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UNRAVELLING THE COLOUR PALETTE: THE RECONSTRUCTION AND ANALYSIS OF SYNTHETIC COLOUR STAINS

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SCIENTIFIC PAPER

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Abstract

Over recent years the Cultural Heritage Agency of the Netherlands (Rijksdienst voor het Cultureel Erfgoed) has conducted several investigations into early synthetic dyes that are used as wood stains. Their poor light fastness means that these dyes are often severely faded. Nevertheless it is usually possible to find parts of a piece of furniture where the original colour is still visible, for example in places that are covered and therefore shielded from light. Against this background a 2007 study looked at 19th century marquetry used on 17th century furniture. These appeared to have been stained primarily with synthetic dyes, detectable particularly on the rear of the inlay work. What was striking, however, was the difficulty encountered in identifying the dyes, even in areas which were not heavily faded. The reason for this was unclear; was the concentration of the dyes applied to the wood low, or was the method used to extract the dyes from the wood unsuitable? Pronouncing judgements about the original colour also proved troublesome, while that is often the primary reason to conduct colour research. It is not only the characteristics of the dye which play a role in determining the original colour of a piece of furniture: the colour of the wood, the concentration of the dye, additives included in the recipe for the stain and other factors also need to be taken into account. That is why a research program was launched involving reconstructions: veneers were coloured with a representative selection of dyes. Studying and following historical recipes and varying various parameters allowed us to make more informed judgements about the original colours. Subsequently, these reconstructions were also used to optimise the analytical method. The results of this research are described in this article.

1 Introduction

Organic dyes obtained from vegetable or animal materials have been used to colour furniture for centuries.[1] The result is a transparent colour, through which the wood grain remains visible. Synthetic dyes were introduced during the second half of the 19th century, initially for the dyeing of textiles.[2] The Cultural Heritage Agency of the Netherlands has initiated extensive research into these early synthetic dyes, which involved the collection of historical information, the development of analytical techniques, the study of degradation behaviour and the investigation of a large number of objects. These dyes were used in numerous applications: as well as the dyeing of textiles and the staining of wood they were also used in drawing and writing inks, in the leather and paper industries and in fine art. In the case of textile dyes the transition from natural to synthetic dyes proceeded fairly rapidly; our research has shown that within a few decades synthetic dyes had almost entirely replaced the natural ones. Whether the transition was equally rapid in the case of furniture stains is as yet unknown. The first recipes for synthetic dyes for wood staining date from 1867, but that is not to say that they were used on a large scale at that time.[3] There are even earlier references to indigo carmine and picric acid, both semi-synthetic dyes with indigo as the original substance, but the majority of the recipes are for natural original

substances. The number of pieces of furniture studied was too small to enable a well-founded judgement about when the replacement of natural dyes by synthetics took place in relation to furniture.

Earlier research does however demonstrate that these synthetic dyes were indeed in use. Research into furniture designed by Piet Kramer between 1912 – 1935[4] from the collections of the Stedelijk Museum in Amsterdam and the Cultural Heritage Agency of the Netherlands indicated that methyl violet, malachite green, nigrosin and probably orange II were used to stain furniture.[5] Crocein orange, nigrosin, picric acid and a variety of red and blue synthetic colorants were encountered on clock cases dating from 1715-1745; the presence of these dyes indicate later conservation work.[6]

In 2007 extensive research was also carried out into the use of dyes on late 19th and early 20th century marquetry. This type of inlay work was extremely popular during that period, and was also used to decorate existing pieces of 17th and 18th century furniture. As well as fragments of marquetry pieces from the workshop off Johannes Lodewijk Miner in the collections of the Amsterdam Museum, the Rijksmuseum Amsterdam and the University of Amsterdam, this research also took in a selection of furniture including pieces from Het Loo Palace.[7] Miner was a furniture inlayer who was active in the early decades of the 20th century. He provided antique furniture with new inlay work, and a collection of prepared inlay work from his workshop has survived. In addition to natural colorants, synthetic dyes such as fuchsine, picric acid, flavazine L and Victoria blue B were principally found during this research.

While a satisfactory answer was found to the primary (chemical) question in the above study, namely "which dyes were used?", another important question remained unanswered: could a judgement be pronounced about the original colour of the piece of furniture in question? Of course some indication could be provided given the fact that the colour of the dyes was known. For example: methyl violet gives an intense purple colour while malachite green gives a strong green. But the question remains: how purple, and how green? It proved impossible to answer this question without additional studies involving reconstruction. What was clear was that the dyes are now severely faded, so much so that in some cases only the colour of the wood was visible.[8]

As well as the question about the original colour there was also an issue of an analytical chemical nature: the responses found during analysis were generally fairly weak. This means that only a small amount of dye was being recovered in relation to the sample size (generally some scrapings taken from an unfaded area). This low response could of course simply be the result of a low level of dye in the sample. The dye may already have faded, or the quantity of dye required to obtain a particular colour may have been small. This latter hypothesis can also be tested by means of reconstruction research. There is however another possible explanation for the low response: the analytical technique used is optimised for samples of textiles and paints, but not for wood. Before the analysis can be carried out the dye must first be placed in a solution. This is achieved by way of extraction using a strong acid, such as hydrochloric acid. This is an effective method for textile and paint samples, certainly for synthetic dyes.[9] In the case of wood stains however it is known that the colorant penetrates the wood. It is not clear whether the extraction medium also does so, to allow effective extraction of the dye. In addition, the binding mechanism between the dye and wood is not the same as in the case of textiles, so that a different method may be required to break that bond.

The aim of this study is therefore twofold. Following study of the historical sources, reconstructions were carried out in order to gain a better understanding of the original colour of items on furniture. This can assist conservators and curators in their understanding of the original appearance of a piece. The same reconstructions may also be used for analytical research, to optimise sample preparation for wood.

2 Recipes and reconstructions

A selection of historical sources were investigated in order to allow good reconstructions to be made. One important source was *Vom Färben des Holzes* by Hans Michaelsen and Ralf Buchhol, which consists primarily of descriptions from other sources.[1,10] This book contains recipes and transcriptions of recipes in which synthetic dyes were used. Another important source was *Beitsen, kleuren en oppervlaktebehandeling van hout* by C P van Hoek.[11] This book was based on a German publication by W Zimmerman from 1907, but adapted for the Dutch market.[12] This book sets out not just recipes for stains but also other treatments applied to wood before or after staining. *A practical handbook to marquetry, woodstaining and kindred arts* by Eliza Turck was published towards the end of the 19th century.[13] Another practical manual is the *Pocket Guide to the Application of Dyestuffs from the Badische Anilin & Soda Fabrik*, published by the dye manufacturers BASF themselves.[14] We must note that this book of over three hundred pages deals primarily with textile dyeing, the staining of wood occupying only a couple of pages, which offers some indication of the relative importance of textile dyeing and wood staining for the manufacturer. Finally, one Italian source was studied, *Coloritura, verniciatura e laccatura del legno*, by A Turco, 1985.[15]

Rather than providing a complete survey, the primary objective of the study was to identify similarities and differences in the recipes, in order to determine the most important parameters and to arrive at a standard recipe. The standard recipe developed during the study had in any event to cover the most significant parameters, and the effects of these parameters could then be investigated by varying them individually.

While there are clear differences between the different recipes, the number of parameters for the synthetics is limited compared to those in the case of natural dyes. This is only to be expected: one reason for the rapid replacement of natural dyes with synthetics (in addition to lower costs) was that the synthetics allowed simplified recipes, which could also be produced more quickly. While the dyeing of a textile with natural dyes could take anything from a day to several weeks (including a period of fermentation when applicable), it could be carried out in less than an hour using synthetics. The number of separate actions and of ingre-

dients were also smaller. Study of the historical sources suggests that the situation was similar in the case of wood stains.

One important parameter, if it can be called a parameter, is the wood itself. Wood has its own colour, which can affect the final colour. The porosity of the wood also plays a role, as this affects the degree to which the dye penetrates it. Oak and maple were selected for use in this study, both timbers having been encountered in objects previously studied. The degree of acidity of the wood can also play a role, as will be shown later. Before staining, the wood must first be wetted to prevent deformation form taking place during the staining process. This can be done simply using water, but often ammonia or a salt solution are used instead. In Van Hoek 1953 it is explicitly stated that this opens the pores of the wood so that the colorant can penetrate more deeply.[11]

The chemistry of the dye also plays a significant role. In the first place there are basic and acid dyes, so called because they are used in a basic or acidic dye bath, respectively. These dyes have basic or acid sidegroups which enter into the bond with the substrate (textile or wood). As well as the effect of these sidegroups on the bonding mechanism, the solubility of the dye also plays a role. Hydrophobic dyes are also soluble in organic solvents such as ethanol. Obviously the concentration of the dissolved substances also plays a role: the higher the concentration, the stronger the colour, although this is not necessarily a linear relationship. Additives may also be included in the dye bath to improve adhesion. Additives commonly mentioned include aluminium sulphate, ammonia and acetic acid. The staining method also has effects: smaller pieces of veneer can simply be dipped, resulting in a homogeneous colour. The duration of the dye bath also affects the final colour. Larger pieces were often stained using a brush or a sponge, and one would need to work quickly to achieve a homogeneous colour. In such cases it is not only the concentration of the dissolved dye that plays a role but also the number of times the brush or sponge passes over the surface. In addition, mixtures of dyes may be used: the manufacturer may supply a mixture of colorants to achieve a certain shade, but the person applying the stain can also choose to mix several dyes together. Finally there is the finishing coat of wax or varnish to consider, which will also affect the way the colour is perceived in the end-product. Such finishing coats have not been included in the scope of this study.

A standard recipe was developed based of the study of historical sources, and the variables within the parameters of this recipe were charted. The parameters listed in the following table have been numbered, the numbers referring to Tab. 1, which sets out the variables. The standard recipe consists of the following stages:

First the wood (1) is sanded very finely. It is then thoroughly wetted (2), and subsequently dried. The colorant (3) is placed in a solution (4) at the correct concentration (5a/b). Depending on the recipe additives may also be added here (6). The dye bath is heated to the correct temperature (7). The stain is applied to the wood using one of two methods. The dipping method (8) entails the wood being placed in the heated dye bath, ensuring that the wood is free on all sides (that is to say it is not in contact with the walls of the dye bath or with other pieces of wood). Following dipping (9) the dye bath is removed from the heat source and allowed to cool (10). The wood is then removed from the dye bath and dried. A sponge was used in the method where the colorant is applied directly to the wood (8), as this gave the most homogeneous result. Following this treatment the wood was dried. In all cases the wood received no post-treatment.

It is of course possible to combine several different parameters, but this would lead to a completely unmanageable outcome with more than a thousand reconstructions. It was therefore decided to employ the standard recipe with two colorants, one acidic and one basic, to apply this to both types of wood (= four reconstructions) and subsequently to vary all other parameters only in relation to the standard recipe, and not to carry out any further combinations. In the four reconstructions mentioned above an acidic and a basic dye were applied to both oak and maple wetted with, respectively, water, 5% ammonia and common salt. Of these however, only the reconstructions dampened with water were further investigated using the other parameters. For each colorant/wood combination this resulted in ten reconstructions for the dipping method (making a total of forty), and five for the sponge application method, where only the concentration is varied.

Nr	Parameter	Variable 1	Variable 2	Variable 3
1	Wood species	Oak	Maple	
2	Pre wetting	Water	5% ammonia	100 g/l common salt (NaCl) in water
3	Dye	Acid dye, Ponceau 2R	Basic dye, Methyl violet	
4	Solvent	Water	20% ethanol in water	100% ethanol
5a	Concentration dye, dipping method	1.0 g/l acid dye	0.1 g/l basic dye	
5b	Concentration dye, sponge method	Range of 1.0 to 15 g/l acid dyes	Range of 0.1 to 5 g/l basic dyes	
6	Additives to the dye bath	No additives or ammonia for acid and basic dye	Aluminium sulphate for acid dyes	Acetic acid for basic dyes
7	Temperature	90 °C aqueous solution	70 °C for 20% or 100% ethanol	
8	Method	Dipping in dye bath	Apply directly with a sponge	
9	Duration	Dipping: 15 min	Dipping: 30 min	Sponge: As fast as possible
10	Cool dye bath with wood inserted (dipping only)	1 h	2 h	

Table 1. The various parameters in the recipes (corresponding to the numbering in the text) and the associated variables.

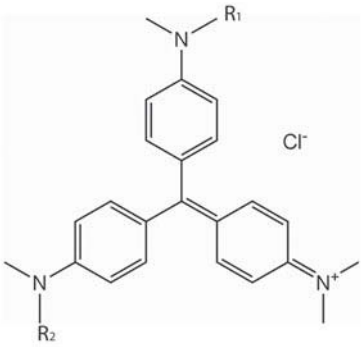

Figure 1. Structural formula for methyl violet, consisting of a mixture of the above structure where R_1= H or CH_3 and R_2= H or CH_3. The components are therefore tetramethylated, pentamethylated or hexamethylated.

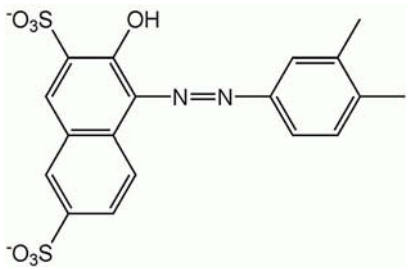

Figure 2 Structural formula for Ponceau 2R, a monoazo dye characterised by a double nitrogen bond.

Name	C.I.-name	C.I.-no.	Dye class	Reference no.
Naphthol yellow S	Acid yellow 1	10316	Nitro dye	6923
Orange I	Acid orange 20	14600	Monoazo dye	6928
Methylene blue	Basic blue 9	52015	Thiazine	4453
Cochineal red A	Acid red 18	16255	Monoazo dye	5311
Methyl violet	Basic violet 1	42535	Triarylmethane	4434
Ponceau 2R	Acid red 26	16150	Monoazo dye	5000
Flavazine L	Acid yellow 11	18820	Monoazo dye	5349
Christal violet	Basic violet 3	42555	Triarylmethane	3742
Diamond green G	Basic green 1	42040	Triarylmethane	3231
Water blue IN	Acid blue 93	42780	Triarylmethane	4518
Eosin A	Acid red 87	45380	Xanthene	4328
Nigrosin	Acid black 2	50420	Azine	3712
Indigo carmine	Acid blue 74	73015	Indigoid	1735

Table 2. Summary of the dyes used for the reconstructions.

This approach limited the work involved while still providing a good impression of the effects of the individual parameters on the final colour.

The research covered only a limited number of colorants. Methyl violet was chosen to represent the basic colorants and Ponceau 2R was selected as the representative acidic colorant. Methyl violet (*Colour Index* Name Basic Violet 1, C.I. no. 42535) is a dye in the triarylmethane class (Fig. 1).[16] It is very widely used in textile dyeing, as a drawing ink, for the staining of furniture and as an artist's dye.[17] Methyl violet has poor light fastness on textiles (ISO 1) and is easily soluble in both water and ethanol.

Ponceau 2R, also known as Ponceau RR (*Colour Index* Name: Acid Red 26, CI no. 16150), belongs to the class of monoazo dyes (Figure 2). It is a typical representative of this class of dyes. The Ponceau dyes belong to a group used in the 19th century to dye textiles and stain furniture. Ponceau 2R is reasonably light fast (ISO 4-5) and is easily soluble in both water and ethanol.

Methyl violet and Ponceau 2R were used to carry out the experiment investigating the recipe parameters. Additionally, a small selection of representative dyes were selected (see Tab. 2) and applied to both oak and maple using the dipping method, and also in five different concentrations using the sponge method. This allowed us to obtain a good impression of the colour variations and the colour palette.

3. Research methodologies

The assessment of the effects of the different recipes on the end-colour of the reconstructions was carried out primarily with the naked eye. Transverse sections were also carried out on a limited number of samples in order to study the penetration of the colorant into the wood. Sections of veneer were taken, embedded in epoxy resin, polished and studied under a microscope at magnifications of 40x and 100x.

Samples were also taken for use in the study of different extraction methods, the aim being to identify which method delivered the highest yield. The sampling was complicated by the quantitative nature of the research. The problems with the wood samples are that it is not known precisely what concentration of colorant is present and, above all, how deeply the colorant has penetrated the wood. Normally a scraping would be taken from a piece of furniture, but because this makes it difficult to determine the sample size it was decided to take relatively large samples by making a large transverse section right through the whole veneer. These samples were then weighed. While this sampling is of course not representative of the normal method of taking samples from objects, it does allow quantification of the results. Each analysis was performed 5 times.

Samples were then extracted using a variety of solvents. Extraction is necessary to detach the dyes from the wood and get them into the solution. Six different extraction methods were compared:

- Extraction using hydrochloric acid, water and methanol;
- Extraction using concentrated acetic acid;
- Extraction using ethanol;
- Extraction using ammonia (for acidic dyes only);
- A two-stage extraction process, using dimethylformamide (DMF) and then hydrochloric acid;
- A two-stage extraction process, using DMF and then ammonia (only tested in combination with acidic dyes).

The first method is the same as that used for the earlier research on the furniture. The sample was transferred to a 300 µl small insert vial, followed by the addition of 30 µl of a solution of concentrated hydrochloric acid, water and methanol (ratio 2:1:1). The vial was then transferred to a boiling water bath and heated for ten minutes. The hydrochloric acid solution was then evaporated to dryness with the aid

of nitrogen, hydrochloric acid not being compatible with the analytical system in use. Following evaporation to dryness, 30 µl of DMF was added to produce a solution of the dye. The sample was centrifuged to prevent small particles entering the analytical system. The extraction using acetic acid, ethanol and ammonia was performed using the same method, except that the temperatures of the water bath were 95 °C, 55 °C and 25 °C respectively. The two-stage extraction used a different method. First 35 µl of DMF was added to the sample and the vial was then transferred to an oven at 140 °C. Following 10 min of extraction the DMF solution was set aside temporarily, and the hydrochloric acid solution described above was added to the remaining wood sample. The vial was then heated for ten minutes in a boiling water bath and evaporated to dryness using nitrogen. The DMF solution from the first stage was then added, so the two extracts were combined, in other words. This sample was then centrifuged and subsequently analysed. The two stage extraction with ammonia was carried out using the same method, apart from the fact that the ammonia stage was carried out at 25 °C.

The analyses of the dissolved dyes were carried out using liquid chromatography linked to a photo diode array or PDA detector, a technique described in detail elsewhere.[18] Briefly summarised, the basic components of the sample were separated on a Luna C_{18} column (150 x 2 mm, 3 µm particles) using a gradient of water, methanol and 0.5% phosphoric acid. Following separation, the components were detected using the PDA detector. This detects spectra in a range from 200 to 800 nm, so that both the ultraviolet and the visible regions are included. Identification was carried out on the basis of reference materials.

The acidic dyes were analysed using the same system, but with the phosphoric acid replaced with 0.5 millimoles of tertiary butyl ammonium hydroxide (TBA). TBA is a positively charged ion which forms a complex with the negatively charged acidic dyes. These complexed dyes have much better chromatographic properties than the unbound dyes.[9]

4 Results and Discussion of the Reconstruction Study

The colour effects of the different parameters were primarily assessed in terms of their visual appearance. It was decided to use maple and oak with a reasonably similar starting colour, light yellowish brown. The veneer was first sanded and then wetted with water, or 5% ammonia, or a solution of 100 g/l of common salt in water. It was found that, when the veneer is stained with methyl violet or Ponceau 2R, the different wetting agents have almost no effect on the final colour (Fig. 3).

Only the combination of oak moistened with ammonia and stained with methyl violet produced a somewhat lighter colour and a somewhat less even staining effect than the other contributions. This could possibly be explained by the fact that oak is fairly acidic and that the basic ammonia adheres so strongly to it that the (similarly basic) methyl violet no longer adheres well. Far more striking is the colour variation between maple and oak: the maple veneer appeared to be far more evenly stained than the oak veneer. This is particularly apparent in the annual rings in the oak veneer, where the basic methyl violet adheres less than the acidic Ponceau 2R. As a result of this the late wood was more lightly stained than the rest of the wood, while it were the annual rings that were darker in the case of Ponceau 2R. No satisfactory explanation can as yet be given for this phenomenon. This effect is far less visible in the case of maple, which has a finer structure. Sections were also made of the reconstructions, which were then viewed under the microscope.

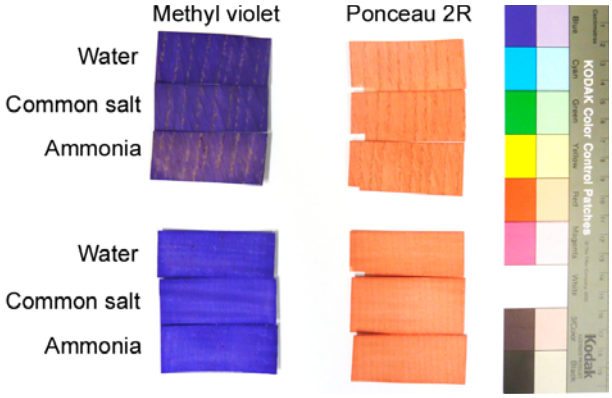

Figure 3. Effect of different pre-wetting agents on the colour of oak (above) and maple (below) stained with methyl violet and Ponceau 2R, respectively.

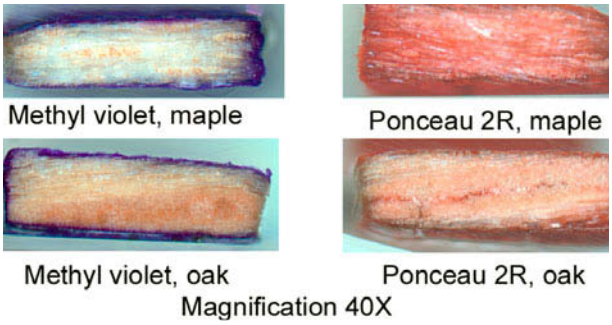

Figure 4. Section of veneer following staining with methyl violet and Ponceau 2R, respectively.

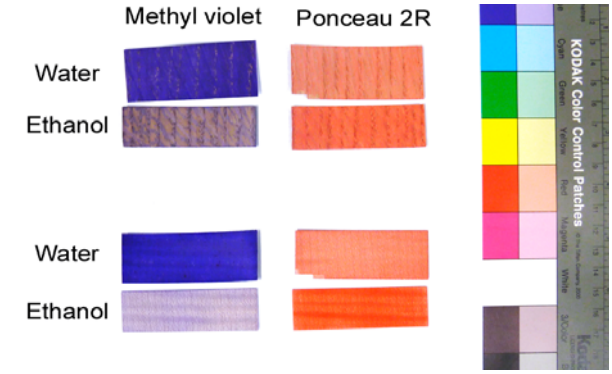

Figure 5. Effect on the colour of oak (above) and maple (below) after staining using methyl violet and Ponceau 2R dissolved in water or ethanol.

The difference in penetration of the two dyes is clearly visible: the basic methyl violet primarily adheres to the surface while the acidic Ponceau 2R penetrates far more deeply into both types of wood, with penetrative staining particularly apparent in the maple, staining it through and through. An explanation could perhaps lie in the structure of the dyes: the basic dyes adhere strongly to the acid present in the wood and do not stain it through and through, as the acidic dyes do. This hypothesis needs to be investigated further, by taking

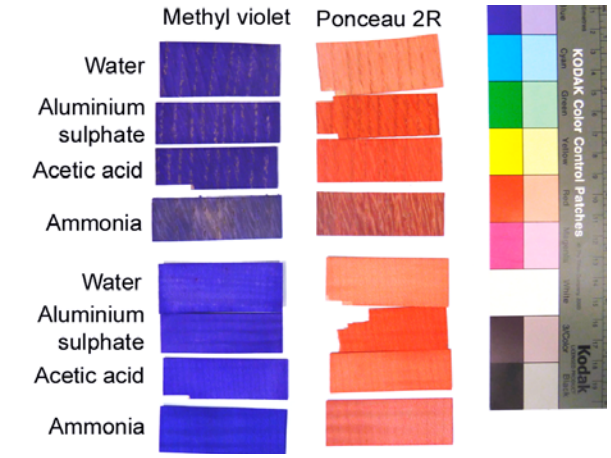

Figure 6: Effect of different dye bath additives on the colour of oak (above) and maple (below) following staining with methyl violet and Ponceau 2R, respectively.

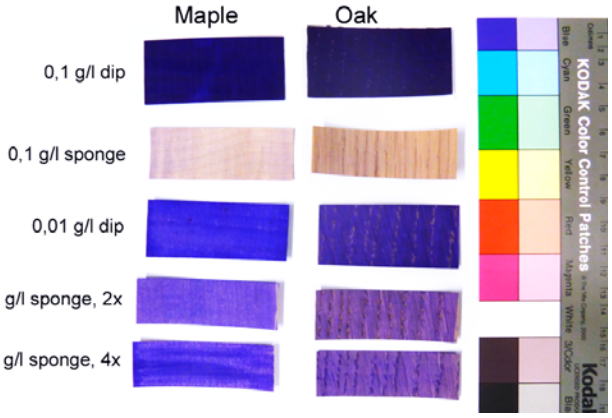

Figure 7. Colour variation following the staining of maple and oak with methyl violet using the dipping method and brush application, at different concentrations.

sections of the reconstructions where other dyes were used. It must be noted that in general the stained wood is sanded before a finishing layer, such as wax or varnish, is added. A deep penetration of the dye is therefore preferred; otherwise the stain is easily scraped off.

The colour variation that results from the dye being dissolved in water or ethanol was investigated next (Fig. 5). In this case the wetting was done with water, with both wood types treated similarly.

In this experiment the colour difference was particularly striking in the case of methyl violet dissolved in alcohol, resulting in a much weaker staining effect in both the oak and maple. In the case of Ponceau 2R the resulting colour is actually darker if it is dissolved in ethanol. It is conceivable that the solvent itself might affect the wood, but that did not appear to be the case here, since the effect would not then be different for the two dyes. Both dyes are in principle easily soluble in both water and ethanol, and the solutions were also unsaturated (that is to say, all the dye was in fact dissolved). It is possible, however, that the methyl violet dissolves so effectively in ethanol that this results in a relatively low affinity for the wood. For Ponceau 2R the situation would be precisely the reverse, as it dissolves more effectively in water than it bonds with the wood. We can find an explanation for this when we look at the chemical structure: Ponceau 2R, with its two strongly acidic groups, is far more hydrophilic than methyl violet. It is also worth noting that many suppliers of these staining materials indicate how the dye can best be dissolved.

In a subsequent experiment a variety of chemicals were added to the dye bath in order to investigate their effects on the staining. The effects of ammonia, aluminium sulphate and acetic acid were investigated (in a concentration equivalent to the quantity of dye): see Fig. 6.

In the case of methyl violet the effect of the additives to the dye bath is limited, and only in the case of ammonia on oak can it be seen that the staining is reduced, while with maple the colour in that case is somewhat more intense. The additives have more effect with the acidic dye Ponceau 2R, with aluminium sulphate in particular intensifying the staining of both oak and maple. Probably a so-called "salting out" effect is involved here, where the solubility of the dyes is reduced through the addition of salt, resulting in better adhesion to the wood. Stronger staining was also observed in the case of acetic acid, particularly in the oak. The addition of ammonia to the Ponceau 2R dye bath had a particularly marked effect on the oak, in which a clear colour difference was could be observed and the wood grain appeared to be accentuated.

The manner in which the stain was applied also had strong effects on the final colour, as can be seen in Fig. 7.

This experiment demonstrated that the dipping method, which involves the wood being fully immersed in the dye bath, produced colours that were far more intense than in the case of application using a brush or sponge. An explanation for this can be found in the duration of the dye bath. In the case of dipping the wood was left in the dye bath for fifteen to thirty minutes. The longer the staining period, the higher the colour intensity of the wood. A pronounced change in colour can be observed particularly during the first few minutes of staining; as the staining lasts longer the colour appears to become saturated. When a brush or sponge is used the staining process is very rapid. The concentration in the dye bath needed to be increased to obtain a good colour. With methyl violet it can be observed that the dipping bath method requires a concentration lower by a factor of 100 than the concentration required when a brush or sponge are used.

When using the brush or sponge the colour can be subtly varied by repeating the process. It is clear that the total immersion of the wood in a dye bath results in a more homogeneous and intense colour than can be obtained with the use of a brush or sponge. The latter method is however particularly suitable for larger areas, in addition to which the final colour can be determined much more easily and shading is simpler. That having been said, it is also possible to effectively control colour shades when using the dipping method. If the concentration in the dye bath is not too high the final colour can be determined by the duration of immersion (after frequent checking). A fairly subtle control can even be exercised, if, following heating, the dye bath is allowed to cool with the wood immersed in it and the colour is then checked frequently.

The above experiments show that the application method, the concentration and the duration of the staining are the most significant factors in determining the final colour. Additives like ammonia and aluminium sulphate have subtle effects on the colour, while pre-treatment with water, a solution of common salt or ammonia hardly affect the final colour. It is difficult to achieve homogeneous results when staining with basic dyes. The basic dyes adhere strongly to acids found in the wood. If the acid is not uniformly distributed, an even staining effect will not be achieved. This is not a problem in the case of acidic dyes, which probably explains why they were used far more frequently than basic dyes.

Figure 8: Selection of colours obtained from the application of the wood stain specified in Tab. 2.

The effect of the concentration on the final colour was subsequently investigated for the series of dyes specified in Table 2. The standard recipe was followed, with a sponge used to apply the dyes, with a concentration range of 1 to 15 g/l for the acidic dyes and 0.1 to 5 g/l for the basic dyes, applied to both oak and maple. Unfortunately it is not possible to show all the reconstructions, but a selection is presented in Fig. 8.

5 Preparation of Samples

The second objective of this research was to investigate whether the extraction method could be improved. Maple veneer was used in this investigation, stained with, respectively, methyl violet, Ponceau 2R, methylene blue and naphthol yellow S. Methylene blue is a basic dye in the thiazine class, while naphthol yellow S is an acidic dye in the nitro class. Staining was carried out using the standard recipe with the dipping method: this provides the most homogeneous stain and therefore the most homogeneous sampling.

The four dyes used are very different from a chemical point of view, and a suitable extraction method would need to be effective for all four. All extractions were repeated 5 times to obtain an indication of the reproducibility. As stated above the samples were accurately weighed and the results were subsequently corrected for the weight difference.

The degree of extraction was affected by three parameters. Firstly, the stability of the dyes in the extraction media. It is possible for the dyes to have decomposed, which would mean the original substances are no longer detectable. This is mainly a problem relating to natural dyes, some of which are not able to withstand hydrochloric acid for example. Research on this topic for this set of dyes has however already been completed and published.[9] In that study both the pure dyes and wool dyed with them were treated with hydrochloric acid using an identical method to that employed with the veneer samples. The research indicated that the majority of these dyes are stable.

The second parameter is the solubility of the dyes: depending on their structure they can be hydrophobic or hydrophilic, therefore dissolving better in organic or in aqueous solvents, respectively. Since this cannot be determined in advance, DMF was used as the solvent in all cases, since it is able to effectively dissolve both hydrophobic and hydrophilic dyes. The third and crucial parameter is the degree to which the extraction agent is able to loosen the dye from the substrate, in this case wood. It is possible that the degree to which the solvent penetrates the wood also plays a role. The results of the extraction tests, by measuring the peak area of the dyes extracted, are presented in Fig. 9.

On the basis of these measurements it appears that methyl violet is best extracted with acetic acid, with the combined method (DMF and hydrochloric acid) coming a close second. There are however only minor differences between the four extraction methods. The differences are much greater for methylene blue, with the yield resulting from the use of hydrochloric acid extraction the highest by far. Here, again, the combined extraction method using first DMF and then hydrochloric acid comes a close second, while extraction with ethanol and acetic acid delivers a clearly infe-

rior result. The acidic dyes Ponceau 2R and naphthol yellow S are best extracted with a combination of DMF and hydrochloric acid, as the other methods all produce poorer results. In the case of these two dyes, extractions were also carried out using ammonia, on the assumption that the basic solution would effectively dissolve the acidic dyes. However, this proved not to be the case.

This investigation showed that the combined extraction method, using DMF and subsequently a solution of hydrochloric acid, produced the best results for all dyes. As a final test a second extraction was carried out on all the extracted samples, in order to determine how much dye could then be found. This investigation revealed that the initial combined extraction using DMF and hydrochloric acid extracted more than 90% of the dye: the method is therefore highly efficient. These extractions were carried out using pieces of wood, while it is more customary to use scrapings. The expectation is that extraction using scrapings would produce better rather than worse results, because the solvent would not then be required to fully penetrate the wood. It is worth noting that these days the combined extraction method is also frequently applied to textile samples.

The method described above was subsequently used for an analysis of the staining of an object from the collection of the Cultural Heritage Agency of the Netherlands. This was a desk made of oak, mahogany and coromandel, dating from 1930 and made in the Amsterdam School style of Eibink and Snellebrand. The desk now looks brown in appearance, but a red colour is still clearly apparent on the insides of the doors. The fading of the finish is particularly evident in the sliding desk top. The further the desk top is exposed, the more pronounced is the effect of fading, with the desk top appearing almost white in places. Two samples were obtained by scraping, one from the faded area and one from the area where the colour finish is still in good condition. The two samples were treated with the combined extraction method and subsequently analysed using HPLC. Analysis indicated that a mixture of Ponceau G and Ponceau 2R was used for the staining. Some other components with comparable spectra were also found, but at far lower concentrations. These were probably subsidiary components of Ponceau G. The Ponceau dyes were found in both the faded and unfaded (or less faded) areas; however, the concentration in the faded area was much lower. Ponceau G (C.I. Acid Orange 14, C.I. 16100) is an azo dye; very similar to Ponceau 2R in its chemical composition, this stain has a vivid reddish orange colour. The light fastness of Ponceau G on textiles is good at ISO 6. Nevertheless in places the colour had disappeared completely, particularly where it was exposed to light. Further research will be required to demonstrate whether the light fastness of this colorant on wood is identical to that on textiles.

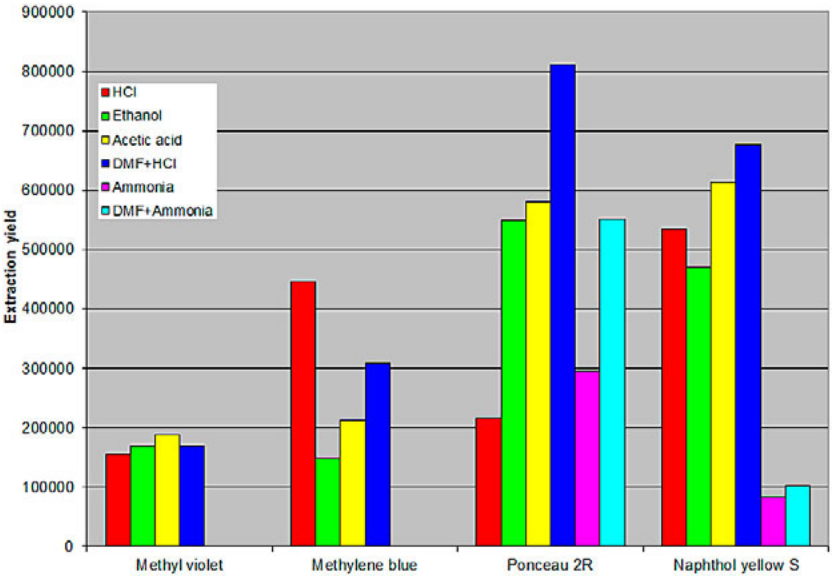

Figure 9: Yield from different extraction methods for various dyes, corrected for the weight of the sample.

6 Conclusion and Further Research

While this study has not produced an exhaustive survey of recipes, it seems clear that the number of parameters within the recipes is limited. The recipes are far less complex than in the case of natural dyes. The most significant parameters are the application method (dipping or brush/sponge), the duration of the staining process, the concentration of the dye and the actual dye used. If the recipes are followed this often results in very intense colours, which are no longer visible today. More object-based research is required to establish what effect this has on the appearance of late 19th and early 20th century furniture. Whether furniture from that period could and should be returned to its original colour is in part an ethical discussion. Reconstructions, digital and otherwise, would also be useful here in providing a better understanding of these items of furniture. This would however require supplementary research on items furniture in order to establish the original colour as precisely as possible. The extraction technique has been optimised in the interim and an initial analysis of a desk from 1930 shows that the dye can be effectively analysed using this method. It would be interesting to conduct a study looking at the minimum quantity of sampling material required for an accurate analysis based partly on reconstructions and partly on furniture.

A follow-up investigation should also consider the ageing of dyes. The light fastness of most dyes is known, but this is when they are used on textiles. Whether their light fastness on wood is comparable has still to be investigated. It is not only the fading of the dye which of interest, as colour changes in the wood itself will alter the appearance of the furniture. As well as ageing due to the effects of light, the ageing of dyes in dark conditions must also be investigated. In many items of furniture it is possible to find areas that were stained but which have had very little or no exposure to light. It is tempting to assume that the original colour will be visible in such areas, but it has still to be investigated whether that is actually the case and whether the wood and the dye have not changed in colour.

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9 Note

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