The colour in the leather finishing

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1. Abstract

Dyeing, pigmenting, coloring, adjusting hues, make a bicolor, to dye crests ... terms widely used in finishing leather to get the color and appearance of the desired finish, with coverage, transparency, fashion, intensity etc. that makes them, commercially interesting and technically strong.

In this presentation we will discuss how the products used for these purposes, that is, dyes and pigments, have been modified over the years. We will talk on how fashion, fastnesses, European regulations or other environments have changed the presentation of dyes and pigments and even more, we will explain the changes suffered by these compounds to make them more environmentally friendly, with better resistances and better colorful performances.

Keywords: Pigments, dyes, finishes, fastness, fashion.

Introduction

In 1942, it was said that:

"Leather can be dyed:
With vegetable materials;
With animal materials;
With metallic dyes;
With synthetic colorants, generally called anilines "...

"Formulations intended to impart the desired coloration to hides and skins can be applied:
By means of common brushes
With the help of a mechanical brush
By spraying;
By means of liquors placed in one or several vats."

What remaining of these words 70 years later? Little or nothing. Basically, that we must dye, that leather should be dyed.

In the 80s of the last century, the same idea prevailed, to dye. So speaking of dyes in finishing it was said: "A dyeing formulation consists of a dye, a polar solvent and water. The polar solvent acts as a surface active agent favouring the penetration, so that its proportion should be experimentally determined, while ensuring stability of the solution so it is essential for some dyes whose solubility in water is limited." [2]

In this last paragraph, the characteristics of the dyes are not mentioned, nor the danger of the used polar solvents, nor the fastness properties of dyeing obtained and many other parameters that are now essential to work properly.

The changes that have taken place in dyeing and finishing operations of leather in the last years are so huge that we thought it would be interesting to give an update of these operations, focusing on the colour in the finishing of leathers. We leave the interesting topic of drum dyeing to our colleagues which are specialists on this subject.

Colour in the finishing operation

Speaking of the colour in finishing operations, we should refer to dyes and pigments, but mainly to their fastness properties, to their environmental performances and dyeing behavior.

How should these products be that bring colour into the finishing operation?

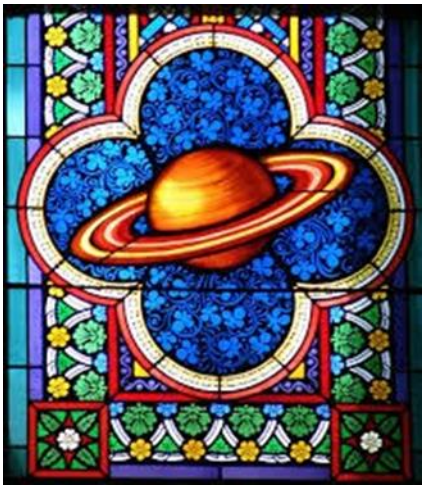
Dyes

- They should have good fastness properties mainly to water spotting, to the light and low migration to PVC
- Free of arylamines
- Dissolved in solvents of low toxicity
- Miscible in aqueous solutions and solvents and with high tinting strength.
- Of clean, vivid and intense hues.

Pigments
- Free of heavy metals.
- Aqueous micro-dispersions free of ethoxylated alkylphenols and volatile organic components
- Of good fastness properties to light and low migration to PVC
- Of clean and vivid hues, with good coverage and luminosity

Dyes and pigments

Currently in the industrial finishing of leather all the dyes used are synthetic, called "aniline" 70 years ago, mainly acids or solvent metal complexes, solubilised in polar solvents, glycols/water, high flash point and low toxicity.
In the 80s, the metal complex dyes were considered as the great novelty. These dyes, in its liquid form, gave to the finisher: versatility, ease of use and fastness indexes generally high. Consider a text of that time:
"Modern liquid metal complex dyes meet three important features that justify its rapid adaptation by the finisher: a fastness index generally high; versatility of use, water or solvent; and the significant advantage of allowing always have on hand a "ready solution" of uniform quality and easy incorporation into finishing formulations to make an unexpected and urgent work, or to correct a colour on the fly
It can be also stated that never before the existence of these dyes, the dyeing of crust leather or the achievement of certain effects were so easy."[3]
Currently versatility, ease of use and colour strength are fully assumed by the finisher. The current challenge of the finisher is "fastness", but not to water spotting or light, which were the most important several decades ago, but to migration to PVC. Are these dyes possible?
Dyes are substances that give colour. For a substance to be a dye should have an unsaturated molecular structure, should be electronically unstable, and should contain in their structure a chromophore group, responsible for absorption of light. Furthermore, this substance should contain an auxochrome group responsible for fixing the dye molecule to the substrate, giving rise, in fact, to a new compound which is equal in all to the undyed substrate except in the colour.
Thus a dye may be defined as the substance that brought into contact with a suitable support, binds to it stably and transmits colour.
For example, a stained glass window



Pigments are poorly reactive substances with colour. These insoluble substances require a binder to incorporate onto the substrate surface. For example, a drying oil in oil paintings.
In the tanning industry, pigments are used in disperse form mainly in water. This allows a simple incorporation to the formulation to be used and they are bound by the polymers of such formulation.

The different chemical-physical behaviour between dyes and pigments allow us to say that the dyes are diaphanous and pigments are opaque, meaning opaque materials those that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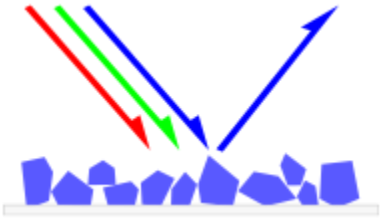
impede the passage to the light and diaphanous which permitted.

Light and colour

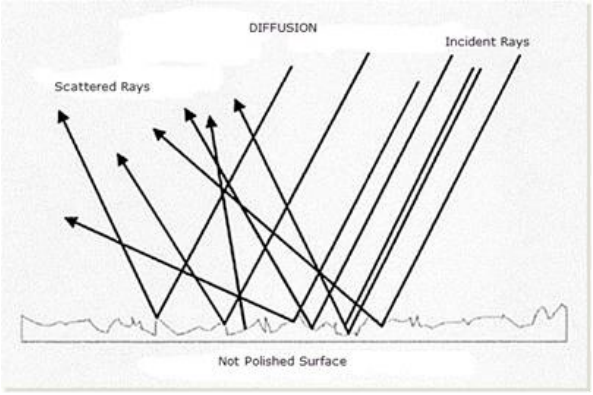
Dyes and pigments produce colours because they selectively reflect and absorb some light waves. White light is approximately equal to the entire light visible spectrum. When such light contact with a dye or pigment some waves are absorbed by the pigment or dye whereas others are reflected. This new spectrum of reflected light creates the appearance of colour. For example, a blue pigment reflects the blue light and adsorbs all the others colours.



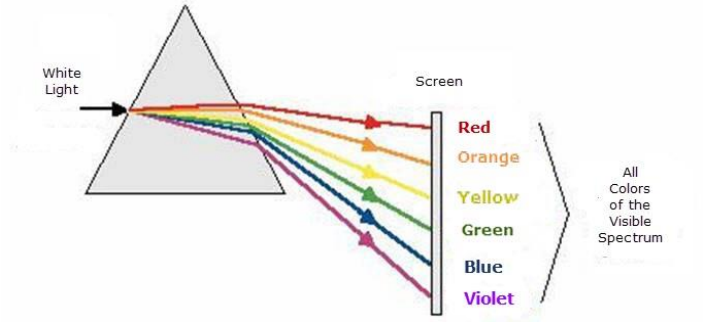
This is, in our opinion, a misrepresentation of the reflection of light on a pigment, since another difference between dyes and pigments is the way in which they reflect the new light resulting from the absorption. Dyes reflect light at an almost perfect angle of 90 º while pigments reflect diffuse light.

"In contrast to dyes (only absorption) pigment colours act by absorption and dispersion, giving rise to an overall reflection." [4]

In our opinion one should refer it as diffusion, which is an optical phenomenon consisting of light distribution in all directions when reflected on unpolished or irregular surfaces.

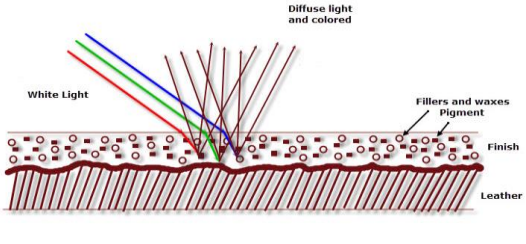


This diffusion of light that contains scattered rays, hence, perhaps, the above confusion, is the cause, along with opacity, of the coverage effect of pigments compared with dyes in the finishing coats.
Light scattering is a phenomenon that occurs when a beam of white light passes through a transparent medium (e.g. a prism) and refracts, showing the respective constituent colours.



Covering power, tinting strength

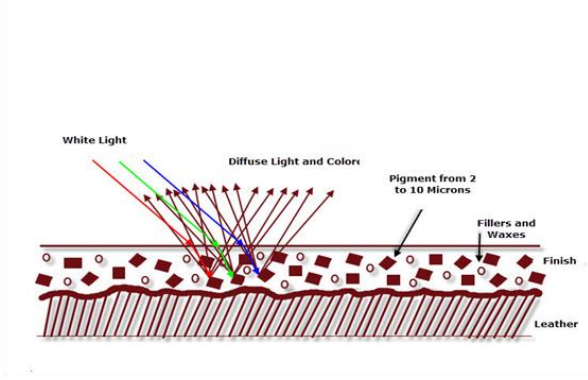
So far we have spoken of white light shining on colored more or less rough surfaces.
But what happens when this light shines on a film of a given thickness, containing pigments and dyes deposited on leather? In other words, what happens when a beam of white light falls on a coating of several layers of different materials with different refractive indices containing, among these materials, pigments and dyes and which is been applied on a unpolished substrate with great power of diffuse light called leather?
For similar other components of the coating, this is more or less covering depending on the particle size of the pigment; these larger particles that diffuse light and are also opaque. The dye will give colour and brightness whereas pigment will provide colour and coverage.



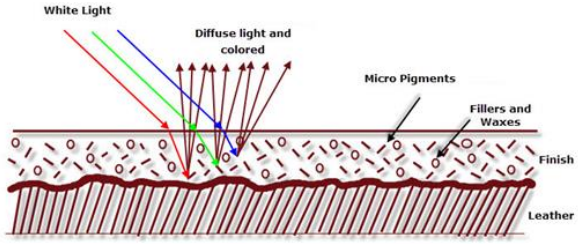
Light behaviour in the finishing

Particle size of the pigment dispersions

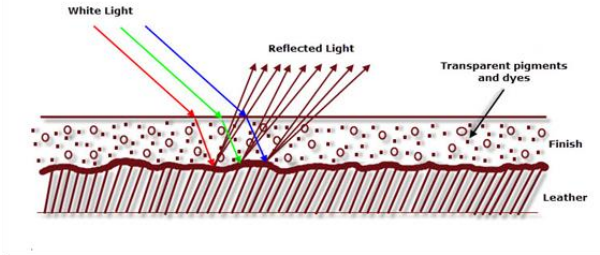
Given that it seems that the particle size of the pigment dispersions is the differentiator element, let us to have a look at this point:
In the 80s, it was said that: "Conventional pigment dispersions have a particle size between 2-10 microns and the so-called micro dispersed pigments can reach 0.2 to 0.5 microns"[5]
Currently, the leather industry uses pigment dispersions of quality which all of them are micro dispersions. Their average particle size is lower than 1 µm, including white and micronized iron oxides. Consequently, these pigments give finishings glossier, tinting, bright, transparent and naturals that 30 years ago and, in addition, with the advancement of surfactants and dispersants, are environmentally less aggressive and more stable. Such surfactants and dispersants, themselves less aggressive to the environment are better wetting agents, that allows omitting the use of glycols in pigment dispersion formulations; dispersions obtained without volatile organic compounds (VOC free) which comply without problems the REACH regulation.
These improvements in the dispersion of pigment aggregates up to its primary particles generated the existence of the so-called transparent pigments of high tinting strength and low coverage.
As criticism to this evolution, it could be said that pigments are losing covering power. However, it is not exactly this. The finishes with microdispersed pigments lose the rough, earthy, and lustreless coverage of old ago to produce finishes with good coverage and much more natural, colored and luminous aspect.



Pigments from 2 to 10 microns



Microdispersed pigments



Transparent pigments and dyes

Characteristics of the pigments
According to the literature, pigments must meet at least the following requirements to be used industrially:
"Some attributes that pigments must meet to determine their suitability for certain manufacturing processes and applications are the following:

- Thermal stability
- Toxicity
- Tinting strength
- Resistance to light exposure • Dispersion
- Opacity or transparency
- Resistance to alkalis and acids
- Reactions and interaction between pigments

We also would add low migration to PVC and easiness of mixing and compatibility of its dispersions to obtain a wide range of hues.

"In leather application mostly liquid pigment preparations with constant colour strength and coloristic properties are used. By blending

different base colours to the final shade, a high flexibility of colour processing is achieved." [7]

All this evolution is supported by the growing use of organic pigments, free of heavy metals, but with a greater easiness of "bleeding" with plastifying agents. Therefore, before adoption, it is essential to control migration to PVC of a pigment.

Environmental differences

Liquid dyes have evolved in the following way from the environmental point of view:

Flammable chemicals to Inflammable chemicals

Uncontrolled arylamides to Controlled arylamides

Dyes of different types to Selective dyes

Medium fastness properties to High fastness properties

Pigment dispersions have evolved as follows:

Pigments with heavy metals to Pigments without heavy metals

Mainly inorganic pigments to Mainly organic pigments

Dispersions of large particle size to Dispersions of small particle size

Dispersion with APEO surfactants to Dispersions free of APEO surfactants

Dispersions with VOC to Dispersions free of VOC

Medium fastness properties to High fastness properties and low migration to PVC

Reactive with butadiene resins to Mainly unreactive

Anionic / Cationic dispersions to Nonionic dispersions

Application

From the application point of view, we want these environmentally less aggressive dyes to be as versatile as its predecessors, because with them we wish to obtain:

- Spray Dyes, matched and full.
- Adjustment of hues with solvent or aqueous tops
- Grain padding
- Natural, vivid and transparent finishes
- High fastness finishes

So are chosen among the growing range of existing dyes, those having a nice hue and good tinting strength, are soluble in a water / glycol mixture, which gives high flash points at a dye concentration greater than 20% and have high fastness to water drop, to light and low migration to the PVC.

We finally have compact and short ranges of dyes fulfilling all these requirements.

Likewise, a pre-selection among all market pigments will be carried out in order to have the ranges of microdispersed pigments of high fastness properties. Pigments with the best fastness properties and more balanced in vividness/coverage are selected to prepare mono-component dispersions, since we want:

- Finishes that hide leather defects and give the appearance of naturalness with bright and luminous hues.
- Finishes of good fastness properties even with small amounts of pigment

Transparent pigments

In many cases, it is advisable to use transparent pigments when finishes with transparency and good colour intensity, naturalness, aniline or semi-aniline aspect, high fastness properties to light, low migration to PVC and free of VOC are required.

Transparent pigments can be used in any type of aqueous solutions, from base coat to padding preparations and can replace the dyes in most cases, depending on the desired final effect.

Characteristics of the pigment dispersions

It is known that, in the leather industry, the different manufacturers present their pigment dispersions at the same pigment concentrations, depending on the pigment type. Several years ago, the recommendation was: "The concentration of pigments should be within the following limits.

Pigment Dispersions	*Percentage*
White colour	*45 - 50*
Inorganic colours	*30 - 50*
Organic colours	*15 - 30*
Black colour	*10 - 20*

This equalization of the pigment content in the dispersions is to facilitate their use. The technician formulates with, for example 200 g /L of pigment without needing to have into

account which pigment type is being used. Also, in this way, he does not require to perform difficult calculations to determine the volumetric concentration of the pigment (CVP) in the finishing solution that ensures that all the pigment present in the film is sufficiently bound by the binder.

On the contrary, the presence or absence of binders in the dispersion was a distinguishing element between manufacturers. Originally dispersions were always anionic and, therefore, the presence of casein as stabilizer was common. Later, with the appearance of the cationic dispersions, without binder, the binder-free anionic dispersions became common. In our opinion, the dispersions without binders are more versatile than those with binders, and if, in addition, they are non ionic dispersions, allow the finisher to work with a unique range of pigments in any preparation, both anionic and cationic, which has the following advantages:

- In cationic/anionic finishes, a single study of hue.
- Diminution of the stored amounts of pigments
- Decrease of costs, etc.

Another difference is the viscosity of the dispersion. Each time, the dispersions can be and are less viscous. But the culture in this aspect is another. As stated in the 80s of last century: "The pigment dispersions used in leather finishing have a more or less pasty appearance"[9] and, in this way, is how a sector of the market demands the dispersion pigments, relating viscosity to concentration.

Conclusions

- Dyes of high fastness properties in glycol / water solutions are technically attractive and environmentally sustainable.
- Transparent pigments can be, in some cases, a "green" alternative to dye solutions and with better resistances.
- Micropigments allow covered finishes with good tinting strength, brighter and more natural than using pigments with greater particle size.

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