

# How They Dyed: A CheMYSTERY

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## *Abstract*

In this study, four types of dyes were used to colour eleven types of fibre, and the effectiveness of each dye was examined based on dye uptake and colourfastness. The dyes used were Diamine Fountain Pen Ink (Majestic Purple), ClubHouse Neon Food Colouring (mix of blue, purple, and pink), Rit DyeMore (Royal Purple), and Tulip One-Step Tie Dye (Purple). These are inks, acid dyes, disperse and direct dyes, and reactive dyes, respectively. The fibres chosen for this study were wool, silk, jute, cotton, paper towel, bamboo, nylon, acrylic, polyester, polyurethane, and polyethylene. Eight experiments were performed for each type of dye, to evaluate the impact of temperature and chemical additives on dye uptake. From this experiment, we found that the results could be accurately explained by current literature, demonstrating the importance of chemical structure in dyeing and the potential for textile colouration as a valuable teaching tool.

As a further demonstration, a multi-material colour-work hat was knitted and then dyed to demonstrate the differences in chemical structure to create a “secret pattern” reveal.

**Keywords:** Ink, Acid dye, Disperse dye, Direct dye, Reactive dye, Wool, Silk, Cotton, Jute, Paper, Bamboo, Polyester, Polyurethane, Polyethylene, Acrylic, Nylon, Vinegar, Salt, Detergent, Resist dyeing

## *Introduction*

Often, people wear clothes that have been chemically coloured in some way. Whether various types of pigments are used or removed through bleaching, the textile industry — and the adjacent fashion industry — places huge emphasis on picking colours to maximize form utility, and, consequently, marketability. This is why trends like Pantone’s Colour of the Year exists; why colour theories like the use of opposite colours are helpful; and why people have favourite colours, in general. We carry colour with us everywhere we go. But what are the chemical mechanisms that allow us to do so? And how can we capitalize on this chemistry, to ensure the longevity of colours in clothing?

There is already a great deal of literature, both academic and hobbyist in nature, regarding the effectiveness of various dyes. A review of the literature revealed that in general, acid dyes penetrate best into polyamide fibres, reactive dyes are most permanent on cellulosic fibres, and disperse dyes are the only effective post-production colouration method for hydrophobic synthetic fibres.

In order for the eye to perceive colour, a chromophore must be present in the molecule. The chromophore is the part of a molecule which causes something to be coloured. Thus, based on the chemical structure of a molecule, a different colour will be perceived. Colour is typically produced in molecules with a significant number of conjugated pi bonds. Therefore, the addition of pi bonds helps to create colour, and their destruction heralds the removal of colour. In the process of dyeing, a chromophore is in some way attached to the subject that is coloured. This can occur through a number of different mechanisms.

One of the largest classes of dyes is reactive. These are colourants which form covalent bonds with the fibres. Since there are very few limitations on chromogens which can be converted to reactive dyes, there is an eclectic range of available shades for reactive dyes. The specific mechanism through which covalent bonds are formed depends on the exact formulation of the product. Since they are water-soluble dyes, they perform best on hydrophilic fibres. In general, they are anionic dyes, and thus prefer to bind to less electronegative fibres, such as wool. However, the addition of electrolytes (e.g., NaCl) to the dyebath can promote attraction between more electronegative cellulosic fibres and the anionic dyes.

Acid dyes are the most popular choice for polyamide fibres such as wool, silk, and nylon. Generally, these fibres have a vast array of choices for colouration methods; since they are hydrophilic fibres, they can be dyed with a great many water-soluble dyes. These include chemical structures such as acid dyes and reactive dyes. However, especially for natural protein fibres, acid dyes are used most often. These are anionic sulfonated chromophores; the structure of a simple acid dye is  $D(-SO_3^- Na^+)_n$ , where D represents a chromophore entity (e.g., azo, anthraquinone, phthalocyanine, etc.), and  $n$  is an integer generally ranging from 1 to 3.

When colouring wool, dyeing is typically carried out at the boil for 1 hour in an acidic dyebath. The uptake of dye has a negative correlation to bath pH (i.e., a more acidic dyebath has greater uptake). Conversely, temperature and uptake have a positive correlation.

One of the primary mechanisms to drive the dyeing process is the Coulombic attraction between anionic sulfonated dyes and protonated amino sites. The wool polyamide contains lysine primary amino groups, histidine secondary/tertiary amino groups, arginine guanidino groups, and  $\alpha$ -terminal amino groups. Overall, there is a molar concentration of about 820  $\mu\text{mol/g}$ ; this is a significant total, which increases the rate of uptake and final saturation value.

The outside of the wool fibre is very hydrophobic. Consequently, it is more difficult for reactive dyes to penetrate them deeply; these dyes attempt to form covalent bonds. They are, however, able to react with the proteins in the endocuticle and endocuticular intercellular regions – thus, they demonstrate some modicum of effectiveness.

Some other fibres are entirely hydrophobic, and therefore require non-water-soluble dyes in order to be effectively coloured. These include polyester, cellulose acetate, nylon, acrylic, and polyolefin. While nylon is a polyamide – and thus has primary amino end-groups that give them some scintilla of substantivity to water-soluble acid dyes – most of these other fibres are not so fortunate. Consequently, most of the time, these synthetic fibres are dyed using mass-colouration before the

solution is spun into filament. However, in the absence of the need for mass-production of a single shade, or if a home-dyeing alternative is desired, the only viable options are disperse dyes.

Disperse dyes are water insoluble dyes which are applied from fine aqueous dispersion, and which have substantivity for hydrophobic fibres. To colour the fabric, they form a solid solution with the fibres. They have very low molecular weight in order to facilitate dye uptake. Most frequently, they comprise colourants derived from azo, anthraquinone, and diphenylamine materials. They are combined with a dispersing agent in order to increase stability; they reduce the particle size of the disperse dyes and increase their aqueous solubility. While some may have weak solubilising groups, they all have a marked lack of strong solubilising groups (e.g., sulfonic, carboxyl, etc.) and ionic charge. Nonetheless, it is possible that Van der Waals forces and dipole interactions help dye retention post-diffusion. When dyeing with disperse dyes, the process should be carried out at the boil. The ideal dyebath pH varies depending on the specific disperse dye; for example, amino azobenzene dyes see an increase in dye uptake as the pH increases, whereas azo dyes with hydroxyl groups do best in slightly acidic environments, and yet other dyes remain unimpacted by pH levels. The actual transfer mechanism for disperse dyes is not fully understood. Some sources speculate that heat allows the fibres to loosen and allow dyes to enter, and that upon cooling, they re-tighten around the colour. However, this is just conjecture.

When sold commercially for home-dyeing use, disperse and acid dyes are often mixed with direct dyes to create “all purpose” solutions. Direct dyes are also known as substantive dyes, since the mechanism by which they function capitalizes on substantivity between dye and cellulose fibre. Consequently, they tend to perform best on fabrics with high cellulose content – and thus, plant materials will take them most effectively. The ideal application environment tends to be at high heat with a basic dyebath. However, since these dyes do not form covalent or ionic bonds with the fabric, they have poor wash-fastness.

While this wealth of information is beneficial to anyone seeking to decide which dye to use, it is also potentially an overwhelming amount of technical specifications that do not necessarily translate well into practical applications. This study seeks to give a visual representation of the implications of this chemistry, and to draw conclusions regarding the effectiveness of household dye products.

## *Experimental*

This study was carried out over a series of experiments. 32 dyebaths were prepared, each boasting a different combination of properties. The variables were temperature (hot, cold), dye structure (ink, acid, disperse/direct, reactive), and additives (none, vinegar, salt, detergent). Each dyebath received 11 fabric swatches, in wool, silk, jute, cotton, paper towel, bamboo, nylon, acrylic, polyester, polyurethane, and polyethylene.

Dye uptake was measured qualitatively using visual analysis of the colouration of the fibres. Analysis of the dye-bath exhaustion proved futile, as all of the dye-baths were unable to experience any significant exhaustion.

## Materials

The fibres dyed in the experiment are as follows:

- + 3-ply (S-plied) wool yarn, 9 wpi, 212 yds/100 g
- + 4-ply (S-plied) acrylic yarn, 8 wpi, 188 yds/100 g
- + 16-ply (8 by 2 S-cable plied) bamboo yarn, 12 WPI, 241 yds/100 g
- + 100% jute burlap, loosely woven, plain weave, 7 warps per inch, 6 wefts per inch
- + Cotton fabric, plain weave,
- + Polyester chiffon
- + Polyurethane faux leather
- + Polyethylene fabric
- + Nylon organza ribbon
- + Silk curtain fabric
- + 2-ply paper towel, 365 gsm

In preparation for the experiment, fabric yardage (jute, cotton, polyester, polyurethane, polyethylene, nylon, silk, and paper towel) was cut into strips 1" by 6". Yarn lengths (wool, acrylic, bamboo) were cut to 24", then doubled back on themselves, secured at midpoint with an overhead knot, and folded at the knot.

The following comprises the dyes used for dyeing samples:

- + Majestic Purple Diamine Fountain Pen Ink
- + Royal Purple Rit DyeMore (C.I. Disperse Red 17, C.I. Disperse Violet 1, C.I. Disperse Blue 3, C.I. Direct Red 16, C.I. Direct Blue 71, C.I. Direct Black 22)
- + Blue, Purple, and Pink ClubHouse Neon Food Colouring (C.I. Food Red 17, C.I. Acid Red 51, C.I. Acid Blue 9)
- + Purple Tulip One-Step Tie Dye (C.I. Reactive Blue 4, C.I. Reactive Red 2)

The additives used in the dyebaths are as follows:

- + White vinegar, 5% acetic acid concentration (2.5 mL per dyebath)
- + Laundry detergent (2.5 mL per dyebath)
- + Table salt (2.5 mL per dyebath)

Finally, the component materials for the hat sample:

- + Stranded colourwork hat, knit from 3-ply (S-plied) wool yarn, 9 wpi, 212 yds/100 g; and 4-ply (S-plied) acrylic yarn, 9 wpi, 205 yds/100 g
- + Golden Yellow, Pink, Violet, Royal Blue, and Teal Wilton Icing Colours (C.I. Food Red 17, C.I. Acid Yellow 23, C.I. Acid Blue 9, C.I. Acid Red 51, C.I. Food Yellow 3, C.I. Acid Blue 74); 3/8 tsp. diluted in 80 mL water
- + White vinegar, 5% acetic acid concentration; 15 mL diluted in 1 L water

### **Immersion-Dyeing Application to Swatches**

In order to mix the dyes with more consistency, a dye stock was prepared in advance of the experiment. 1 mL (20 drops) of Diamine Fountain Pen Ink was diluted into 80 mL water; 10 mL of this solution was added to each dyebath. 80 mL water was added to the Tulip One-Step Tie Dye, and the solution was agitated to dissolve the powder; 10 mL of this solution was added to each dyebath. 3.75 mL Rit DyeMore was added to each dyebath at full concentration. 10 mL of ClubHouse Food Colouring was diluted with 6 mL water; 2 mL of this solution was added to each dyebath.

The dyebaths were prepared inside glass mason jars with capacities of approximately 475 mL. 80 mL water, the relevant dye stock, and additive was added to the jar. (Note that one sample for each dye type and temperature was left without additive.) For dye applications carried out at the boil, this elevated temperature was achieved by placing the dyebath into a pot of boiling water. Once the desired temperature was attained, one swatch of each fibre was added into the dyebath. Dyeing was carried out in full immersion for 20 minutes, after which the fabrics were removed from the dyebath and rinsed in cold water until the water ran clear. The samples were then laid flat to dry.

### **Low-Water Immersion Dyeing Application to Hat**

The hat was presoaked in about 500 mL cold water. 1 L water was brought to a simmer in a large pot, at which point 15 mL white vinegar was added. The hat was then added to the dyebath, and colorant was applied using squirt bottles. After approximately 15 minutes, the fabric was flipped, and the same process was carried out on the reverse side. The water was drained and replaced with clean water; following this, the hat was left to set for 15 minutes. It was rinsed with cold water until the water ran clear, then with warm water and a gentle detergent.

## *Results + Discussion*

We found that overall, the results were consistent with the literature. Some deviations were recorded; however, it is uncertain whether this was due to experimental flaws. For the colour cards in this section, the shades were obtained by photographing the samples, then using the eyedropper tool in paint.NET to ascertain the HEX value. This is not a perfectly accurate system, as the lighting environment was not perfect during photography, and it is difficult to deduce which point is the “true” colour, since there are a myriad of shadows and highlights present in a photograph of fabric or yarn. Where possible, colour cards are used to provide clearer demonstrations. In some cases, however, such as with the nylon organza ribbon, sample pictures are included, since the fabrics are sheer and thus harder to place numerical values on. This will allow the reader to draw their own conclusions regarding the optics of the subjects in question.

Nonetheless, the following are some general observations.

### **Impact of Vinegar on Hue**

Due to resource constraints, we were unable to accurately measure either the pH of the dyebaths or the hue of the resultant samples. However, in general, there seems to be a correlation between

acidity and uptake of red colour. This is similar to pH indicators such as red cabbage (which turns pink in acidic solution, and blue in alkaline solution), indigo (which turns yellow in acidic solution and blue in alkaline solution), and litmus paper (which turns red in acidic solution, and blue in alkaline solution). It should be noted that not all substances follow this same trend of acids creating warm tones and bases creating cool tones (e.g., hydrangeas grow blue in acidic soil, and pink in alkaline soil; phenolphthalein turns pink as pH increases; etc.).

It is also possible that this trend is related to the overall uptake of colour; in the following two examples, the samples dyed with vinegar are both more red and more saturated in general.



*Nylon organza ribbon dyed in hot acid dyebath with vinegar (left) and detergent (right)*



*Acrylic yarn dyed in a hot disperse/direct dyebath with vinegar (left) and detergent (right)*

### Acid Dye Hue

For acid dyes, the uptake of the red colourant was far faster than blue. When wiping down the finished product, the decomposition of the blue dye was evident. This tends to be especially problematic in purple dyes, which happens to be the colour we used in this experiment.





Left: Violet Wilton Icing Colour broken on a tissue after wiping down a surface

Right: jars with remnants of dyebaths after the swatches were dyed; the left is a purple hue similar to the original colour of the dyebath, and the right is a blue hue with a significant decrease in red from the original dyebath

We observed that despite using a purple dye solution, most of the fabrics dyed pink. There were a few exceptions to this observation, such as the silk swatches dyed at high heat with salt and vinegar, as well as the wool swatch dyed in hot solution with vinegar. We hypothesize that the elevated temperature and acidity allowed faster dye uptake, which consequently allowed the blue dye to have time to strike.



Left: samples dyed in hot acid dye with salt added; from left to right, acrylic, polyethylene, polyurethane, polyester, paper towel, cotton, bamboo, nylon, wool, silk, jute

Right: wool samples dyed in acid dye, in cold medium on the left and hot medium on the right; from foreground to background, with the addition of detergent, with the addition of salt, with the addition of vinegar, with no additives

cold acid vinegar	cold acid	cold acid salt	cold acid detergent	cold acid vinegar	cold acid	cold acid salt	cold acid detergent
hot acid vinegar	hot acid	hot acid salt	hot acid detergent	hot acid vinegar	hot acid	hot acid salt	hot acid detergent

*Left: silk colour card for acid dyes; additives from left to right, vinegar, none, salt, detergent; from top to bottom, cold, hot*

*Right: wool colour card for acid dyes; additives from left to right, vinegar, none, salt, detergent; from top to bottom, cold, hot*

## Dyebath Temperature

Disperse dyes struck best at high heat; there is an incredibly noticeable difference in dye uptake when applied cold vs. hot. In the case of polyurethane, the uptake is barely present at cold temperatures. Even if it does dye at cold temperatures, such as in the case of wool, the saturation is far greater at high temperatures.

cold disperse vinegar	cold disperse	cold disperse salt	cold disperse detergent	cold disperse vinegar	cold disperse	cold disperse salt	cold disperse detergent
hot disperse vinegar	hot disperse	hot disperse salt	hot disperse detergent	hot disperse vinegar	hot disperse	hot disperse salt	hot disperse detergent

*Left: polyurethane colour cards for disperse/direct dye; additives from left to right, vinegar, none, salt, detergent; from top to bottom, cold, hot*

*Right: wool colour cards for disperse/direct dye; additives from left to right, vinegar, none, salt, detergent; from top to bottom, cold, hot*

The same is true of most dyebaths. In most cases, heat speeds up chemical reactions, since it adds energy to the system. Furthermore, heat tends to increase solubility. As a result, dye uptake occurs much faster in hot environments.

In general, the synthetic fibres struggled to accept any dye. Nonetheless, hot dyebaths of disperse dyes had promising results. The hot acid dyebath with the addition of vinegar was able to take some dye; however, it does appear to be particularly washfast, and the texture of the fibre is markedly crunchier. Consequently, this is still not a viable option for practical textile dyeing.

cold reactive vinegar	cold reactive	cold reactive salt	cold reactive detergent	cold ink vinegar	cold ink	cold ink salt	cold ink detergent
hot reactive vinegar	hot reactive	hot reactive salt	hot reactive detergent	hot ink vinegar	hot ink	hot ink salt	hot ink detergent

*Left: acrylic colour cards for reactive dye; additives from left to right, vinegar, none, salt, detergent; from top to bottom, cold, hot*

*Right: acrylic colour cards for ink; additives from left to right, vinegar, none, salt, detergent; from top to bottom, cold, hot*



cold disperse vinegar	cold disperse	cold disperse salt	cold disperse detergent	cold acid vinegar	cold acid	cold acid salt	cold acid detergent
hot disperse vinegar	hot disperse	hot disperse salt	hot disperse detergent	hot acid vinegar	hot acid	hot acid salt	hot acid detergent

*Left: acrylic colour cards for disperse/direct dye; additives from left to right, vinegar, none, salt, detergent; from top to bottom, cold, hot*

*Right: acrylic colour cards for acid dye; additives from left to right, vinegar, none, salt, detergent; from top to bottom, cold, hot*

While in most cases, heat and saturation were positively correlated, there are some cases where the opposite was true. This includes the application of acid dyes to cellulosic fibres. It is likely that this is the case since heat promotes the breakdown of weak bonds, whereas it aids setting in cases where there is high substantivity between dye and fibre.

cold acid vinegar	cold acid	cold acid salt	cold acid detergent	cold acid vinegar	cold acid	cold acid salt	cold acid detergent
hot acid vinegar	hot acid	hot acid salt	hot acid detergent	hot acid vinegar	hot acid	hot acid salt	hot acid detergent

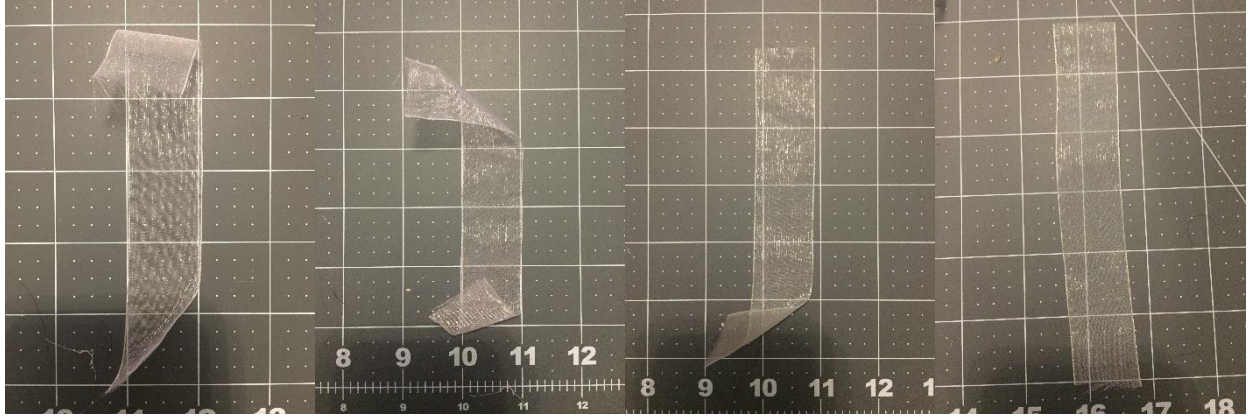
*Left: cotton colour cards for acid dye; additives from left to right, vinegar, none, salt, detergent; from top to bottom, cold, hot*

*Right: polyurethane colour cards for acid dye; additives from left to right, vinegar, none, salt, detergent; from top to bottom, cold, hot*

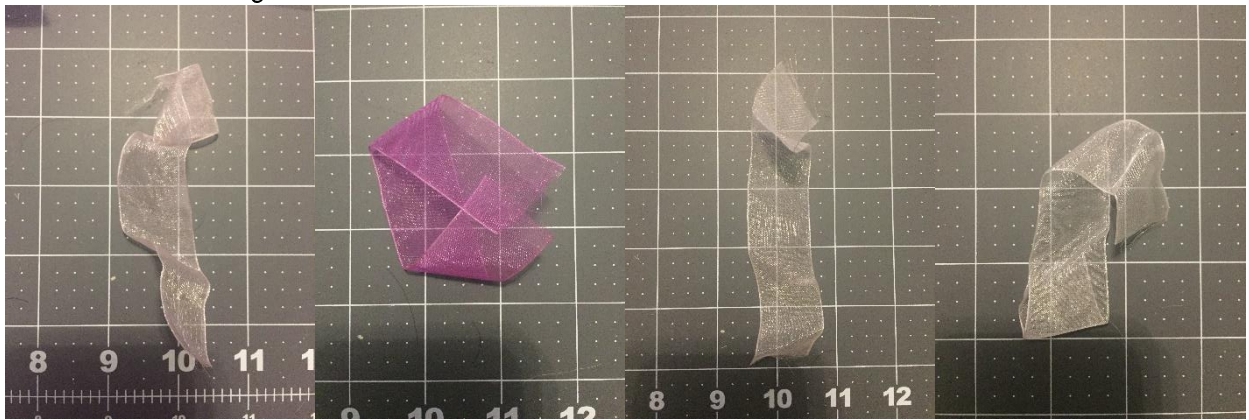
## Ink Uptake

In most cases, the ink was unable to bond to the fabric samples. We were unable to ascertain the chemical composition of the Diamine Fountain Pen Ink, so the reasoning behind this is dubious. However, given that the product was not formulated for textile colouration purposes, it is likely that there is an absence of binding agents, and that the chemical structure is not optimized for permanent application.

In general, nylon took the dyes extremely well, but in the case of ink, it was only able to take any colour in the hot dyebath with vinegar.



*From left to right: nylon organza ribbon dyed in a cold ink bath with no additives, with vinegar, with salt, and with detergent*



*From left to right: nylon organza ribbon dyed in a hot ink bath with no additives, with vinegar, with salt, and with detergent*

### Hat Dyeing

With the hat, we found that the wool took the dye well, and the acrylic did not take the dye at all.



*Left: hat in the process of low-water immersion dyeing*

*Right: tight shot of hat after dyeing and washing*

## Conclusions

Based on the obtained results, it is evident that there is no “ideal” solution to which dyes are most effective. Depending on goals, various dyes might have the desired effect. Acid dyes, while brilliant in applications, are difficult to set if using blue shades. For more colourfast results, dyeing at high heat is superior – however, if wash fastness is not required, it may be best to dye at low heat in some cases. In general,

In future, most experiments should be performed with different colours and brands of dyes, as well as in various increments of dye/additive concentration and temperature. Furthermore, instruments should be obtained to more accurately measure properties such as temperature, weight, colour, and pH.

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