

# COVALENT FIXATION OF DRUM DYES ON COLLAGEN\*

by

GERHARD WOLF, HARALD KIESOW, LASZLO SOMOGYI\*\*

<sup>1</sup>BASF AG,

67056 LUDWIGSHAFEN, GERMANY

## ABSTRACT

Covalent fixation of performance chemicals on various substrates of natural or synthetic origin is a well-known and thoroughly investigated principle since decades. Taking a deeper look into the literature of collagen, though, there are only a few examples found to this topic. Immobilisation of process chemicals is of great importance for leather as well. Especially dyes play a crucial role, since their mobility within the substrate matrix may lead to visible staining of other materials upon contact. In order to meet these challenges in leather manufacturing a new dyeing concept has been developed: covalent fixation of drum dyes to the collagen fibre. The dyes react with collagen under mild alkaline conditions at moderately elevated temperatures, thus reaching a fixation rate of above 95%. Due to the fact that only covalently fixed dye molecules remain in leather, unprecedented fastness properties are achieved even on leather dyed to very deep shades.

## ABSTRACTO

El principio tras la fijación covalente de productos químicos de desempeño sobre varios sustratos de orígenes sintéticos o naturales es bien conocido y ha sido investigado a fondo durante varias décadas. Examinando más profundamente la literatura específica al colágeno, sin embargo, se encuentran pocos ejemplos sobre el tema. La fijación de químicos del proceso es de una gran importancia en el cuero también. Colorantes especialmente juegan un papel decisivo, ya que su movilidad dentro de la matriz del sustrato puede conducir a manchar otros materiales en contacto. Para cumplir con estos retos en la fabricación del cuero un nuevo concepto de teñido ha sido desarrollado: fijación covalente de los colorantes ofrecidos en fulón sobre la fibra del colágeno. Los colorantes reaccionan con colágeno bajo

condiciones suavemente alcalinas y a temperaturas moderadamente altas, así alcanzando tasas de fijación superiores al 95%. Debido al hecho que solo moléculas del colorante covalentemente fijadas permanecen en el cuero, las propiedades de solidez alcanzan valores sin precedente aún en cuero teñido a tonos muy intensos.

## INTRODUCTION

Exodus 25,5

Offerings for the Tabernacle

“...ram skin dyed red...”

Dyeing of animal skins and hides is probably as old as tanning<sup>1</sup>. Since vegetable tanning agents have dominated leather manufacturing until the end of the 19<sup>th</sup> century, it is not surprising that among the first chemical substances used for dyeing leather solutions of metal salt forming coloured complexes with these vegetable extracts played an important role<sup>2</sup>. Iron salts produced grey to black shades on leather; copper salt gave leather a dark brown shade, whereas titanium salts were responsible for orange shades.

Another large group of substances used for centuries to colour leather was the extracts of different plants, dominated by the extracts of dyewood, mainly brazilwood, logwood, redwood and fustic<sup>3</sup>. These dyewood extracts also served as tanning agents and had a great advantage to dye both the grain and flesh side of leather equally well without tendency to accentuate or hide defects on the grain side.

Metal salt solutions and dyewood extracts were also known as natural and mordant dyes. The invention of the first synthetic dye, Mauveine by a young Englishman in 1856 was a milestone marking the decline of the long lasting dominance of natural and mordant dyes (mordanting: fiber treatment with metallic salts usually resulting in poorly soluble colored complexes). William Henry Perkin was only 18-years-old when he synthesized mauve or aniline purple (Figure 1) from chemicals

\* A Technical Note based on a presentation at the 102<sup>nd</sup> annual meeting of the American Leather Chemists Association at the Hyatt Regency, Milwaukee, WI, on June 24, 2006.

\*\* Corresponding author - E-mail: laszlo.somogyi@basf.com

Manuscript received July 7, 2006, accepted for publication October 8, 2006

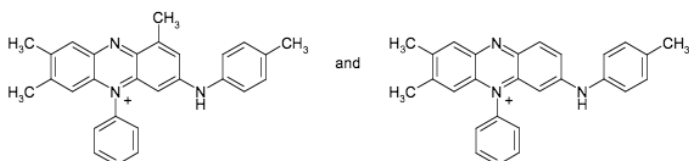


FIGURE 1. Mauvein or aniline purple, the first synthetic dye invented by W.H. Perkin

derived from coal tar. Like in many other cases in chemical discoveries, his intention was to produce a quite different compound, quinine, an antimalarial drug. Perkin realized the potential of his discovery in the rapidly growing textile industry and developed a process for the production. With the financial help of his father he opened his factory already in 1857 and started commercializing the first synthetic dye.

Inventions of furtherer synthetic dyestuffs have rapidly followed not only in England but also on the old continent. In 1865 Friedrich Engelhorn founded the Badische Anilin & Soda-Fabrik (now better known as BASF and hereafter referred to as the "Company") to produce coal tar dyes and precursors. The famous textile dyes, indigo (Figure 2) and later the indanthrene dyes were highlights of the company's success on the world dye market.

Whilst the textile industry has profited from the discoveries of synthetic dyestuffs from the very beginning, the leather industry has remained reserved. It was not until the first International Leather Congress in 1897 in London that synthetic dyestuffs gained wider acceptance for the colouring of leather. From then onwards, the use of synthetic organic dyestuffs has increased steadily and nowadays they dominate leather coloration. Table I summarizes the dye classes listed in the Colour Index as suitable substances for the colouration of leather.

The first synthetic dyestuffs used for leather were basic or cationic dyes. These dyes are characterized by high brightness but their light fastness is usually poor.

The invention of Chrome tanning by Augustus Schulz in 1884 has paved the way for the application of a new class of synthetic dyes suitable especially for chrome tanned leather, the so called acid or anionic dyes. Nowadays, about 85-90% of the world's leather production is tanned with chromium salts. Consequently, acid dyes became by far the most important colorants in leather manufacturing. The majority of acid dyes are azo dyes, which represent the largest group of synthetic dyes at all. (Figure 3)

### Challenges in leather dyeing

"Most of these dyes [leather dyes] are chosen from the huge textile dye ranges. Only a minority of the dyes used was designed only for leather <sup>4</sup>."

In the year 2000 the estimated demand for leather dyes was somewhere between 30 and 50 thousand tons. In the same year the estimated demand for textile dyes grew to about 1 million tons <sup>4</sup>!

**TABLE I**  
Classes and number of leather dyes listed in Colour Index

Acid dyes	1031
Direct dyes	283
Mordant dyes	76
Reactive dyes	53
Sulfur dyes	25
Solvent dyes	4
Basic dyes	2

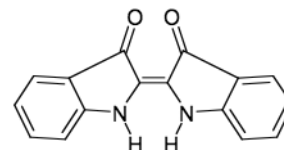
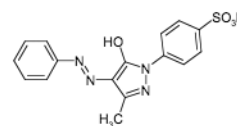
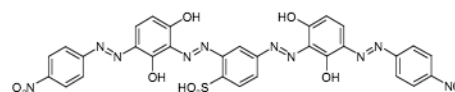


FIGURE 2. Indigo, a blue textile dye marketed by BASF in 1897



*C.I. Acid Yellow 11, 18820*



*C.I. Acid Brown 123, 35030*

FIGURE 3. Conventional acid dyes

These data clearly underline the above citation. The textile industry with its huge demand for synthetic dyes concentrated far more research capacities than the leather industry. This is also reflected in the Color Index, which is almost exclusively listing colorants for textiles, whereas leather dyes only appear in supplementary chapter.

Today almost every dye manufacturer has its own tailor made range of leather dyes, which are mostly selected textile dyes that have been found to be suitable for leather as well. Nonetheless, leather chemists and tanners are equally challenged when it comes to meeting the criteria set forth especially for high-grade leather articles.

Leather drum dyes are not only expected to dye both the grain and the flesh side in the same shade but also they are supposed to penetrate evenly through the cross section of leather. Dyeing must fulfill high fastness standards, such as migration-, wash- or perspiration fastness, should be reproducible and applicable on wet white, wet blue or on crust leather, not to mention the various raw hide defects that are also expected to be highly covered by the dye.

In order to better understand the properties of leather dyeing and the limitations of the current technology we need to take a

deeper look at the interactions or in other words binding forces working between the collagen fiber and the chemical substances applied on leather. Focusing on the largest group of leather dyes used today, namely the acid dyes, four major types of interaction can be distinguished that play a substantial role in binding the dye molecules to the collagen fiber. (Figure 4)

1. Metal salts would fix to the carboxylic acid groups of collagen through coordinate bonds. Typical examples are the Chromium salts used in the tanning process, but the metal centre of metal complex acid dyes can also coordinate ligands from amino acids bearing carboxylic acid groups in their side chains.
2. Hydrogen bonds play an important role in the stabilization of the triple helix structure of the three polypeptide chains. Dye molecules bearing functional groups capable of hydrogen bond formation (like OH, NH<sub>2</sub>, NH etc) could also form hydrogen bonds with the backbone of the polypeptide chain (shown also on Figure 4) or with appropriate side chain functionalities of the individual amino acids (like Lysine, Arginine, Asparagine or Glutamine)
3. Almost all acid dyes possess at least one water solubilizing sulfonic acid group. The sulfonic acid groups are usually in a salts form (most often sodium, potassium or lithium salts) meaning that they are capable of ionic interactions with cations of the collagen fiber (like ionic primary amines), or with the tanning salts.
4. The chromophoric systems of leather dyes are usually built out of differently substituted aromatic molecules. The aromatic ring systems could interact with dipolar groups of the polypeptide backbone (amide bonds) or of the side chains.

Hydrophobic interactions are relevant for fat liquors, whereas covalent bonds are formed for example between amino functionalities of the amino acids and aldehyde tanning agents.

Interactions 1-4 can be made responsible for the fixation of conventional acid dyes. These interactions are pH dependant, though, meaning that this kind of fixation

**TABLE II**  
**Comparison of dyeing conditions commonly used for textiles with conditions required in reactive leather dyeing**

	Textile	Leather
pH range	> 12	< 10
Temperature	80 - 100 °C	< 60°C
Fixation rate	up to 80%	> 95 %

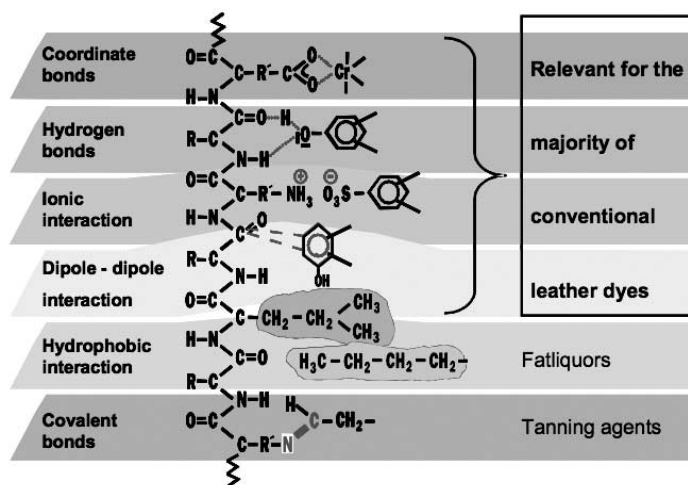


FIGURE 4. Types of interaction between chemical substances and collagen

is reversible or in other words, the dye can be theoretically washed out of leather or can migrate out of leather again under certain conditions.

It is important to keep in mind that due to their manufacturing procedures synthetic dyes usually consist of a limited number of main components (mostly only one), plus, to a lesser extent, several other side components. These side components may have different properties, like hydrophobic or hydrophilic character, solubility or shade, which influence their affinity to the collagen fiber differently. As a result, they would also behave differently under conditions like for

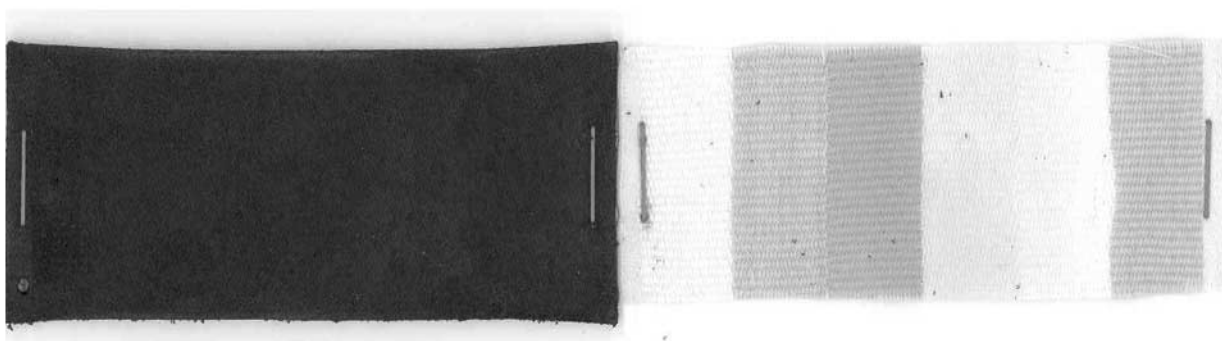


FIGURE 5. Perspiration fastness according to DIN ES ISO 11641 of bovine split suede shoe upper leather dyed with conventional acid dye (Multi-fibre test material from left to right: cellulose acetate - cotton - nylon - polyester - acrylic - wool)

example perspiration fastness testing. Figure 5 shows the result of a perspiration fastness test of a conventional black dye. Dye components with blue or red shades are clearly distinguishable on the multi-fiber test material.

### Vision and reality: covalent fixation of drum dyes on collagen

“Since 1951, when the first reactive dyes were designed for cotton, many reactive dyes including complete ranges have been offered for leather. However, no major breakthroughs have been achieved to date<sup>3</sup>.”

A few years ago a visionary project has been started at the Company with the task of designing new, colored chemical entities that would irreversibly fix to the collagen fiber. The goals were not only to develop highly innovative, new dyestuffs for the drum dyeing of leather but also to work out their application processes in the wet end phase. Besides trying to reach fastness levels found only at textiles, improvement of leather image in general through a quantum leap innovation was clearly envisaged, too.

Today's reality is that the Company has introduced the world's first reactive dyestuff to the market, which is specifically designed for leather drum dyeing applications. Having to consider the high research costs, as well as the cost for the registration of each new chemical compound, the Company has clearly committed itself to innovation in the leather industry alike all other industry sectors it is working with.

Reactive dyes are colored compounds that contain reactive groups capable of forming covalent bonds between the chromophoric system of the dye molecule and appropriate target groups of the substrate. Figure 6 schematically shows the reaction of a reactive dye with the suitable group of the substrate.

The trichlorotriazine molecule (see Figure 7) was the first reactive compound that was found to be able to form a covalent bond between dye and substrate. One chlorine atom reacts with a primary or secondary amino group of the dye molecule; the other two chlorines are then available for interaction with the appropriate nucleophilic groups (OH in the case of textile) of the substrate or with water (hydrolysis).

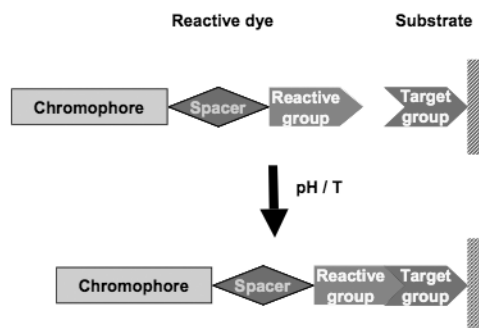


FIGURE 6. Reactive dyeing process

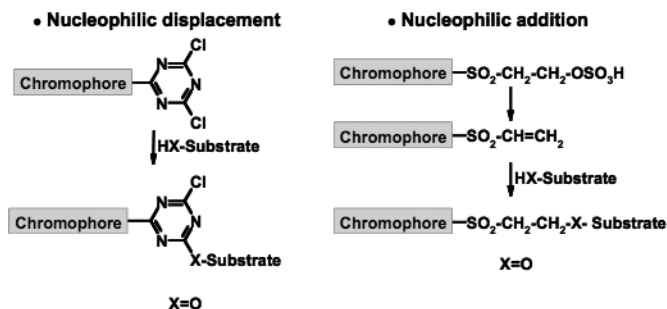


FIGURE 7. Reactive anchors commonly used in textile dyes

Another reactive group common in textile dyes is the beta-sulfatoethylsulfonyl group, better known as vinylsulfone group. The vinylsulfone group is actually the activated form bearing a double bond that can perform Michael type addition reactions with the nucleophilic groups of the substrate or with water.

Why have reactive textile dyes failed in the case of leather? Tanners have basically done the same as they have done with conventional, non-reactive textile dyes: tried to select the ones suitable for leather. But under which conditions should reactive dyes be applied on leather?

In Table II typical conditions of reactive textile dyeing are compared to those of the limitations set forth by leather. Textile dyes react with the substrate under highly alkaline conditions, at high temperatures and exhibit a fixation rate of up

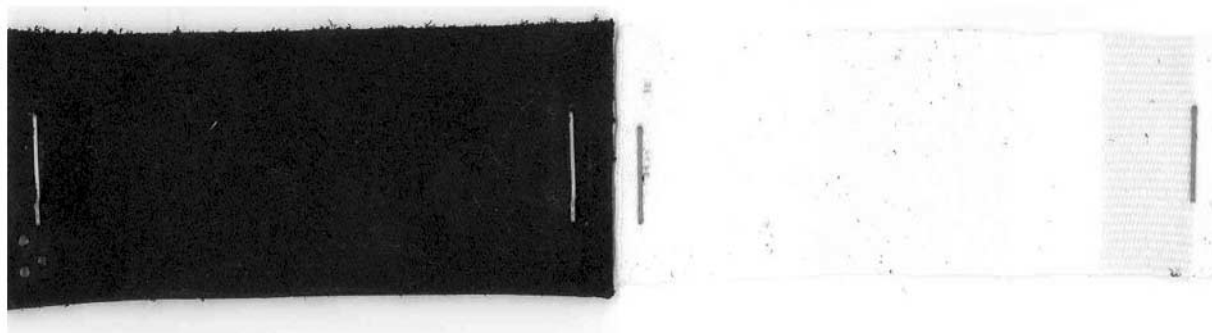


FIGURE 8. Perspiration fastness according to DIN ES ISO 11641 of bovine split suede shoe upper leather dyed with reactive dye (Multi-fiber test material from left to right: cellulose acetate - cotton - nylon - polyester - acrylic - wool)

to 80%. It means that at least 20% dye hydrolyses or remains unfixed during dyeing and has to be washed off at the following steps of the application process.

Tanned collagen, though, should not be treated at pH ranges above 10 or temperatures above 60°C, as it would suffer irreversible structural changes that would ultimately lead to the complete destruction of leather. On the other hand one should also consider that;

“...the reaction of the electrophilic group of reactive dyes with water (hydrolysis) competes with the fixation reaction of forming a covalent bond between the dye and the substrate. The hydrolyzed dye cannot react with the fiber. Leather absorbs the non-covalently bound dye like a conventional anionic dye. Unlike on textiles, these hydrolyzed dyes cannot be easily washed off<sup>3</sup>.”

Therefore reaching high fixation rates (above 95%) is a must when trying to dye collagen with reactive dyes.

The Company has developed a completely new reactive system that meets these requirements set forth for reactive leather dyes.

The dyes react with collagen under mild alkaline conditions at moderately elevated temperatures, thus reaching a fixation rate of above 95%.

The innovatively new wet end processing also ensures that the small amount of non-fixed dye components can easily be washed off from leather in the wash process following the dye fixation. Due to the fact that only covalently fixed dye molecules remain in leather, unprecedented properties are achieved even on leather dyed to very deep shades including perspiration fastness levels demonstrated on Figure 8.

The covalent fixation of dye molecules on the collagen fiber makes the process uniformly applicable on wet white, wet blue or on crust leather. The simple processing ensures high reproducibility of dyeing from batch to batch as well as excellent levelness and coverage of row hide defects. There are no shade differences between the flesh and the grain side of leather even the cross section is easily dyed through the same shade.

As far as the environmental and health issues of the new reactive dyestuffs and the new dyeing technology are concerned tanneries can handle the dyes just like any conventional acid dyes. Due to the high fixation of the dyes, total dyestuff emission from the tannery is not expected to increase. A great advantage for the leather article manufacturers and consumers is that no dye release to the environment or onto contact material or skin would take place during the lifetime of the final leather article.

The new dyestuffs are of course designed to meet all requirements needed to dye also high-grade leather articles. They are free of solvents and contain no components listed among banned amines.

The new wet end processing can readily be applied in the existing manufacturing apparatus of the tanneries, thus the implementation of the new technology requires no investment into production facilities.

## SUMMARY

This research has succeeded in developing new reactive dyeing technology for the drum dyeing of leather. The technology implies not only the design and large-scale synthesis of new chemical entities together with their toxicological evaluation and registration, but also the development of innovatively new wet end processing.

The technology is suitable to prepare high quality leather from a wide variety of raw material and it is also indifferent of the tanning process (wet white, wet blue or crust). Basically all kinds of leather articles are possible.

Besides excellent leather quality it ensures unprecedented fastness properties even at leathers dyed to very deep shades.

The new technology is a quantum leap innovation in leather dyeing, thus creating a new State of the Art in the manufacture of leather!

## REFERENCES

1. G. Otto, Das Faerben des Leders, Eduard Roether Verlag, Darmstadt, 1962
2. H. Schweppe, Handbuch der Naturfarbstoffe, Landsberg, 1992
3. Industrial dyes, Klaus Hunger (Editor), Wiley-VCH Verlag, Weinheim, 2003
4. A.G. Püntener, Leather Dyes, Colorants for non-textile applications, H.S.Freeman and A.T. Peters (Editors), Elsevier Science B.V., 2000

## CONVENTION DISCUSSIONS

*David Rabinovich, Herman Lowenstein and Sons Co. - In the early part of the presentation you speak about the anionic sulphonic group of the dye electro-statically being attracted to a charged amino. Your Dr Otto, as BASF has been ahead of all of us for many years, points out that is an inverse square attraction whereas the coordination forces that you mention, dipole interaction in other forms, are inverse six power or inverse twelve power: some of the forces involved in Van der Waals. So really the most important attraction is electrostatic.*

Yes, that is right.

*And, if you look at that carefully, Viankovitch says that you not only have that electrostatic attraction but there is also three hydrogen bonds involved between the oxygen's and the hydrogen's of the aminos. So I think the most important step, according to Dr. Otto, occurs with that electrostatic attraction which is pH dependant.*

Yes that is correct. I may not have emphasized it correctly - I just skipped through these details. Thank you for your comments.

*Jerry Maffia, Weidner University -*

*A question about the terminology. The fixation rate is at 90 to 95 %. Maybe you could define what that means in terms of a fiber. Does that mean that all the fibrils within that are going to be fixed at that rate? Or, as an engineering question, have you done radial profiles?*

Yes, that refers to 95 % of the dyestuffs are fixed, but that does not mean that there are no more target groups in the collagen. You can increase the dye amount up to a certain extent before you saturate the collagen. And, of course, this is more than we need for normal leather dyes.

*We sort of do the opposite. We attach biomolecules to the collagen: hopefully that will release and so sort of a controlled release of biomolecules. So rather than keep it on there permanently we hope it comes out of there - sometimes it comes out faster than we would like it to. Thank you. Molecule*

*Bill Marmer, USDA -*

*Reactive dyes have been around for a long time (tape unclear) ... and they have been applied to other protein materials, especially wool. Does your line of reactive dyes differ from the wool dyes?*

Yes. Wool has other target groups. Wool is like hair. In wool the target groups are -SH groups. They are much more nucleophilic than the collagen target groups.

*So, would your line also be applicable to wool.*

Theoretically yes, after certain pretreatment of the wool fibers. But wool was not in focus of the project"

(remainder of tape unclear)