

Evaluation of Dye Fixatives – A Comparative Study

by

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Abstract

Dyeing is the important unit process in leather manufacturing, which adds value to the leather. Although formic acid is used for fixing of dyes in leather processing, difficulties do arise in fixation of certain dye stuffs. Further high quantities of formic acid used do create health issues and adds to high cost of production. Compounds such as formic acid, acetic acid, mixture of organic acids and quaternary ammonium compounds have been found to function as dye fixatives. The efficacy of these compounds to function as dye fixatives for various dye stuffs and substances either alone or along with formic acid has been studied in detail in this work. The physical and color characteristics of leather and spent liquor analysis have been carried out.

Introduction

In leather making dyeing is one of most important process because it gives aesthetic look to the leather. Dyeing is necessary to satisfy the sophisticated tastes of the modern person and should keep abreast of the changing fashion trends in color. The final appearance and value of leather is decisively influenced by the color characteristics. Dyeing assumed much greater significance in modern leather finishing particularly with increase in demand for leather for lifestyle products.¹ Conventionally, the following dyes are used in leather processing - acid dyes, direct dyes, metal complex dyes, basic dyes, natural dyes and reactive dyes. The characteristics of dyestuffs have great impact on the color of leather.² The main characteristics of dyestuffs can be described as:

- Shade build-up properties and saturation limit
- Affinity of the dyestuff
- The migration power of a dyestuff
- Fastness and other properties

Dyeing parameters such as dye concentration, temperature, float, initial pH, penetration, fixation time and fixing agent, fixation pH are not the same for all cases and all these have effect on the color of the leather.^{3,4} Unlike textile dyeing, one deals with a three dimensional matrix in leather dyeing and hence the problems become more complex.⁵

Around the turn of the 20th century, mineral acids were being replaced by less destructive weak acids in the leather dyeing process.^{6,7} Formic acid is one such weak acid and has been a popular choice for the dyeing process. Formic acid is traditionally used by the tanning industry during the retan, dyeing and fatliquor processes in order to lower the pH, for the uptake of dyes (particularly acid dyes and anionic dyes) during the dyeing process.⁸ Weak acids have also been selected over mineral acids due to greater dye levelness and penetration. Unfortunately, like mineral acids, workers in the tanning industry must handle concentrated formic acid with extreme care since it is a relatively corrosive liquid and exudes noxious vapors. Other limitations of formic acid as a fixative are its inability to provide the same level of fastness and exhaustion for all types of dyes and its cost.⁹

A safe alternative to formic acid in the dyeing process would be highly desired if the alternative not only demonstrated to be an equally efficient but also cost effective replacement. Lots of research has been taken up to evaluate various auxiliaries for dye fixing.¹⁰⁻¹⁶ In this study an attempt has been made to study the efficacy of different dye fixing agents in order to find their usefulness in leather dyeing.

Experimental

Commercial dyestuffs have been purchased from Clariant (India) Ltd for the study. Commercial grade chemicals are used as fixing agents. The main objective of this study is to analyze different dye fixing agents in order to find their efficacy. Experiments were performed using following fixing agents.

Table I
Types of fixing agents

| Experiments | Chemicals used |
|-------------|--|
| Expt 1 | Formic acid |
| Expt 2 | Benzyl triethyl ammonium Chloride |
| Expt 3 | Tetra butyl ammonium bromide |
| Expt 4 | Acetic acid |
| Expt 5 | Formic acid and Acetic acid mixture (in 1:1 ratio) |

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Preparation of Leather Samples

Chrome tanned goat skins were neutralized, fatliquored, retanned and dried. The crust leathers were rehydrated uniformly and taken for dyeing experiments. The dyeing process is given in Annexure.

Exhaustion Studies

The leathers are dyed with 5% (on the crust weight) of all type of dyes and fixing was done with all the fixing agents (5% on the crust weight) except acetic acid which was used at 7% level (based on preliminary studies to match the exhaustion behavior of formic acid). The spent liquor was analyzed through Spectrophotometer for exhaustion levels. Optical Density (OD) values for different dyes were taken and calibration curves were prepared.

Color Value of Dyed Crust Leathers

Quantification of the color values of conventional and experimental dyed crust leathers were made by reflectance measurements. This assessment is more accurate and it signify hues (h^*), Chromaticity (C^*) and actual color difference (DE). In this assessment, color values can be determined by using Gardner's tristimulus colorimeter and measured in terms of 'L', 'a', 'b'. The values indicate, the greater the **b** value more yellow and lesser the **b** value greater the blueness. Greater the **L** value, greater its brightness and lesser the **L** value, lesser the brightness or more darkness, lesser the **a** value, greater is the greenness and greater the **a** value more of redness of samples. From the color value of our experimental leather color difference was calculated on basis of comparison with the Experiment - 1 as standard.

$$E = \sqrt{(L_s - L_{T1})^2 + (a_s - a_{T1})^2 + (b_s - b_{T1})^2}$$

L_s, a_s, b_s – standard color

L_{T1}, a_{T1}, b_{T1} – Experimental color values

Plotting of graph

$$\text{Chromaticity} = \sqrt{a^2 + b^2}$$

Color Fastness

Wet rubbing, dry rubbing and light fastness tests were done to ascertain the fastness of dyed leathers fixed by different chemicals.¹⁷

Physical Testing of Leathers

Testing is a very important part of the leather manufacturing process. When trying to improve the quality of leathers, testing is necessary in order to ascertain the functional properties. Hence tensile strength, elongation at break, tear strength, fastness of color to wet and dry rubbing have been analyzed according to standard procedures.^{18,19}

Results and Discussion

Exhaustion of Dyes

The dye spent liquor was analyzed and described in Table II. It is observed that formic acid is consistent in exhaustion levels with each class of dyestuffs. Use of acid mixture resulted in better exhaustion when compared with acetic acid with all dye stuffs. Benzyl triethyl ammonium Chloride and Tetra butyl ammonium bromide yielded moderate with acid, direct, metal complex 1:1 and poor with metal complex 1:2 dye stuffs. Better exhaustion of dyes also results in effective dye removal in the effluents.²⁰⁻²²

Table II
Spent Liquor Exhaustion

| S.No | Dyes | Expt-1 | Expt-2 | Expt-3 | Expt-4 | Expt-5 |
|------|----------------------|--------|--------|--------|--------|--------|
| 1 | Acid dye | 97±2% | 90±2% | 87±2% | 92±2% | 97±2% |
| 2 | Direct dye | 97±2% | 89±2% | 85±2% | 92±2% | 97±2% |
| 3 | Metal complex 1:1 | 96±2% | 84±2% | 80±2% | 90±2% | 96±2% |
| 4 | Metal complex 1:2 | 96±2% | 78±2% | 71±2% | 87±2% | 96±2% |

Table III
Acid Dyes

| S.No | Sample | L* | a* | b* | c* | h | DE _{CIE} | DE _{CME} |
|------|--------|--------|-------|--------|--------|---------|-------------------|-------------------|
| 1 | Expt-1 | 37.549 | 7.805 | 15.892 | 17.705 | 296.156 | – | – |
| 2 | Expt-2 | 33.456 | 8.034 | 15.978 | 18.456 | 298.493 | 3.782 | 2.256 |
| 3 | Expt-3 | 33.167 | 8.734 | 15.988 | 18.652 | 298.794 | 3.812 | 2.351 |
| 4 | Expt-4 | 38.516 | 7.334 | 15.671 | 17.416 | 296.123 | 2.814 | 1.658 |
| 5 | Expt-5 | 36.730 | 8.523 | 15.985 | 18.115 | 298.066 | 3.887 | 2.173 |

Table IV
Direct Dyes

| S.No | Sample | L* | a* | b* | c* | h | DE _{CIE} | DE _{CME} |
|------|--------|--------|-------|-------|-------|---------|-------------------|-------------------|
| 1 | Expt-1 | 43.280 | 2.528 | 6.931 | 7.378 | 249.958 | – | – |
| 2 | Expt-2 | 40.076 | 3.392 | 8.749 | 9.621 | 248.042 | 4.095 | 2.454 |
| 3 | Expt-3 | 40.022 | 3.738 | 8.894 | 9.822 | 248.981 | 4.395 | 2.765 |
| 4 | Expt-4 | 45.471 | 2.836 | 7.598 | 7.829 | 249.089 | 3.095 | 2.015 |
| 5 | Expt-5 | 44.476 | 3.632 | 8.590 | 9.326 | 247.082 | 4.295 | 2.665 |

Table V
Metal Complex Dyes 1:1

| S.No | Sample | L* | a* | b* | c* | h | DE _{CIE} | DE _{CME} |
|------|--------|--------|--------|--------|--------|--------|-------------------|-------------------|
| 1 | Expt-1 | 63.280 | 18.741 | 50.447 | 53.815 | 69.620 | – | – |
| 2 | Expt-2 | 60.456 | 20.345 | 52.789 | 55.897 | 69.484 | 2.456 | 0.984 |
| 3 | Expt-3 | 60.176 | 20.045 | 52.397 | 56.126 | 69.184 | 2.563 | 1.045 |
| 4 | Expt-4 | 65.677 | 18.156 | 46.447 | 50.818 | 69.326 | 2.063 | 0.945 |
| 5 | Expt-5 | 63.771 | 19.101 | 51.884 | 55.288 | 69.789 | 2.115 | 0.840 |

Table VI
Metal Complex Dyes 1:2

| S.No | Sample | L* | a* | b* | c* | h | DE _{CIE} | DE _{CME} |
|------|--------|--------|-------|--------|--------|--------|-------------------|-------------------|
| 1 | Expt-1 | 70.988 | 1.377 | 37.030 | 37.055 | 87.870 | – | – |
| 2 | Expt-2 | 67.647 | 2.045 | 41.214 | 41.476 | 86.644 | 3.365 | 1.494 |
| 3 | Expt-3 | 66.491 | 2.141 | 41.146 | 41.765 | 86.471 | 3.568 | 1.584 |
| 4 | Expt-4 | 71.677 | 1.745 | 36.214 | 36.476 | 86.142 | 3.252 | 1.894 |
| 5 | Expt-5 | 70.323 | 2.470 | 40.414 | 40.489 | 86.503 | 3.168 | 1.719 |

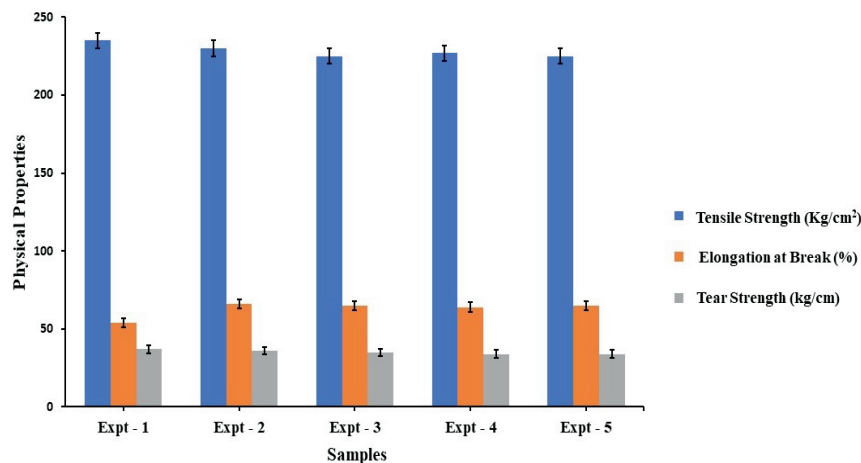


Figure 1. Physical Properties of Leathers

Color Value of dyed crust leathers

From the Tables III-VI it was observed that there are no significant changes in the hue for all the dye fixing agents. Quaternary ammonium compounds treated leathers gave slightly darker shade. There is not much improvement in the shade of acid mixture treated leather.

Physical Strength Characteristics of Leathers

The physical testing values of crust leathers are listed in Figure 1. In order to assess the strength characteristics of experimental leathers acid dyestuff was chosen. It was observed that there are no significant changes in strength characteristics for dye fixing agents.

Fastness Properties of Leather

The fastness property values for leathers of four different fixing agents with direct dye are listed in Table VII. From the results it could be inferred that acid mixture gives results similar to formic acid. Quaternary ammonium compounds yielded better wet and dry fastness. Acetic acid gives moderate fastness properties. Light fastness for TBAB treated leathers was moderate.

Table VII
Fastness Properties of Leather (Direct Dye)

| S.No | Fastness Properties | Expt 1 | Expt 2 | Expt 3 | Expt 4 | Expt 5 |
|------|---------------------|--------|--------|--------|--------|--------|
| 1 | Dry rub | #4 | #4-5 | #4-5 | #4-5 | #4-5 |
| 2 | Wet rub | 4 | 4 | 4-5 | 4-5 | 4 |
| 3 | Light | 6-7 | 6 | 5-6 | 6 | 6-7 |

*Grey Scale Readings (5-8 is excellent, 1 is poor, #Polished effect)

Table VIII
Fastness Properties of Leather (Acid Dye)

| S.No | Fastness Properties | Expt 1 | Expt 2 | Expt 3 | Expt 4 | Expt 5 |
|------|---------------------|--------|--------|--------|--------|--------|
| 1 | Dry rub | #4 | #4 | #4-5 | #4-5 | #4-5 |
| 2 | Wet rub | 4 | 4 | 4-5 | 4-5 | 4 |
| 3 | Light | 6-7 | 6 | 4-5 | 5-6 | 6-7 |

*Grey Scale Readings (5-8 is excellent, 1 is poor, #Polished effect)

The fastness property readings of acid dye treated leathers are listed in Table VIII. The results show fastness properties of acid mixture and formic acid treated leathers were more or less same. Quaternary ammonium compounds give better fastness than other agents. Acetic acid gives only moderate fastness properties when compared to other agents. TBAB treated leathers have only moderate light fastness.

The fastness property readings for metal complex dye 1:1 are listed in the Table IX. From the results it is inferred that acid mixture gives good results as formic acid when used for fixing of dyed leathers. Quaternary ammonium compounds give better wet and dry fastness but moderate light fastness. Acetic acid gives moderate fastness properties.

Table IX
Fastness Properties of Leather (Metal-Complex Dye 1:1)

| S.No | Fastness Properties | Expt 1 | Expt 2 | Expt 3 | Expt 4 | Expt 5 |
|------|---------------------|--------|--------|--------|--------|--------|
| 1 | Dry rub | #4-5 | #4-5 | #4-5 | #4-5 | #4-5 |
| 2 | Wet rub | 4 | 4 | 4 | 4-5 | 4 |
| 3 | Light | 6-7 | 5-6 | 6 | 5-6 | 6 |

*Grey Scale Readings (5-8 is excellent, 1 is poor, #Polished effect)

Table X
Fastness Properties of Leather (Metal-Complex Dye 1:2)

| S.No | Fastness properties | Expt 1 | Expt 2 | Expt 3 | Expt 4 | Expt 5 |
|------|---------------------|--------|--------|--------|--------|--------|
| 1 | Dry rub | #4-5 | #4-5 | #4-5 | #4-5 | #4-5 |
| 2 | Wet rub | 4-5 | 4-5 | 4-5 | 4-5 | 4-5 |
| 3 | Light | 6-7 | 6 | 5-6 | 5 | 6-7 |

*Grey Scale Readings (5-8 is excellent, 1 is poor, #Polished effect)

The fastness property values for metal complex dye 1:2 are listed in the Table X. The leathers fixed with acid mixture and formic acid yielded same results. Quaternary ammonium compounds give better wet and dry fastness but moderate light fastness. Acetic acid gives moderate fastness Properties.

Conclusions

Extensive studies were carried out to ascertain the ability to fix different dye stuffs with different fixing agents in comparison with formic acid. The results indicate that acid mixture could replace formic acid as dye fixative based on color properties and exhaustion levels. While quaternary ammonium compounds give better fastness properties, the exhaustion levels were found to be much lower compared to formic acid.

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Annexure

Dyeing Experiments

The experimental procedure given below was followed for all types of dyestuffs and fixing agents (acid dyes, direct dyes, 1:1 metal complex dyes and 1:2 metal complex dyes). Full chrome goat crust leathers were chosen for the experiments. All quantities are based on crust weight.

Wetting back

| | | |
|-----------------|------|----------------------------------|
| Water | 150% | |
| Wetting agent | 0.5% | |
| NH ₃ | 0.2% | Run for 1 hr then left overnight |
| Next Day | | |

Washing

| | | |
|-------|------|--------|
| Water | 100% | 15 min |
| Drain | | |

Dyeing

| | | |
|--------------------------|------|-----------------------------|
| Hot Water | 300% | @50°C |
| Synthetic fatliquor | 2% | 30 min |
| Dyestuffs | 5% | 30 min |
| Synthetic fatliquor | 2% | |
| Semi-synthetic fatliquor | 2.5% | - 60 min Checked exhaustion |

Fixing

| | | |
|---------------|----|---------------------------------|
| Fixing Agents | 5% | - 5 × 5 min + 30 min pH 3.8-4.0 |
|---------------|----|---------------------------------|

Leathers were rinsed in water and aged for 8 hrs. Then hooked to dry, staked, toggled and assessed for fixing efficiency.