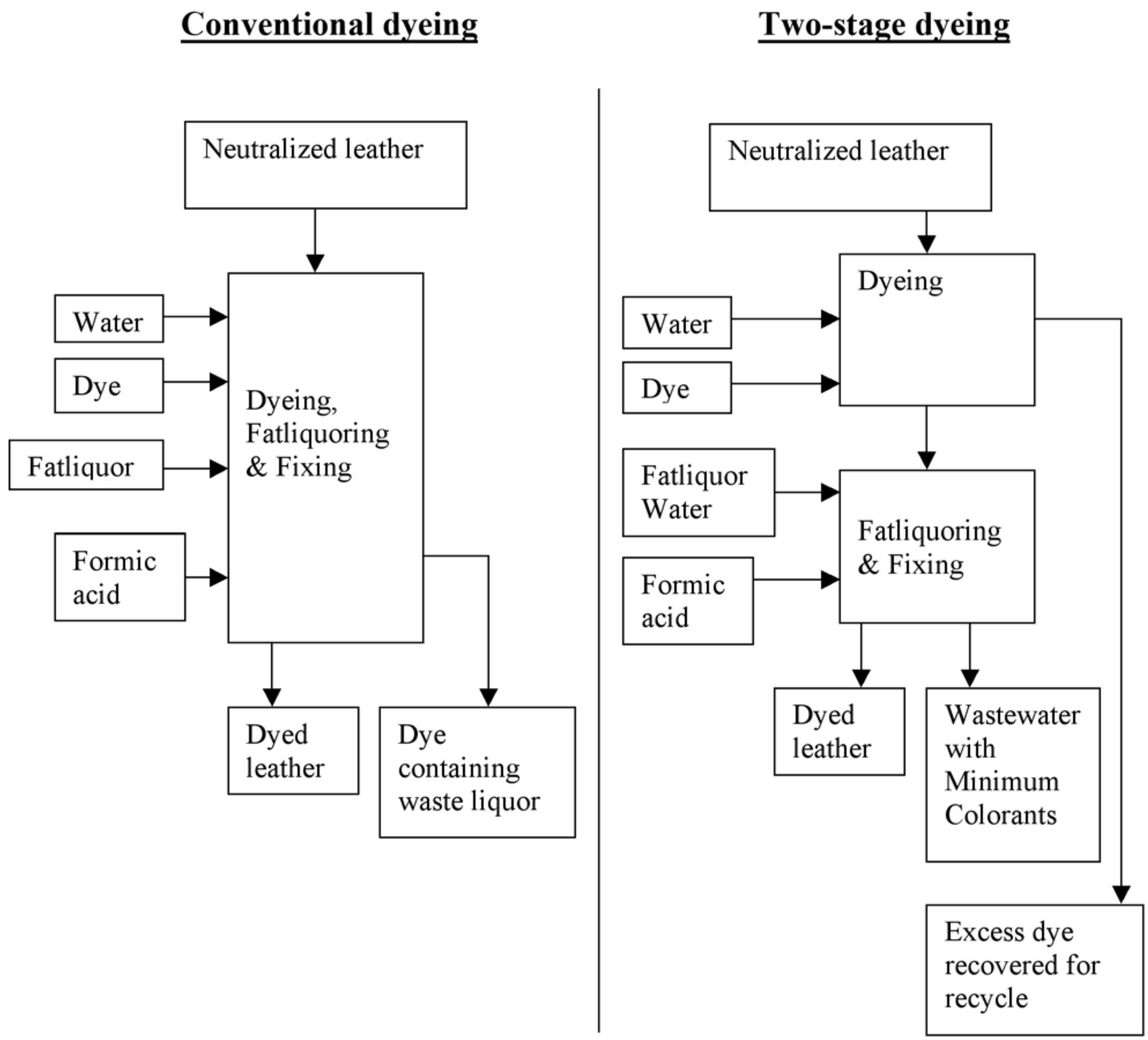


Figure 1. Conventional dyeing vs. Two-stage dyeing

However the equilibrium dyeing produces shades much lower than the target shade, which may not be acceptable.

Figure 3 shows the amount of dye present in dye bath at the end of dyeing process for 4% dye offer. In conventional dyeing, at the end of dyeing process 23.5% of dye was still present in solution without fixing on the substrate whereas in equilibrium dyeing the dye content was 3.9% In case of 20% excess over equilibrium dyeing, dye present in water is about 4.5% higher than the equilibrium dyeing.

Table 3 shows the color values obtained by various dyed pieces. Two-stage dyed leathers lies towards whiter region compared to control while 20% excess and control lie around the same value towards the black region. The dyed pieces in conventional and the 20% excess stages are reddish. The color angles of both, in 20% excess and in conventional dyeing, lie in the same quadrant. The color intensity of 20% excess matches that of control but color intensity of two-stage method varies from control. Thus it can be concluded from this table that the colors of leathers by conventional dyeing and the 20% excess over equilibrium dyeing match to a reasonable extent. However the equilibrium dyeing produces shades much lower than the target shade. The results are similar to the results obtained with 2% dye input.

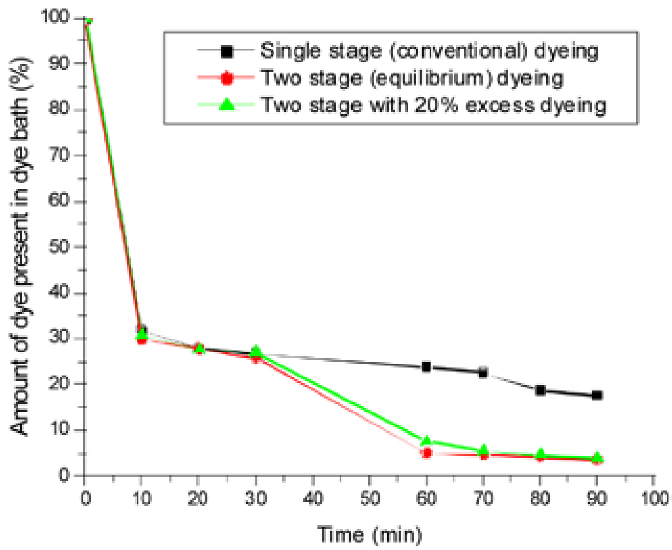


Figure 2. Amount of dye present in solution (2% dye offer)

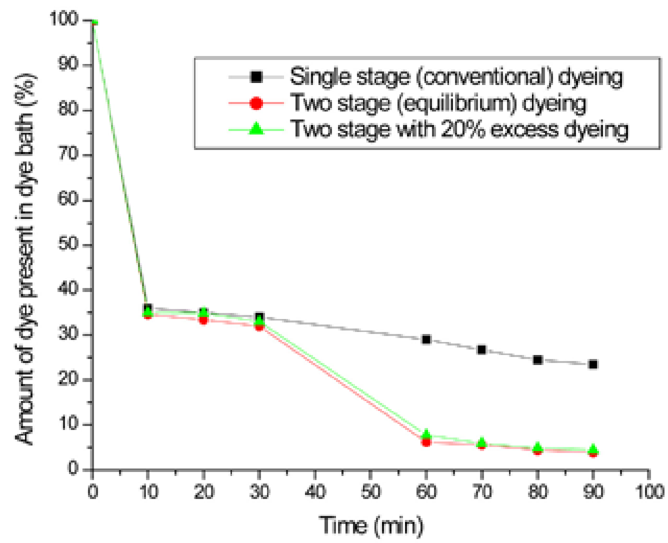


Figure 3. Amount of dye present in solution (4% dye offer)

**TABLE 2**
**Color value of dyed leathers (2% dyeing)***

| Dyeing method | CIE and CH color values | | | | |
|---|---|---|---|---|---|
| | **L** | **a** | **b** | **c** | **h** |
| Single stage | 5.52 | 4.57 | 2.63 | 4.21 | 39.50 |
| Two stage | 16.50 | 7.75 | 8.70 | 1.14 | 47.46 |
| Two stage with 20% excess | 3.86 | 3.97 | 4.56 | 5.14 | 40.10 |

*These values are the average values of 3 measurements

**TABLE 3**
**Color value of dyed leathers (4% dye offer)**

| Dyeing method | CIE and CH color values | | | | |
|---|---|---|---|---|---|
| | **L** | **a** | **b** | **c** | **h** |
| Single stage | 4.52 | 3.37 | 2.52 | 4.21 | 36.80 |
| Two stage | 10.50 | 7.34 | 8.72 | 1.14 | 49.92 |
| Two stage with 20% excess | 4.86 | 3.87 | 3.381 | 5.14 | 41.10 |

*These values average values of 3 measurements

## CONCLUSION

The leather manufacturing industry produces a large quantity of effluent that often include unfixed dye and this may cause health and environmental problems. There are several physico-chemical methods reported and they are mainly to remove or degrade the dye from the effluent. In the present study an effort has been made to modify the dyeing process in such a way that discharges in the final effluent will contain minimum dye. This study leads to the following conclusions:

- Two-stage equilibrium dyeing discharges much less dye in the effluent compared to conventional dyeing, but the shade obtained by this method does not match the conventional dyeing.

- Two stage with 20% excess dyeing in the fatliquoring also discharges much less dye in the effluent compared to conventional dyeing and the shade obtained by this method closely matches with conventional dyeing. So this method of dyeing not only meets the final shade requirement but also discharges less dye effluent (77 to 81% reduction) compared to conventional dyeing. The dye recovered by this method can be used for subsequent dyeing that will lead to economic gains apart from minimizing environmental losses.

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