ABSTRACT

STEWART, CHARLES WAYNE. A Comparative Study of the Environmental Impacts of Standardized Dyeing Systems Using Natural and Synthetic Dyes on Knitted Cotton Fabric. (Under the direction of Dr. Warren Jasper.)

Cotton apparel is universally accepted, comfortable to wear and remains in high demand. The 2016-17 global forecast for cotton consumption is 21.81million metric tons and has remained relatively stable since 2014-2015. Traditional manufacturing practices for cotton consumes large amounts of water, energy and chemicals as well as discharging large amounts of polluted effluent. Textile dyeing has been blamed for up to 20% of all global industrial wastewater pollution.

With cotton apparel, we are faced with the multi-faceted and complex balancing act of strong market demand for the end product versus the negative environmental impact resulting from old and traditional manufacturing technologies. The challenge is to find new synergies in dyes, colorants and manufacturing technology to apply color to cotton while reducing the negative environmental impact from manufacturing. The objective of the research is to identify select processing parameters for use in comparing the dyeing efficiency and environmental impact of various dyeing systems for cotton.

Cotton was originally dyed using natural colorants coupled with toxic heavy metal mordants. Synthetic versions of natural colorants were introduced and used before the introduction of direct dyes. Direct dyes provided the mills a more robust means of applying color using electrolyte and temperature. Early direct dyes were limited by their moderate to poor wet fastness and eventually were replaced with fiber reactive dyes. Fiber reactive dyes have evolved to provide satisfactory results using lower amounts of water and energy. A

recent improvement in fiber reactive dyes increased the dyeing efficiency, which results in more color going on the fabric and less color going down the drain as waste.

Water usage, steam consumption, cycle time, impact of effluent, and dyestuff efficiency were the processing parameters selected for comparison using a Weighted Parameter Evaluation. A representative set of dyeings from the study was submitted for a limited panel of apparel fastness testing. Since fastness testing is not directly related to dyestuff efficiency and impact on the environment, the data from fastness testing was used only for relative comparison of the various types of colorants and dyes and was not included in the Weighted Parameter Evaluation.

When the Weighted Parameter Evaluation data for natural colorants was compared to data for synthetic dyes, the petroleum based, synthetic dyes produced the best overall scores, thus confirming the hypothesis.

When the petroleum-based synthetic dyes were compared to each other, the sequential improvements made over time were apparent. Direct dyes performed better than natural colorants. First generation fiber reactive dyes displayed improved performance and lower environmental impact than direct dyes. And finally, the newest iteration of fiber reactive dyes, poly-functional dyes, recorded the lowest amount of water usage, steam consumption, and cycle time, plus had the highest dyestuff yield of all systems evaluated.

A Comparative Study of the Environmental Impacts of Standardized Dyeing Systems Using Natural and Synthetic Dyes on Knitted Cotton Fabric

by
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DEDICATION

To my late father, Charles M. Stewart, thank you for introducing me to your wonderful world of dyeing and color.

To Donna and Ashley Stewart, thank you for the many years of encouragement, pushing, and prodding. Thank you. I could not have done it without the both of you.

BIOGRAPHY

Charles Wayne Stewart (August 1955) earned his BS degree in Textile Chemistry from North Carolina State University in 1977 and his MS degree in Textile Engineering from The Georgia Institute of Technology in 1979. His professional textile career was highlighted by 17 years as the owner and operator of Tumbling Colors (1999-2016) in Raleigh NC. Charles is currently employed as a Principal Scientist with Eastman Chemical, Kingsport TN.

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Thank you to Eastman Chemical for providing me the time and resources to complete the journey started in 2006 while operating Tumbling Colors in Raleigh, NC.

A special thank you goes to the many wonderful students and interns from The College of Textiles, North Carolina State University that helped with both gathering data for the research and keeping Tumbling Colors running while I was busy with this, my final degree.

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1. INTRODUCTION

One Trillion, 500 Billion is the estimated value of the 2015 global apparel retail market. The US apparel retail market contributes 20% (300 Billion) to the total. The volume of individual transactions required to achieve this monetary value is astronomical. How do retailers move enough products to generate these numbers?

…COLOR…

Color is the primary driver in retail sales. Color is the magnet that attracts the consumer to the product, thus starting the selling/buying process: See, Touch, Try, and Buy.

Color has been used since before the beginning of recorded history on all major continents and by all cultures. Cave art using minerals for color has been dated to 15000 BC. Fabrics woven from flax and linen and dyed with Tyrian purple were discovered in Turkey and dated to 8000 BC. Early archaeological finds show that colored animal furs and hides, and woven fabrics were used for protection from the elements.

Wild cotton was indigenous to a vast global growing belt that included the American Southwest, Mexico, Central and South America, Africa, Persia, and India. Mexican Indians cultivated cotton for textile applications as early as 5000 BC. Fragments of cotton textiles have been found in the Indus River Valley of Pakistan that date to 2000 BC. Linen (spun from flax) was limited to Egypt, Russia, Europe and areas surrounding the Mediterranean.

Natural colors and natural fibers are not new and were integral to the development of civilization.

The earliest colors were most likely to have been red and brown stains caused by physical contact with objects such as clay or tree bark. Blocks of ochre, compounded into crayons and dating back as early as 100000 BC have been unearthed in the Blombos Caves in South Africa. When these stains were exposed to metal containing compounds, the stains became darker and more permanent colors.

Yellows were common and easy to apply since they dyed ‘directly’ and did not require high temperatures or metal mordants. Bright yellows were available from indigenous plants and flowers such as turmeric and safflower.

Many ancient civilizations processed excellent knowledge of local colors and dyeing procedures. From 1500 BC, the Phoenicians were known to have a thriving royal purple dyeing industry based on a species of shellfish processed in the city of Tyre (Tyrian purple) until destroyed by invading armies in 638 AD.

Ancient India was advanced with regards to applying color to cotton. India had the advantage of a large population for labor, the presence of wild cotton, and was surrounded by excellent natural color producing plants. Plus the Indian dyers were very patient and willing to spend the days and weeks necessary to develop the rich colors now associated with the ancient Indian culture.

Everything changed in 1856 when William Henry Perkin accidently synthesized Mauve from aniline. From this point on, synthetic colors steadily replaced natural colors due to their improved color gamut, ease of application, and reduced costs. There are no references of their environmental impact of applying natural colorants in early literature, however one can expect the impact to both the environment and dyers was very bad. Many of the early synthesized dyes were developed to mimic natural colors such as Madder and Indigo. The synthetic versions had improved color yield, color consistency, could be produced in large volumes as needed and were not limited by growing seasons or the weather.

There was a short return to natural colors and traditional techniques in the 1920's (World War I) with the embargo of German dyes and chemicals. American manufacturers were jolted into producing synthetic dyes to supply the growing textile industry. The global demand for natural colors as the primary source of color for textiles soon went away and never recovered.

Synthetic dyes have become the standard for the global textile industry. The global colorant industry (organic dyes and pigments) for 2016 is valued at $19-$24 billion dollars. Reactive and disperse dyes account for more than 50% of the global market value. Natural colors make up a very small percentage of the already very small 'others' category of dyes.

There are no commercial scale applications of natural colors in the modern textile industry. Natural colors continue to be used only by the local craft and cottage industries.

The renewed and current interest in natural colors is due in large part to the Sustainability and Green Movements driven by retail marketing organizations attempting to differentiate themselves from others.

The objective of the work is to determine which standardized dyeing system: natural or synthetic, has the best color efficiency with lowest environmental impact when applied to 100% cotton knit. There have been many papers written about applying natural dyes to protein fibers (wool and silk), however the literature has limited references for natural color on cotton. For petroleum based, synthetic dyes, there are countless papers and textbooks covering the dyeing of cotton with azoic, sulfur, vat, direct, and fiber reactive dyes.

A primary concern from the beginning of the research was where to set the boundaries. The decision was reached to set the boundaries at the ‘dye house walls’ and focus only on the inputs and outputs that can be directly measured and quantified in the dye house. The selected metrics are water usage, steam consumption, cycle time, impact of effluent, and dyestuff efficiency. The data accumulated from the work can be normalized and compared to findings in various Life Cycle Assessments for Cotton.

2. LITERATURE REVIEW

2.1 Fibers: Global Market

The global market for textile fibers in 2015 was 86.71 million metric tons (1, 2). Table 1 details the distribution of petroleum-based synthetic fibers and natural fibers.

Table 1. 2015 Global Fibers Market

Fiber Type	% of Total	Million Metric Tons
Synthetic	62.1	53.85
Cotton	25.2	21.85
Wood Based	6.4	5.55
Other Natural	5.1	4.42
Wool	1.2	1.04

Polyester is the dominant petroleum-based fiber, accounting for 82% of the global synthetic fibers market. Acrylic (10%), polypropylene (6%) and nylon (2%) make up the balance of the petroleum-based fibers (3).

Of the 32.86 million metric tons of natural fibers, cotton's share was 21.85 million metric tons, wood based fibers was 5.55 million metric tons, wool was 1.04 million metric tons, and other natural fibers were 4.42 million metric tons (1, 4).

The cotton sector of the global market is projected to consume more fiber than produced for the third consecutive year, further depleting the excess ending stock of cotton fiber available (4). See Table 2 for global cotton production and consumption data.

Table 2. Global Cotton Markets (million metric tons)

	2014-15	2015-16	2016-17	2017-18
Produce	23.8	19.1	20.7	21.2
Consume	21.9	21.6	21.8	22.0
Excess Stock	20.2	17.6	16.3	15.5

The top ten cotton producing countries generate over 90% of the world's supply of cotton fiber (5). In 2016, India surpassed China as the largest producer of cotton. Table 3 contains details of global cotton production.

Table 3. Top Cotton Producing Countries (2016)

Country	Million Metric Tons	% Global Supply
India	5.29	26
China	4.06	20
USA	3.25	16
Pakistan	1.62	8
Brazil	1.22	6
Africa	1.02	5
Uzbekistan	0.82	4
Australia	0.82	4
Turkey	0.61	3
Rest of World	1.62	8

2.2 Cotton

2.2.1 History of Cotton

Natural fibers can be divided into two primary classes: cellulose and protein based fibers (6). Wool and silk are the primary protein based fibers. Table 4 details the different types of cellulose fibers (7).

Table 4. Different Types of Cellulose Fibers

Fiber Type	Examples
Seed	Cotton and Kapok
Bast	Flax, Ramie, and Hemp
Leaf	Sisal and Abaca
Nut Husks	Coir

Cotton is both the most popular natural fiber and the most publicly scrutinized fiber in the world (8, 9). Biologists speculate that cotton has been growing on earth for as many as ten million years (10). Cotton has evolved from a locally harvested wild plant (6000-3000 BC) in the Indus River Valley region of Pakistan (10) to an international business conglomerate supplying over 20 million metric tons of fiber annually to the textile industry (4, 11).

From what was once a simple cottage industry, today's textile industry is now a vast and global series of loosely connected segments producing 400 billion square meters of fabric from 100 million metric tons of natural (38%) and synthetic fibers (62%) (12).

Cotton is the largest revenue generating nonfood crop grown and is an important agricultural product for both large and small economies. Cotton contributes financial income to over 250 million people around the world (11).

Approximately 2.4% of the world's available arable land is used to grow cotton (8, 11). The amount of land used to grow cotton has been consistent for the past 80 years, however the yield per acre has more than tripled since 1930 (8). Cotton requires 180 frost-free days per crop cycle (5). Cotton is a thirsty crop and requires 550-950 liters of water per square meter of area planted from rainfall and/or irrigation. Irrigation is used in the growing of 73% of the global cotton crop (13). The critical environmental impacts resulting from growing cotton are agrochemical use (11% of all pesticides and 25% of all insecticide) and excessive amounts of water (11, 14). James Pruden of Cotton Inc. recently refuted many of the numbers commonly associated with the negative agricultural impact of cotton, including use of pesticides and amount of water required (77).

2.2.2 Chemistry of Cotton

Cotton is classified in 3 genera based on fiber staple length (7, 15, 16).

1. Gossypium Barbadense has lustrous, extra-long staple fibers (30-60mm) and is known as Egyptian, Pima, or Sea Island Cotton (17). Pima Cotton is used to produce very fine cotton yarns for high-end (expensive) applications. See Figure 1, right image.

2. Gossypium Hirstum has medium length staple fibers (25-33mm) and is known as Upland Cotton. Upland Cotton makes up over 95% of cotton grown for textiles. See Figure 1, center image.

3. Gossypium Herbacem has short staple fibers (10-25mm) and has limited use for textile fibers and fabrics. See Figure 1, left image.

Figure 1: Cotton Fiber Lengths (21)

Cotton is a bush that grows to a height of 1-2 meters and produces blossoming flowers. When the blossoms drop from the bush, a cotton boll (seed pod) develops that contains 7-8 cotton seeds. Each seed is covered by several hundred thousand individual fibers (15). As the boll ripens, it splits open and the white cotton fibers are exposed to the environment.

After harvesting the ripe boll, the long cotton fibers are separated from the seeds at the gin. Lint (long fibers) compose about 12% of the total cotton plant with stalk 66%, linters (very short fibers) 10%, cottonseed oil 10%, and waste 2% making up the balance.

Cotton fibers are flat, ribbon like single cell structures growing from the cotton seed with regular twists (50-100 convolutions/inch) that run the length of the staple (18). Cotton is the only seed fiber with convolutions which allow it to be twisted and spun into fine yarns. The width of cotton fibers is uniform at 12-20μm (7).

The layers comprising a cotton fiber (Figure 2) are as follows:

Cuticle – outer waxy layer made up of pectin and proteinaceous materials (removed during scouring) that protect the fiber and make it water resistant.

Primary Wall – thin cell wall containing a network of fine fibrils (small strands of cellulose) capable of moving water.

Winding Layer (S1) – thickening layer made of cellulose fibrils aligned at 40-70° angle to the fiber axis.

Secondary Wall (S2) – reversing, concentric layers of cellulose formed at 70-80° angle to the fiber axis that form small capillaries.

Lumen Wall (S3) – chemical resistant layer between the secondary wall and the lumen.

Lumen – a hollow canal, running the length of the fiber that transports nutrients during growth. The lumen collapses at maturity, leaving a central void in each fiber.

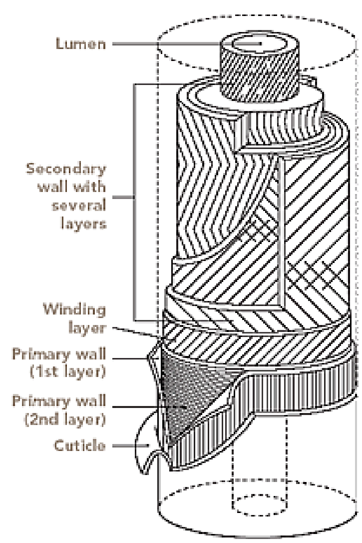


Figure 2. Cotton Fiber Physical Structure (16)

At 90-95%, cellulose is the primary component of cotton fibers (see Table 5). Cotton fibers contain more cellulose than wood pulp (40-50%), dried hemp (50-60%) or flax (60-80%) (16). Cellulose is the principle building material of the vegetable world and is the most abundant of all naturally occurring organic polymers. Thousands of millions of tons of cellulose are produced annually by photosynthesis.

Table 5. General Composition of a Cotton Fiber (7, 19)

Component	%
Cellulose	94.0
Protein	1.3
Pectin	0.9
Ash	1.2
Wax	0.6
Other Substances	2.0

Cellulose is a linear condensation polymer made of 2000-4000 anhydro-glucose units connected by 1,4 oxygen bridges (20). The repeat unit is anhydro-beta-cellulose (21). Figure 3 shows the cellulose repeat unit where n-2 = degree of polymerization.

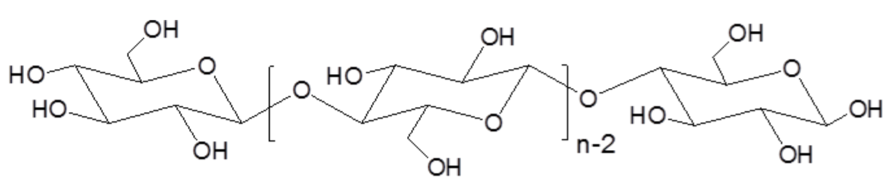


Figure 3. Cellulose Repeat Unit (78)

Cellulose $(C_6H_{10}O_5)_n$ contains 44.4% carbon, 6.2% hydrogen, and 49.4% oxygen. Cellulose from cotton has a higher degree of polymerization (DP) and average crystallinity than viscose rayon and wood pulp (Table 6). Fiber strength is directly related to DP and crystallinity (21).

Table 6. Comparison of DP and Crystallinity for Cellulosic Fibers

Fiber	Average DP	Average % Crystallinity
Cotton	9,000-15,000	73
Rayon	250-450	60
Wood Pulp	600-1,500	35

Cotton fibers typically have a distribution of one third amorphous to two thirds crystalline. Rayon has a distribution of one third crystalline and two thirds amorphous. When placed in water, cotton experiences a volume increase of roughly 40% as well as a gain in strength. Rayon (regenerated cellulose) has a similar increase in volume, however the tensile strength decreases when wet (21). Cellulosic fibers are highly hydrophilic and can regain up to 15% moisture without feeling wet.

There are 3 hydroxyl groups (-OH) present with each anhydro-glucose unit of the cellulose polymer. The hydroxyl groups, one primary and two secondary, are chemically reactive and will undergo substitution reactions during the application of select dyes and chemical finishes (18).

2.2.3 Dyeing of Cotton

There is no debate that water, energy, chemicals, and colorants have always been used to apply color to cotton (8, 11, 12, 13). The issue is how much is used and how efficient are the procedures. The mechanical and procedural manipulation of these variables to produce satisfactory results with minimal impact on the environment is a daily challenge for dyers around the globe. The textile dyeing industry is faced with producing more and better colors on cotton with lower amounts of water, energy, chemicals, and colorants.

The textile industry currently uses vat dyes, sulfur dyes, direct dyes and fiber reactive dyes to apply color to cotton. There are no known active commercial applications of natural color for cotton.

Natural colors are used mostly for craft and cottage projects that are not production volume driven. Dyeing cycle times for some natural colors on cotton are measured in days and weeks instead of hours making them impractical for commercial use. Natural colors can be applied to cotton through direct dye applications, combined with metal salts (mordants), or through vat reduction techniques.

Direct dyes are used for applications where improved light fastness is required. Direct dyes are applied ‘directly’ from aqueous baths containing electrolyte and bond to the cotton via hydrogen bonds and van der Waals forces.

Fiber reactive dyes are the preferred colorant due to their high wet fastness and excellent color range. The high wet fastness of reactive dyes is the result of strong covalent bonds that are formed between the hydroxyl groups on the cotton fiber and the reactive leaving group on the dye molecule.

2.3 Color

2.3.1 Natural Colorants

Blocks of ochre, compounded into crayons have been unearthed in Blombos Caves in South Africa. The blocks have been dated to 100000 BC. Archeologists believe the indigenous tribes mixed the ochre crayons with water to create art on cave walls and to ‘paint’ their own skin (22).

One of the earliest recorded uses of color in art are the cave paintings by Cro-Magnon man dating from as early as 30000 to 10000 BC. The cave paintings show the use of yellow and red mineral based colorants (23).

Natural colorants based on the local agronomy were simultaneously developed for use with natural fibers in all populated areas of the globe. Following the Industrial Revolution (1760-1840), the global population was growing rapidly and moving toward urban environments. Many of the traditional tasks of farming, spinning, knitting, and weaving were shifted to industrial applications in order to satisfy the growing demand for larger volumes and more unique colored fabrics.

Prior to Perkin's discovery of Mauvine (Figure 4) in 1856, all colorants were of animal, vegetable, or mineral origin (23, 24). Following Perkin's discovery, petroleum based synthetic dyes almost completely replaced natural colorants for textiles.

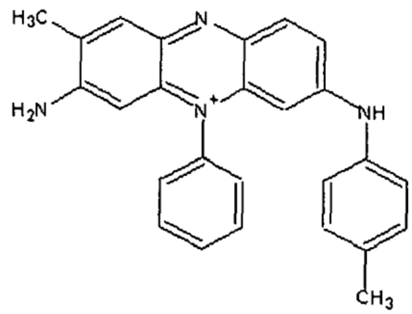


Figure 4. Mauvine (Perkin) Chemical Structure (31)

Synthetic dyes had favorable application procedures, excellent reproducibility, high yields with lower costs, and a wider color gamut for natural fibers. The introduction of commercial synthetic fibers, cellulose acetate (1920), nylon (1938), acrylic (1950) and polyester (1956) demanded new types of colorants that could not be produced from natural materials, which further accelerated the decline of natural colorants for textiles (7).

Today, assuming an average of 1% on weight of goods (of a highly efficient synthetic dyestuff), applied to the 22.68 million metric tons of cotton consumed annually, it will take more than 227,000 metric tons (227,000,000 kg or 500,535,000 pounds) of petroleum based synthetic colorant per year to color the cotton.

The amount of natural material required to produce 1kg of colorant is very large and the extraction process is still very inefficient. Patterson has calculated that 13 acres of farmland are required to produce enough plant material to dye the cotton from a single acre (25). For non-vegetable natural colorants, over 9000 mollusks must be killed to extract 1kg of Tyrian purple dye and one kg of Cochineal requires 150,000 dried insects harvested from 0.4 acres of cactus (26).

Water makes up the vast majority of the vegetable and plant material used for natural colorant and is disposed of during extraction. On a positive note, the solid waste portion of the plant can be composted, provided the extraction method does not use toxic compounds (27).

Bechtold notes that 'a mass of 100 kg of plant material has to be extracted for the dyeing of 100 kg of goods.' (28), which translates to a 100% on weight of goods of plant material prior to dyeing. The extracted color is subsequently dried down to a stable powder with a usable colorant yield of less than 15% from the original plant weight. Besides their low yield, another major drawback to natural colorants is their lack of consistency in shade development. Tutak's experimental design uses 100% on weight of goods of various natural colorants sourced from local Turkish suppliers (9).

The global population explosion has forced agriculture to focus on increased food production and thus non-food items such as natural colorants have been de-emphasized. The incorporation of non-food plants into today's modern farms will also introduce issues with weed and pest control. Suitable pesticides and herbicides for non-food products (natural colorants) have not been developed and properly tested (29).

Natural colorants present a shade matching and applications dilemma to the dyer since each major color group (yellow, red, and blue) is applied using a totally different set of conditions. There are no simple trichromatic combinations of natural color that a dyer can mix to build a normal gamut of colors. To produce a larger color gamut using natural colorants, dyers are dyeing raw fibers and blending them to produce colors unavailable using exhaust procedures on fabric. Each major hue is applied using a different method. Blues and dark browns are applied using a reductive vatting system, reds and flavonoid yellows are applied by coupling with a mordant, and cartotinoid yellows are applied directly to the substrate (23,29, 30).

Depending upon the chemistry of the chromophore, natural yellow colorants can be applied using either a direct dye application or by coupling with a mordant. Tumeric (curcurmin) and saffron (crocin) are carotinoids and are examples of direct application type natural yellows. (23, 29, 30, 31). Figure 5 shows the chemical structure of Curcurmin (derived from Tumeric).

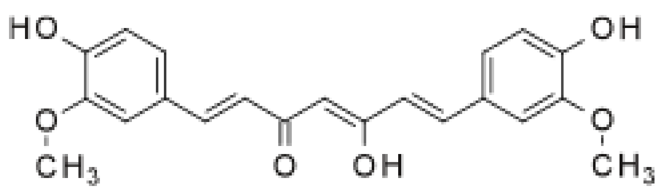


Figure 5. Curcurmin Chemical Structure (31)

Many plants produce flavonoids, natural yellow colorants that can be applied by coupling with a mordant. Flavanoids form a large group of aromatic compounds (flavones and flavonols) and include weld (luteolin), cutch (catachin), and other plants (quercetin). The main source of quercetin is from the inner bark of an oak tree (23, 29, 30). Due to the large number of plants that produce flavonoids, no one plant became a dominant source of supply for natural yellow colorants.

Anthraquinones make up the vast majority of natural red chromophores and are derived from both plant material and insects. The primary source of red colorants from insects are cochineal (carminic acid) and lac (laccaic acid) which are extracted from the Coccidea family of plant parasites (30).

The most important natural colorant in history is Madder, a red colorant that is extracted from the roots of the Rubiaceae family of plants (31). Madder (alizarin and purpurin) is important due to its fastness and diverse range of shades (23). The anthraquinone contents of madder root are complex and vary with both the age and growing conditions of the plant. Nineteen different anthraquinones have been identified in mature roots while only four anthraquinones (Figure 6) are found in young plants. In 1868, Graebe and Liebermann produced a synthetic Alizarin, marking the first natural chromophore to be reproduced in the lab (32).

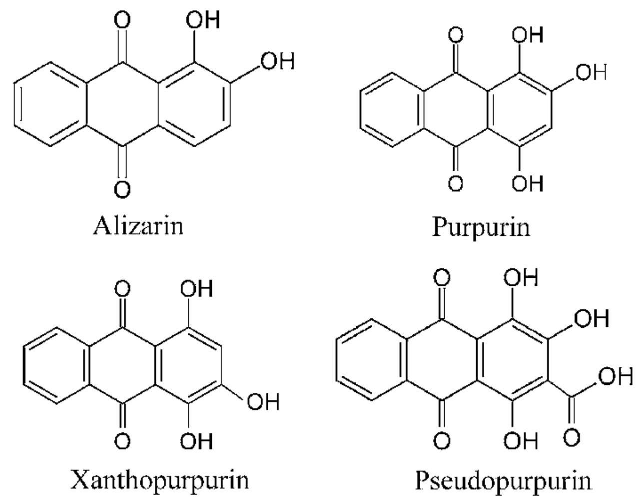


Figure 6. Madder Root, Primary Anthraquinone Structures (23)

Indigo (indigotin) is the primary natural blue colorant. Indigotin bearing plants can be found all around the world with evidence of use in Egypt as early as 2000 BC (30, 31, 33). Indigo is an aromatic compound formed by two molecules of indoxyl. Indigo is insoluble in water and must be converted to a leuco (colorless form) using strong alkali (sodium hydroxide) and reducing agents (sodium hydrosulfite). The leuco form of indigo is applied to cotton and then exposed to air. Oxidation of the reduced indigo renders it insoluble and allows for physical entrapment of the molecule inside the fiber. In 1878, von Bayer established a synthesis route to produce synthetic indigo. Once the synthetic indigo was commercialized in 1897, the market for natural indigo was eventually reduced to small craft markets.

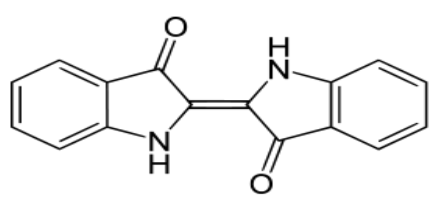
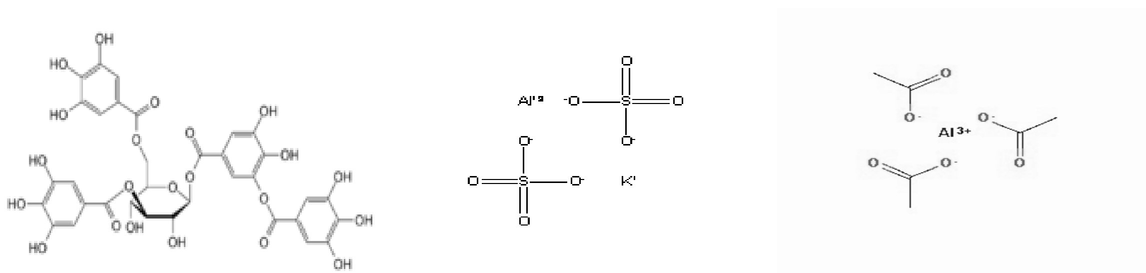


Figure 7. Indigotin Chemical Structure (23)

While the world ‘natural’ is used to describe the non-synthetic source of the color and mordants, it does not automatically imply it is safe for use and disposal. Mercury, arsenic, and asbestos are all ‘natural’, yet highly toxic and not welcomed in commercial dye houses or their effluent waste streams.

The early mordants used to develop colors and fastness on cotton included compounds containing tin, cobalt, chromium, nickel, copper, lead, and mercury (9, 25, 34, 35, 36). None of these compounds can be used in commercial dyeing applications today based on their negative impact on the environment.

The primary mordants used today include tannins, potassium aluminum sulfate and aluminum acetate (35, 37). Figure 8 shows the chemical structures of modern mordants.



Tannin Potassium Aluminum Sulfate Aluminum Acetate

Figure 8. Modern Mordants Chemical Structures (35)

There are numerous application routes for creating a colorant:mordant complex. The fabric can be pre-treated with the mordant prior to the addition of colorant. The colorant and mordant can be applied to the fabric in a single bath (often uses multiple steps). And with post-mordanting, the mordant is added in a separate bath after the application of colorant. Post-mordanting with metal ion is typically used to create a shift in hue not possible with other procedures (26). Compound and multiple mordant systems are also referenced in the literature (38).

Madder Root is extracted from the roots of a common wild flower, Rubia Tinctorum. Madder is a natural red colorant and was a valuable commodity for dyers in ancient Egypt, Persia, India, as well as ancient Greeks and Romans. The coloring components of Madder Root are a variety of anthraquinones (Figure 6). Alizarin and Purpurin are the most significant of the 19 different anthraquinones identified in Madder Root. The ratio of the different anthraquinones varies dramatically depending on moisture during growing season and the age of the root when harvested (23, 30). Madder Root has little to no natural affinity for cotton and requires a mordant to produce a satisfactory dyeing.

Osage Orange is a natural yellow/orange colorant extracted from the bark of the Maclura Pomifera plant (39). The colorant contains lectins, triterpenes, xanthones, and flavones (scandenone and auriculasin). Osage Orange is unique in that the colorant is extracted from the waste stream of the lumber mill (40).

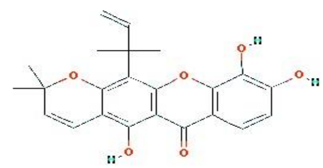


Figure 9. Osage Orange (Macluraxanthone) Chemical Structure (31)

Using black walnut shells to produce color also creates a positive value from what is normally waste. Black Walnut produces a neutral brown when applied to cotton using a pre-mordant procedure. The colorant in Black Walnut is Juglone (Figure 10), which some references classify as a vat dye (9, 41, 42).

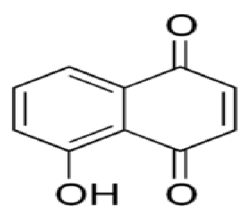


Figure 10. Black Walnut (Juglone) Chemical Structure (31)

2.3.2 Synthetic Dyes

As with natural colorants, synthesized dyes are classified based on their chemical structure and their method of application (primarily time, temperature, and pH).

Petroleum based synthesized compounds are used to produce commercial dyes. The characteristics of a commercial dye are: intense color, soluble or dispersible in water, substantive to the selected fiber, has adequate fastness, is easy to handle and apply, and the effluent has minimal impact on the environment.

Dye molecules are aromatic organic compounds that contain a series of conjugated double bonds. Attached to the dye molecule are chromophores, unsaturated functional groups (electron acceptors) such as azo, nitro, and carbonyl groups. Also included in the structure are auxochromes, saturated functional groups that act as electron donors. Various amino groups, hydroxyls, and ethers are examples of auxochromes. Sulfonic acid groups provide solubility in water for the dye molecule (20, 43, 44, 45, 46).

2.3.2.1 Direct Dyes

The first commercial petroleum based synthetic colors were direct dyes, Malachite Green (synthesized in 1876) and Congo Red (CI Direct Red 1, 1884) (20, 32, 47). Direct dyes are soluble anionic compounds consisting of an aromatic structure with a chromogen and solubilizing groups. Because of their substantivity to cotton, direct dyes were the first dyes to be applied ‘directly to cotton’ without the need of a mordant or other chemical pretreatment. Direct dyes are applied from an aqueous bath at the boil and the only dyeing auxiliary needed is a strong electrolyte (sodium sulfate or sodium chloride) to assist in exhaustion (20).
The common chromogens found in direct dyes are azo, stilbene, pthalocyanine, oxazine, and thiazole. Unmetallised azo compounds account for more than 75% of direct dyes. Disazo compounds (50% of direct dyes) are found in bright yellows and oranges (Figure 11) to blue direct dyes. Polyazo compounds are found in dull green, brown, grey, and black direct dyes.

Dioxazine and pthalocyanine chromogens are used for bright blue direct dyes (excellent light fastness). Stilbene and thiazole dyes are generally found in yellow to red direct dyes (47).

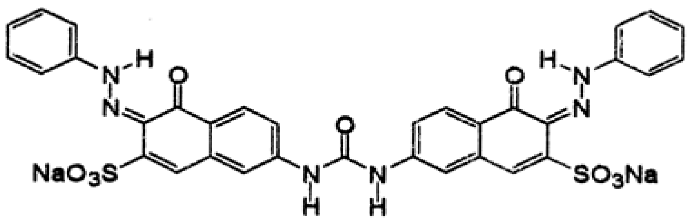


Figure 11. Direct Orange 26 Chemical Structure (20)

2.3.2.2 Fiber Reactive Dyes

Reactive dyes are relatively new to the textile industry with the first commercial products, Procion™ MX from ICI, being introduced in 1956 (20, 32, 48). Reactive dyes are water soluble anionic compounds. Figure 12 details the various parts of a reactive dye: a conjugated chromogen (C), a reactive group (R), a bridging group (B), a leaving group (L), and a solubilizing group (S).

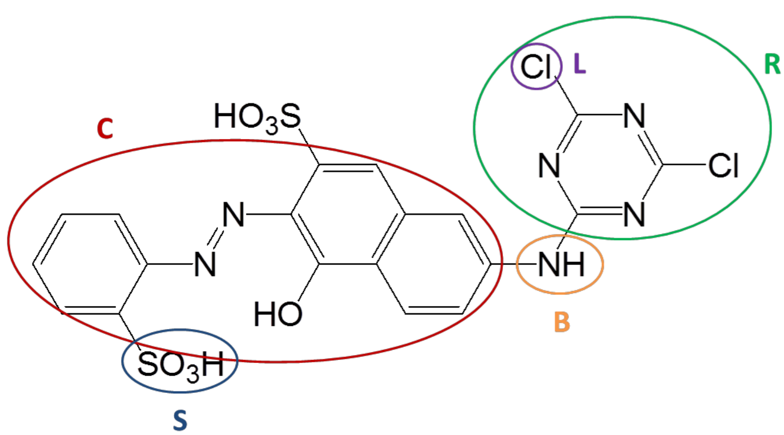


Figure 12. Diagram of Generic Fiber Reactive Dye Molecule (78)

The reactive group on the compound reacts with the hydroxyl groups on the cellulose to form a strong covalent bond. The covalent bond provides the excellent wet fastness that reactive dyes are known for.

A major concern when working with reactive dyes is hydrolysis, a competitive reaction between the dye and a hydroxyl group on water. Once the reaction occurs with water, the hydrolyzed dye will not react and bond with cotton, resulting in excess color discharged in the effluent, wasted dye, lower color yields, potential shading, and negative issues with fastness. Figure 13 details the competing routes between the cellulose (Cell-OH) and the water (OH) for the reactive dye.

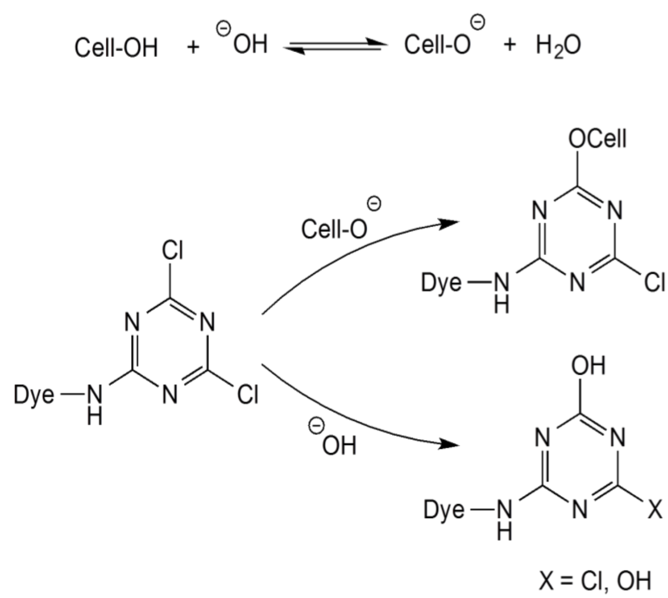


Figure 13. Competing Reaction Routes for Reactive Dyes (78)

There are multiple configurations of the reactive group based on triazine, pyrimidine, and quinoxalin coupled with chlorine and / or fluorine molecules. The original Procion™ dyes were dichlorotriazine based colors (2 Cl molecules attached to a triazine base).

The degree of reactivity of the dye is determined by a combination of the number of halogen molecules present and the level of reactivity of the halogen molecule. The dyeing temperature, the amount of electrolyte, and the amount of alkali are all influenced by the reactive group. Trichloropyrimidine (Drimarene™ X), dichloroquinoxaline (Levafix™ E), monochlorotriazine (Drimarene™ X-N, Cibacron™ E), dichlorotriazine (Procion™ MX), monofluorotriazine (Cibacron™ F, Levafix™ E-N), difluoropyrimidine (Levafix™ EA), and difluoromonochloropyrimidine (Drimarene™ K, Levafix™ EA) are examples of current commercial reactive dyes (48). Figure 14 shows an assortment of reactive groups used in modern reactive dyes.

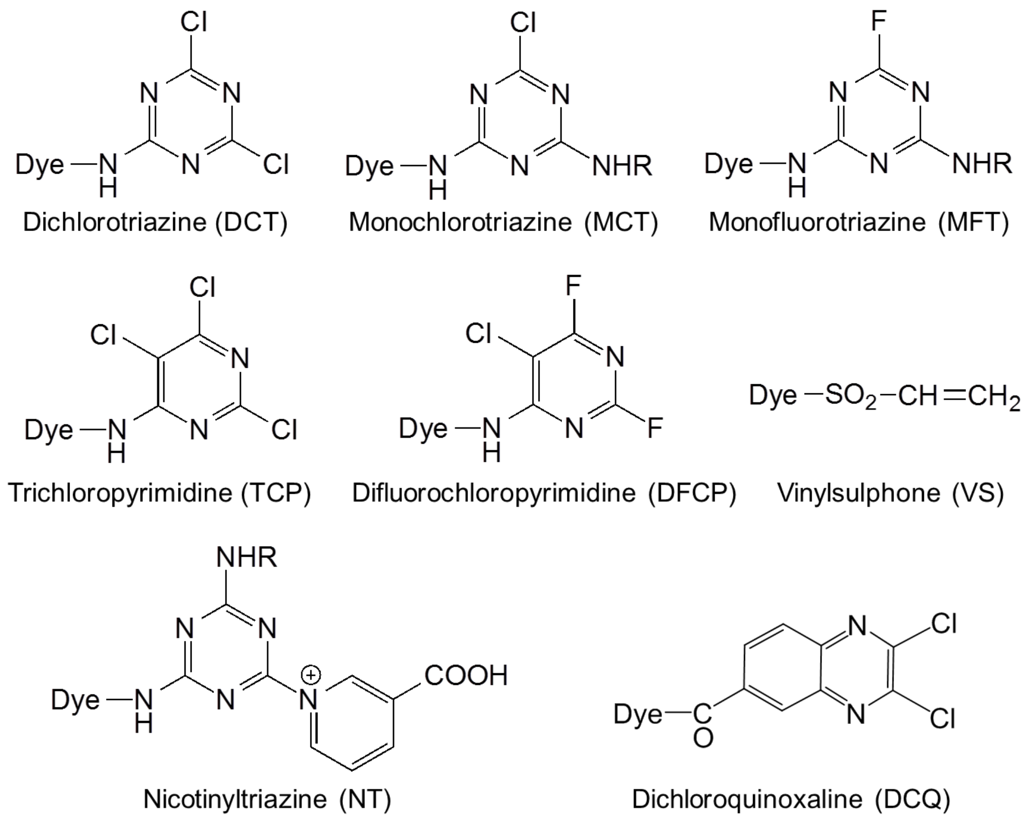


Figure 14. Reactive Dye Structures (18)

A different reactive system is incorporated for vinyl sulfone dyes (Remazol™). Vinyl sulfone dyes contain a sulfato-ethyl-sulfone group. In the presence of a strong alkali, the dye undergoes an elimination reaction to form a vinyl sulfone group. The vinyl sulfone group then combines with the cellulose via an addition reaction. As with conventional fiber reactive dyes vinyl sulfone dyes also have 2 competing routes for the reaction of water and cellulose with the dye (Figure 15).

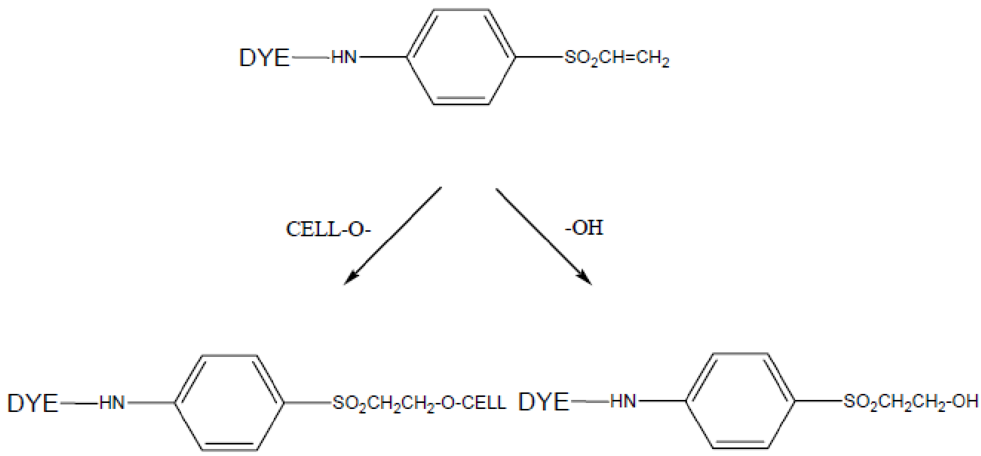


Figure 15. Competing Reaction Routes for Vinyl Sulfone Dyes (78)

Research continues to reduce the amount of color that is discharged as unfixed or hydrolyzed dye by combining reactive groups to form bi-functional (Drimarene™ HF-CL, Sumafix Supra™, Cibacron™ C) and poly-functional (Avitera™ SE) reactive dyes.

The poly-functional fiber reactive dyes represent the latest in dye research. The reactive groups (o-sulfo-para-ester, etheramine, para-ester, N-ethyl-meta-ester, Schwander, sulfo-napthalene-ester, chlortriazine, and fluorotriazine) were screened and paired together to give the maximum reactive and fixation. Each dye contains 2 to 4 selected reactive groups. (49, 50, 51, 52)

2.4 Sustainability

The Bruntland Commission's report (UN World Commission on Environmental and Development and Commission for the Future, 1990) defined sustainable development as 'the ability to meet the needs of the present without compromising the needs of future generations' (53, 54).

There is much confusion over what is sustainable. The term sustainability has different meanings for different people. We are saturated with terms of 'green' and 'organic' and 'natural' and 'recyclable' and yet we have not changed the way we purchase to excess, use minimally, and discard haphazardly (55). We are not behaving in a sustainable fashion. We continue to live today by borrowing from tomorrow and 'kicking the problem further down the street' for someone else to deal with (56, 57).

The textile industry has been highly scrutinized for the excessive amounts of water and chemicals that are consumed in the production of fabrics. There is no consistency in the literature with regards to water consumption required to grown cotton. The water usage ranges from 7,000 - 29,000 liters/ kg of cotton fiber produced (8, 11, 13).

The wet processing of cotton consumes water and energy and discharges effluent contaminated with dye, salt, alkali, and an assortment of ionic surfactants and auxiliaries (8, 11, 55, 58, 59).

With regards to textiles, in 1900 there were 1.9 billion people consuming an average of 2.25 kg of fiber (3.45 million metric tons). All textiles were made from natural fiber and dyed with a combination of natural and synthetic colors. Clothes were valued, mended, handed down, and eventually repurposed into other house hold items (quilts). What was disposed of quickly degraded and was absorbed back into the environment. In 2012, we had 7 billion humans consuming 9.1 kg each (63.5 million metric tons) that went directly to the trash. Textile trash from 2012 contained a significant percentage of petroleum based fibers (nylon and polyester) that do not break down into easily degraded organic waste.

The largest amount of water and energy consumed in the life of textiles is during post-consumer laundry. We cannot continue in this manner. There are not enough available natural resources and the earth is not large enough to hold all of the trash (56).

2.5 Life Cycle Assessment

The World Summit for Sustainable Development (Johannesburg, SA 2002) addressed the need for a program to focus on sustainable production and consumption (60). Environmental Impact Assessment (EIA) and Life Cycle Assessment (LCA) were developed and introduced as analysis tools to access the environmental impacts associated with the many stages of a product's life cycle (61). There are 4 major components to an LCA (62). The first component involves defining the parameters and establishing the boundaries of the study. The second component is inventory analysis. Input-Output data is collected and compiled from raw material extraction, materials processing, manufacturing, distribution, use, and disposal. Impact assessment, the third component, is the compilation of the data to create a concise image of the environmental impacts. The fourth and final component is interpretation of the results and impact assessments of the study (62).

Cotton Inc. compiled data from Life Cycle Inventories (63) from 2005-2009 for:

1. Cotton fiber production (agricultural impact)
2. Cotton fabric production (textile fabric manufacturing plus dyeing)
3. Cotton cut and sew, consumer use, and disposal

The categories used by Cotton Inc. to access the overall environmental impact of cotton are detailed in Table 7.

Table 7. Life Cycle Categories used by Cotton Inc (63)

Category	Description
Acidification Potential	Acid Rain
Eutrophication Potential	Water Pollution
Global Warming Potential	Greenhouse Gas Emissions
Ozone Depletion Potential	Impact on Ozone Hole Covering Polar Caps
Photochemical Ozone Creation	Smog
Primary Energy Demand	Electricity and Other Fuel Consumption
Water Used	Amount of Water Used and Discharged
Water Consumed	Amount of Water Lost through Evaporation
Ecotoxicity Potential	Animal Health
Human Toxicity Potential	Human Health

The data set built from this research can be normalized and compared to similar studies in Life Cycle Assessments (LCA) for processing cotton (62, 63, 64, 65, 66).

3. EXPERIMENTAL

3.1 Hypothesis: *Petroleum based synthesized fiber reactive dyes have a higher color yield with a lower environmental impact than direct dyes and natural colors applied using standardized dyeing conditions on 100% cotton knit.*

The objective of this work is to determine which standardized dyeing system: natural or synthetic, has the best color efficiency with lowest environmental impact when color is applied to 100% cotton knit.

A primary concern from the beginning of the research was where to set the boundaries. The decision was reached to set the boundaries at the 'dye house walls' and focus only on the inputs and outputs that can be directly measured and quantified in the dye house. Once the analysis is complete, the data can be normalized and used to update or validate various published Life Cycle Assessments.

Based on my experiences in color development and dyeing, the processing parameters selected for the Weighted Parameter Evaluation were water usage, steam consumption, cycle time, impact of effluent, and dyestuff efficiency.

The sequence of experimental flow for the research

1. Establish benchmark color palette using natural colorants on 5 meter lengths (1.6 kg) of pre-scoured cotton jersey in sample dyeing equipment. Measure the water usage and steam consumption for each bath and capture aliquots from each machine drain.

2. Match the benchmark natural color palette using petroleum based synthetic dyes in the laboratory on 10 gram swatches of cotton knit. A spectrophotometer and multiple color matching software programs were utilized to match the natural color palette under D65 as primary light.
3. Transfer the 10 gram lab formulas for synthetic dyes to the dyehouse and dye 5 meter lengths (1.6 kg) of cotton knit in sample dyeing equipment. Measure the water usage and steam consumption for each bath and capture aliquots from each machine drain.
4. Measure all 5 meter sample dyeings on spectrophotometer for reflectance spectral profiles and L*a*b* values.
5. Measure all captured machine drain aliquot using HueMetrix Color Analyzer for absorbance / transmission values.
6. Submit select 5 meter sample dyeings for physical fastness testing
7. Submit samples from select dyebath effluent for analytical testing.

4. HARDWARE AND SUPPLIES

4.1 Fabric

A pre-scoured100% cotton jersey (Green Textile Associates, Spartanburg SC) was sourced by Tumbling Colors for use in the dyeing studies. The fabric was made using 18/1 cotton yarn knit to a basis weight of 220 gram per square meter. A 5 meter length weighing approximately 1.6 kg was cut for each coloration trial.

4.2 Rapid Oscillating Lab Dyer

All lab scale, 10 gram dyeings were prepared in the Color Development Lab at Tumbling Colors, Raleigh NC using a Rapid atmospheric oscillating laboratory dyeing machine. The Rapid lab dye units provide the consistent rate of rise and hold at select dyeing temperatures necessary for developing robust and reproducible colors and formulas.

Laboratory dyeings were run for 60 minutes at temperature and a 20:1 liquor ratio following the dyestuff manufacturers recommendations for dyeing temperature, electrolyte, and alkali.

4.3 Tupesa Sample Dye Machine

Sample dyeings were completed using 5 meter lengths of cotton knit (1.6 kg) in an atmospheric Tupesa Garment Dye Extractor (2.5 kg capacity) located at Tumbling Colors, Raleigh NC. (www.tupesa.com)

Sample dyeings were run for 60 minutes at temperature and a 10-12:1 liquor ratio following the dyestuff manufacturers recommendations for dyeing temperature, electrolyte, and alkali.

4.4 Spectrophotometer

A Konica Minolta CM-3220d Spectrophotometer was used for all reflectance measurements. The CM-3220d, connected to a PC running MatchWizard™ Software from Archromawas utilized for formula predictions and establishing spectral profiles with L*a*b* values for all dyeings.

4.5 HueMetrix Color Analyzer

A HueMetrix Dye-It-Right Instrument was utilized for obtaining dyestuff absorbance values for the individual drain samples of the petroleum based synthetic dyes. Each synthetic dye used in the study was calibrated separately prior to the color analysis of effluent streams. The lack of solubility in water and the large particle size of the natural colorants prevented their calibration and measurement on the HueMetrix unit.

4.6 Colorants and Dyes

4.6.1 Natural Colorants

Natural colorants used in the study were provided by Stony Creek Colors, Nashville TN. Osage Orange, Madder Root, and Black Walnut were selected based on previous commercial success at Tumbling Colors with applying natural colorants to cotton (79).

4.6.2 Petroleum Based Synthetic Dyes

The petroleum based synthetic dyes selected for the study were based on both commercial success at Tumbling Colors and the technical recommendations of Cotton Inc.

4.6.2.1 Direct Dyes

Solophenyl™ Yellow ARLE 154%, Red 3BL 140%, and Blue FG 400% (Huntsman) were suggested by Cotton Inc. for use in the study. Each of the selected direct dyes has an SDS Classification of [B]. Class B direct dyes require the controlled additional of electrolyte to ensure level and satisfactory dyeings. Direct dye samples were provided by Cotton Inc.

4.6.2.2 Fiber Reactive Dyes

Five different types of fiber reactive dyes were utilized in the comparison study. Each type has a different reactive group and the manufacturers' recommendations were followed for temperature, electrolyte, and alkali amounts.

Monochlorotriazine (MCT): Drimarene™ Yellow X-4RN and Red X-6BN (Archroma), and Permabril™ Blue H-ER 150% (Standard Colors) were selected to represent fiber reactive dyes applied at 95°C. Commercial samples were obtained from Tumbling Colors' drug room inventory.

Vinyl Sulfone (VS): Remazol™ Golden Yellow RGB, Red RGB, and Navy RGB (DyStar) were selected to represent vinyl sulfone chemistry. Remazol™ RGB dyes are applied at 60°C. Samples were obtained from Cotton Inc.

Difluoromonochloropyrimidine (DFMCP): Drimarene™ Yellow K-2R, Red K-4BL, and Blue K-2RL (Archroma) were selected to represent fiber reactive dyes applied at 60°C. Commercial samples were obtained from Tumbling Colors' drug room inventory.
Bi-functional (MCT-VS and TCP-VS): Drimarene™ Yellow CL-2R, Rubine CL-3BL, and Blue HF-RL (Archroma) are described as bi-functional reactive dyes, meaning they contain two different reactive groups and are constituted in a way to react with the fiber in more than a single way. Drimarene™ HF-CL dyes are applied at 60°C. The exact reactive group combinations of the Drimarene™ HF-CL dyes are proprietary, however examples are a monochlortriazine (MCT) coupled with a sulfato-ethyl sulfone group (VS) or a trifluoropyrmidine (TFP) coupled with a sulfato-ethyl sulfone group (VS). Commercial samples were obtained from Tumbling Colors' drug room inventory.

Poly-functional: Avitera™ Yellow SE, Red SE, and Light Blue SE (Huntsman) were selected to represent the latest in reactive dye chemistry. The Avitera™ SE dyes, described by Huntsman as poly-functional, containing 2-4 different reactive groups, and are applied at 60°C. Samples were obtained from Cotton Inc. and Huntsman.

4.7 Chemicals and Dyeing Auxiliaries

All chemicals used for the study were obtained from the commercial inventory of Tumbling Colors, Raleigh NC.

RucoWet™ FIN Conc (Rudolf Group) is a non-ionic, fatty alcohol ethoxylate wetting agent used as part of the cotton knit preparation.

Verolan™ NBO (Rudolf Group) is an anionic blend of polyacrylates and alkyl phosphonates. Verolan™ NBO is used in all synthetic dyes' baths due to its complexing capacity for heavy metal ions and dispersing ability. Verolan™ NBO was used for all colorants as a post dyeing, clean-up surfactant at 85°C.

Myrobalan (Stony Creek Colors) was incorporated in the pre-mordanting of cotton prior to application of natural colorants as a source of tannin (Figure 16).

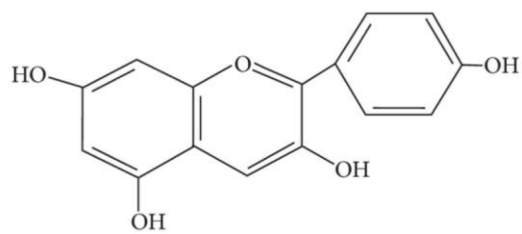


Figure 16. Myrobalan Chemical Structure (79)

Potassium Aluminum Sulfate (Tumbling Colors) was incorporated in the pre-mordanting of cotton prior to the application of natural colorants (Figure 17).

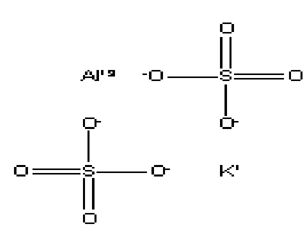


Figure 17. Potassium Aluminum Sulfate ($KAl(SO_4)_2$) Chemical Structure (34)

Sodium Sulfate (Tumbling Colors) was used as the primary electrolyte for both direct dyes and fiber reactive dyes (Figure 18). The amounts used are based on the dye manufacturers recommendations.

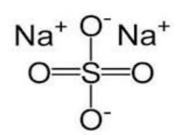


Figure 18. Sodium Sulfate (Na_2SO_4) Chemical Structure (34)

Sodium Carbonate (Tumbling Colors) was used as the primary source of alkalinity for both pre-scour (in conjunction with Rucowet™ FIN Conc) and as the alkali for all fiber reactive dyes (Figure 19). The amounts used are based on the dye manufacturers recommendations.

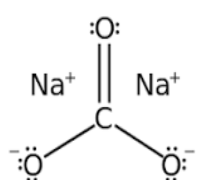


Figure 19. Sodium Carbonate (Na_2CO_3) Chemical Structure (34)

Calcium Carbonate (Tumbling Colors) (Figure 20) was incorporated with Madder Root as source of calcium ions for a more consistent red with better fastness (79).

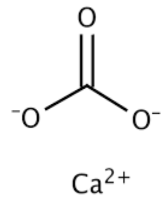


Figure 20. Calcium Carbonate ($CaCO_3$) Chemical Structure (31)

5. PROCEDURES

With few exceptions, applying color to cotton involves water, mechanical action, temperature (energy), time, and chemistry. To reduce the number of variables contributing to the data collection, all trials were run in the same sample dye machine using 5 meter lengths of greige cotton knit (approximately 1.6 kg) cut from a single roll. Liquor ratios, rate of heating, time at dyeing temperature, pre-scouring, and post-rinsing were treated at constants. The process flow for the natural colorants and the synthetic dyes was based upon production experience at Tumbling Colors and held constant for all data collection in this research. All samples were tumble dried for 45 minutes at 85°C.

5.1 Fabric and Load Size

A 100% cotton pre-scoured jersey was use for the dyeing studies. The fabric was made using 18/1 cotton yarn to a basis weight of 220 gram per square meter. All trials were conducted using 5 meter lengths weighing roughly 1.6 kg each. The sample dye machine was loaded to roughly 60% of the machine's rated capacity. The basket rotation was set at 24 rpm, and reversed at 60 second intervals for all cycles and steps which provided level and consistent dyeings.

5.2 Effluent Sample Collection

A 200 ml aliquot of every bath was captured just prior to each drain step. All drain bath samples were later measured for absorbance to determine the amount of color discharged in the step.

5.3 Fabric Preparation

Before applying color, all fabrics were pre-scoured using 0.25% owg (on weight of goods) of a non-ionic surfactant (RucoWet™ FIN Conc) for 10 minutes at 60°C and rinsed with cold water. The pre-scour and rinse baths were both set at 20:1 Liquor Ratio (32 liters of cold fresh water was metered in upon the machine's signal). The scoured fabric was given a short low speed extraction to remove excess water, unloaded from the dye machine, fluffed to eliminate any knots and tangles, and returned to the dye machine.

5.4 Water Levels for Dyeing and Post Rinsing

The microprocessor on the sample dye machine was programmed to deliver a Liquor Ratio of 10:1 for all water fills and rinses used during the dye cycle. When called for by the microprocessor, 16 liters of fresh cold water was metered into the machine. Separate trials were conducted to determine the amount of water that would be retained by the wet fabric in the dye machine. The 1.6 kg original dry weight of the fabric increased to roughly 5.6 kg when wet, indicating 4 kg of water (approximately 250%) was 'trapped' in the fiber and fabric. The cumulative volume of 20 liters resulted in an actual Liquor Ratio of 12.5:1.

5.5 Coloration Procedure for Natural Colorants

Without the chemical treatment of the cotton, the natural colorants have very poor exhaustion and fastness after dyeing. Following fabric pre-scour, the cotton was re-loaded into the dye machine for the first of two mordanting steps. Based on previous commercial success, a two-step pre-mordant procedure was used with the natural colorants.

The goods were first treated with 10% owg of Myrobalan (source of tannic acid) for 30 minutes at 90°C and rinsed with cold water.

The second mordanting step is treatment with 20% owg of Potassium Aluminum Sulfate for 30 minutes at 90°C and rinsed with cold water.

The pre-dissolved natural colorant was added slowly (over 10 minutes) to the fabric, heated at 3°C/minute to 90°C and held for 60 minutes.

At the end of the natural colorants exhaustion/fixation step, the goods received the following series of programmed rinses:

Cold rinse (1) for 5 minutes
Cold rinse (2) for 5 minutes
Hot soap at 85°C using 0.5% owg scouring agent for 5 minutes
Cold rinse (3) for 5 minutes
Cold rinse (4) for 5 minutes
Extract and tumble dry at 85°C for 45 minutes.

Detailed natural colorant dyeing procedure is included in Appendix 1.

5.6 Dyeing Procedure for Direct Dyes

After filling with cold water, 0.5 g/l of a dispersing agent (Verolan™ NBO) was added to the machine and circulated for 3 minutes. The direct dyes were pre-dissolved in warm water and added slowly over 10 minutes. The goods were heated at 3°C/minute to 95°C and held for 3 minutes before the addition of the manufacturer’s recommended amount of electrolyte (sodium sulfate). The electrolyte was divided into 3 portions (1/10th, 3/10th, and 6/10th) and added with 5 minute holds at 95°C. Once the addition of electrolyte was complete, the cycle ran for 60 minutes at 95°C.

At the end of the direct dye exhaustion/fixation step, the goods received the following series of programmed rinses:

Cold rinse for 5 minutes
Cold rinse for 5 minutes
Hot soap at 85°C using 0.5% owg scouring agent for 5 minutes
Cold rinse for 5 minutes
Cold rinse for 5 minutes
Extract and tumble dry at 85°C for 45 minutes.

Detailed direct dyeing procedure is included in Appendix 2.

5.7 Dyeing Procedure for 95°C Fiber Reactive Dyes (MCT)

After filling with cold water, 0.5 g/l of a dispersing agent (Verolan™ NBO) and the manufacturer's recommended amount of electrolyte (sodium sulfate) was added to the machine and circulated for 3 minutes. The MCT reactive dyes were pre-dissolved in warm water and added slowly over 10 minutes. The goods were heated at 3°C/minute to 95°C and held for 3 minutes before the addition of the manufacturer's recommended amount of alkali (soda ash). The alkali was divided into 3 portions (1/10th, 3/10th, and 6/10th) and added with 5 minute holds at 95°C. Once the addition of alkali was complete, the cycle ran for 60 minutes at 95°C.

At the end of the hot fiber reactive dye exhaustion/fixation step, the goods received the following series of programmed rinses:

Cold rinse for 5 minutes
Cold rinse for 5 minutes
Hot soap at 85°C using 0.5% owg scouring agent for 5 minutes
Cold rinse for 5 minutes
Cold rinse for 5 minutes
Extract and tumble dry at 85°C for 45 minutes.

Detailed fiber reactive dyeing 95°C procedure is included in Appendix 3.

5.8 Dyeing Procedure for 60°C Fiber Reactive Dyes (DFMCP, VS, Bi-functional, and Poly-functional)

After filling with cold water, 0.5 g/l of a dispersing agent (Verolan™ NBO) and the manufacturer's recommended amount of electrolyte (sodium sulfate) was added to the machine and circulated for 3 minutes. The reactive dyes were pre-dissolved in warm water and added slowly over 10 minutes. The goods were heated at 3°C/minute to 60°C and held for 3 minutes before the addition of the manufacturer's recommended amount of alkali (soda ash). The alkali was divided into 3 portions (1/10th, 3/10th, and 6/10th) and added with 5 minute holds at 60°C. Once the addition of alkali was complete, the cycle ran for 60 minutes at 60°C.

At the end of the 60°C fiber reactive dye exhaustion/fixation step, the goods received the following series of programmed rinses:

Cold rinse for 5 minutes
Cold rinse for 5 minutes

Hot soap at 85°C using 0.5% owg scouring agent for 5 minutes

Cold rinse for 5 minutes

Cold rinse for 5 minutes

Extract and tumble dry at 85°C for 45 minutes.

Detailed fiber reactive dyeing 60°C procedure is included in Appendix 4.

6. RESULTS

6.1 Description of Colors

Figure 21 is a display of the dyeings utilized for this study.

Figure 21. Photograph of Dyeings Utilized for the Study

The colors in the far-left column of Fig. 21 are the benchmark palette established for the study using natural colorants from Tumbling Colors' inventory (Stony Creek Colors).

Osage Orange

Commercial dyeings of Osage Orange produce a yellow / orange shade with spectral values of: L*=62.19, a*=2.74, and b*=49.45. The spectral profile (400-700 nm) is displayed in Figure 22.

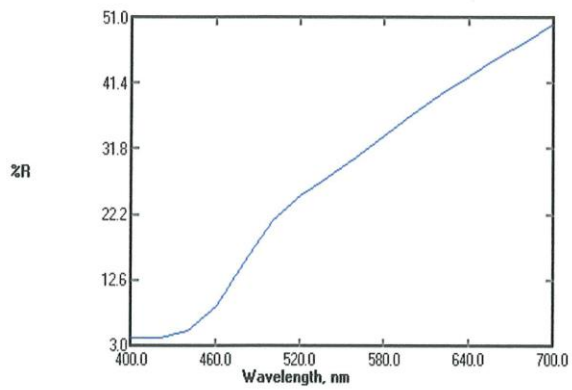


Figure 22. Osage Orange Natural Colorant Spectral Profile

Madder Root

Madder Root (coupled with calcium carbonate, Figure 20) produces a brick red shade with spectral values of: L*=52.34, a*=18.16, and b*=22.35. The spectral profile (400-700 nm) is displayed in Figure 23.

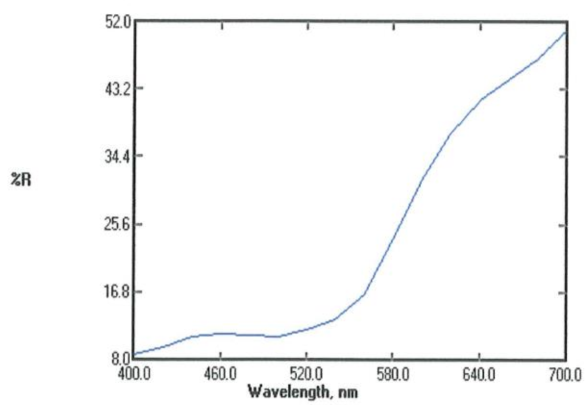


Figure 23. Madder Root Natural Colorant Spectral Profile

Black Walnut

Black Walnut produced a medium brown shade with spectral values of: L*=64.62, a*=1.23, and b*=23.23. The spectral profile (400-700 nm) is displayed in Figure 24.

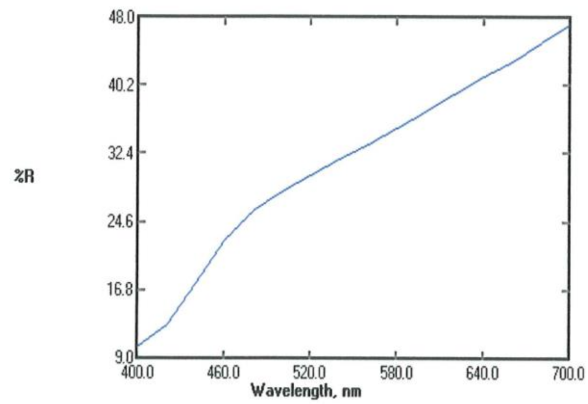


Figure 24. Black Walnut Natural Colorant Spectral Profile

The formulas developed in the lab for reproducing the natural palette using synthetic dyes are detailed in Table 8 (Page 50):

Table 8: Synthetic Dye Formula Used to Match Natural Color Palette

(% on weight of goods)	Osage Orange (yellow/orange)	Madder Root (brick red)	Black Walnut (brown)
Direct Dyes (98°C)			
Yellow ARLE 154%	0.86	0.29	0.13
Red 3BL 140%	0.025	0.36	0.047
Blue FG 400%	0.031	0.025	0.028
Total	0.916	0.675	0.205
MCT (98°C)			
Yellow X-4RN	0.98	0.42	0.23
Red X-6BN	0	0.32	0.038
Navy H-ER 150%	0.098	0.062	0.078
Total	1.078	0.802	0.346
VS (60°C)			
Golden Yellow RGB	1.15	0.72	0.33
Red RGB	0	0.7	0.078
Navy RGB 150%	0.05	0.025	0.046
Total	1.2	1.445	0.454
DFMCP (60°C)			
Yellow K-2R	1.05	0.53	0.25
Red K-4BL	0.06	0.65	0.095
Blue K-2RL	0.105	0.09	0.1
Total	1.215	1.27	0.445
Bi-Functional (60°C)			
Yellow CL-2R	0.95	0.46	0.2
Rubine CL-3BL	0.036	0.58	0.045
Blue HF-RL	0.105	0.03	0.073
Total	1.091	1.07	0.318
Poly-Functional (60°C)			
Yellow SE	0.66	0.5	0.2
Red SE	0.005	0.34	0.03
Light Blue SE	0.09	0.085	0.08
Total	0.755	0.925	0.31

Osage Orange

The spectral profiles for the dyeings of petroleum based synthetic dye combinations used to match Osage Orange natural colorant are shown in Figure 25. Note the similarities in the spectral profiles for the synthetic dyes and the abrupt difference when compared to the smooth spectral profile of the Osage Orange natural colorant.

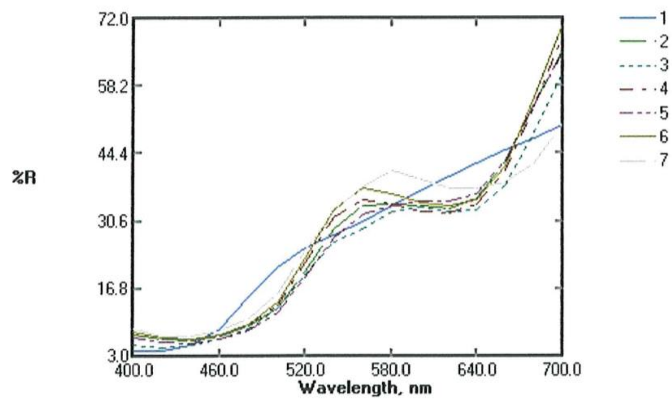


Figure 25. Spectral Profiles for Synthetic Dye Matches of Osage Orange

Line 1 – Osage Orange Natural Colorant
Line 2 – Poly-Functional Fiber Reactive Dye (60°C)
Line 3 – DFMCP Fiber Reactive Dye (60°C)
Line 4 – MCT Fiber Reactive Dye (95°C)
Line 5 – Bi-Functional Fiber Reactive Dye (60°C)
Line 6 – Vinyl Sulfone Fiber Reactive Dye (60°C)
Line 7 – Direct Dye (95°C)

Madder Root

The spectral profiles for the dyeings of petroleum based synthetic dye combinations used to match Madder Root natural colorant are shown in Figure 26. Note the similarities for the synthetic dyes when compared to the smooth spectral profile of the Madder Root natural colorant.

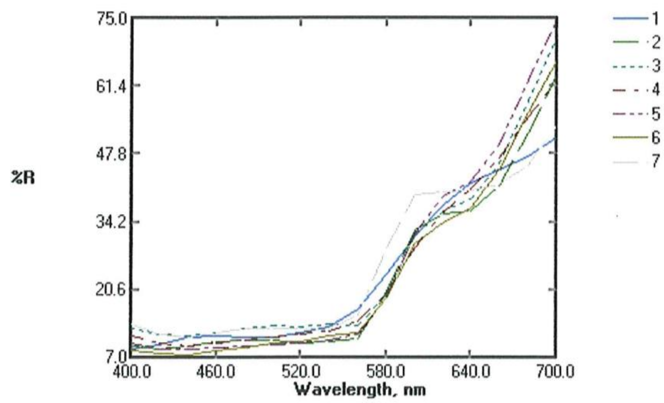


Figure 26. Spectral Profiles for Synthetic Dye Matches of Madder Root

Line 1 – Madder Root Natural Colorant
Line 2 – DFMCP Fiber Reactive Dye (60°C)
Line 3 – MCT Fiber Reactive Dye (95°C)
Line 4 – Bi-Functional Fiber Reactive Dye (60°C)
Line 5 – Vinyl Sulfone Fiber Reactive Dye (60°C)
Line 6 – Poly-Functional Fiber Reactive Dye (60°C)
Line 7 – Direct Dye (95°C)

Black Walnut

The spectral profiles for the dyeings of petroleum based synthetic dye combinations used to match Black Walnut natural colorant are shown in Figure 27. Note the similarities in the spectral profiles for the synthetic dyes and the abrupt difference when compared to the smooth spectral profile of the Black Walnut natural colorant.

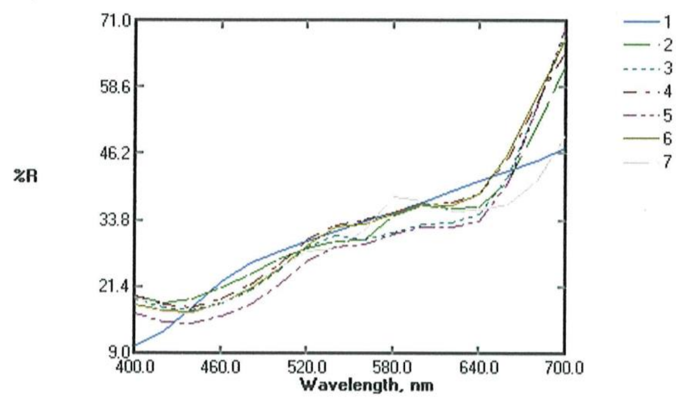


Figure 27. Spectral Profiles for Synthetic Dye Matches of Black Walnut

Line 1 – Madder Root Natural Colorant
Line 2 – DFMCP Fiber Reactive Dye (60°C)
Line 3 – MCT Fiber Reactive Dye (95°C)
Line 4 – Bi-Functional Fiber Reactive Dye (60°C)
Line 5 – Vinyl Sulfone Fiber Reactive Dye (60°C)
Line 6 – Poly-Functional Fiber Reactive Dye (60°C)
Line 7 – Direct Dye (95°C)

All shade matches were prepared using D65 as a primary light source. Color inconstancy will be a significant challenge for dyers trying to match natural colorants using petroleum based synthetic dyes. The spectral profiles for natural colorants are very smooth and absent of steep slopes and sharp peaks. When presented with fabrics dyed to the same color with both natural colorants and synthetic dyes, viewers tend to pick the natural colored samples. Fabrics dyed using natural colors are considered to be more soothing and visually appealing than fabrics dyed with synthetic dyes (67)

6.2 Water Usage

Water is essential for the coloration for cotton. A major challenge for the dyer is minimizing both the amount of fresh water consumed in the dyeing process and the level of contaminants released into the effluent. In general terms, there is a direct correlation between wash fastness and water usage. By reducing the number of rinses, the liquor ratio of the rinses, and the temperature of rinses, the dyer can reduce processing costs, however the resulting wash fastness will also be reduced.

For this study, all dye types and dyeings received identical pre-scour (40 liters/kg) and post rinse (50 liters/kg) treatments.

Following the standardized pre-scour (40 liters/kg), a double mordant procedure (tannin and alum) was used before the application of natural color to cotton, and used a total of 40 liters/kg. The natural coloration step called for 10 liters/kg. The post coloration rinses were standardized at 50 liters/kg. The number of programmed machine fills for applying natural colorant to cotton called for a total of 224 liters to process 1.6 kg of fabric (140 liters/kg).

The number of programmed machine fills was the same for all petroleum based synthetic dyes (direct and fiber reactive dyes). Following the standardized pre-scour (40 liters/kg), the dyebath for synthetic colors used 10 liters/kg. The post coloration rinses were standardized at 50 liters/kg. Table 9 details the total amount of water used for petroleum based synthetic dyes was 160 liters for 1.6 kg of fabric (100 liters/kg).

Table 9. Total Water Usage for Research Dyeings (L/kg dyed)

Colorant	Pre-Scour	Coloration	Post-Scour	Total
Natural Colorants	40	50	50	140
Synthetic Dyes	40	10	50	100

After the coloration process, the 5 meter lengths were centrifugally extracted and tumble dried. The original greige weight of 1.6 kg increased to 3.6 kg wet weight after extraction, indicating 2 kg of water was retained by the knitted cotton fabric (125% wet pick up).

Of the 224 liters of water introduced for natural colorants, 222 liters (99.1%) was discharged as colored effluent and 2 liters (0.9%) was evaporated in the dryer. For petroleum based synthetic dyes, 160 liters was introduced with 158 liters (98.75%) discharged as colored effluent and 2 liters (1.25%) evaporated in the dryer.

Petroleum based synthetic dyes require 28.6% less water than natural colorants to produce a similar shade. Due to the design of the experiment, all petroleum based dyes were processed using the same machine fill/drain procedure.

The improved dyeing and rinsing efficiency of the poly-functional and bi-functional reactive dyes will translate to lower water usage in commercial applications (Table 10).

Table 10. Assigned Values and Rankings for Water Usage

Dye Class	Assigned Value
Poly-Functional and Bi-Functional	5
Direct Dyes, VS, DFMCP, and MCT	3
Natural Colorants	2

5 = Excellent (Lowest usage) and 1 = Poor (highest usage)

Detailed procedures for all dyeings are in Appendix 1-4.

6.3 Steam Consumption

The amount of energy (kJ) required to heat and maintain temperatures during the total cycles was calculated for natural colorants, synthetic dyes at 95°C, and synthetic dyes at 60°C using a program developed at Cotton Inc. (68).

To maintain consistency in the calculations, process standardization and several key assumptions were established (Table 11). As discussed in water usage, all colorations included a standard pre-scour and post dyeing rinse procedure.

Table 11. Assumptions Used for Calculating Steam Consumption

1. All machine fills were programmed based on predetermined Liquor Ratio
2. All machine fills use incoming water at 30°C
3. All machine volumes following a drain and fill were adjusted by 4 liters (retained from previous bath)
4. All water temperatures following a drain and fill were adjusted to account for the temperature of the retained 4 liters.

The formula to calculate energy required to raise the temperature: $Q = (m)(C_p)(\Delta T)$

Q = quantity of energy in kJ (kilo Joules)

m = mass in kg

C_p = specific heat capacity in kJ/kg°C

ΔT = change in temperature (°C)

C_p, Specific heat capacity of water = 4.19 kJ/kg

C_p, Specific heat capacity of cotton = 1.31 kJ/kg

Example calculation for raising the temperature of 32 liters of water containing 1.6 kg of cotton fabric from 30°C to 60°C:

$Q = (m)(C_p)(\Delta T)$

For the water: Q (water) = (32 kg) (4.19 kJ/kg°C) (60°C - 30°C)

Q (water) = (32 kg) (4.19 kJ/kg°C) (30°C)

Q (water) = 4,022.4 kJ

For the cotton: Q (cotton) = (1.6 kg) (1.31 kJ/kg°C) (60°C - 30°C)

Q (cotton) = (1.6 kg) (1.31 kJ/kg°C) (30°C)

Q (cotton) = 62.9 kJ

Combine the Q for water and cotton for a total energy consumption of 4085.3 kJ to raise the temperature of a bath containing 32 liters of water and 1.6 kg of fabric from 30°C to 60°C.

Calculating the amount of energy required to maintain an elevated temperature for a period of time required determining the radiant heat loss of the sample dye machine at multiple temperatures (Table 12). A 5 meter length of cotton was loaded into the sample dye machine, filled with 32 liters of water (LR 20:1) and heated to specific temperatures. The steam was turned off and the drop in temperature due to radiation (°C/min) was measured.

Table 12. Measured Temperature Loss in Tupesa Sample Dye Machine

Temperature (°C)	Measured Loss (°C / Minute)
30	0.000
40	0.050
60	0.275
80	0.625
90	0.825
95	0.975

The equation for calculating the energy required to raise the temperature was modified to predict the amount of energy required to maintain an elevated temperature. To simplify the calculations, mass (m) was assumed to be the combined kg of the contents (33.6 kg) and specific heat capacity (C_p) was assumed to be water (4.19 kJ/kg°C). The change in temperature (ΔT) was determined to be the multiple of (the minutes at the elevated temperature) times (the measured temperature loss due to radiation at the elevated temperature).

Continuing with the earlier example, the energy required to maintain the bath at 60°C for 10 minutes is calculated as:

Q (maintain) = (33.6 kg) (4.19 kJ/kg°C) (10 minutes x 0.275 °C/minute)

Q (maintain) = (33.6 kg) (4.19 kJ/kg°C) (2.75°C)

Q (maintain)= 387.2 kJ

The total energy required to heat a bath containing 32 liters of water and 1.6 kg of cotton for 30°C to 60°C and hold at 60°C for 10 minutes is:

Q (total) = Q (water) + Q (fabric) + Q (maintain)

Q (total) = 4,022.4 kJ + 62.9 kJ + 387.2 kJ

Q (total) = 4,472.5 kJ

Natural colorants required steam to set and hold the temperature for 5 different baths. The total energy requirement for each bath is the sum of the energy required to heat the water (Qw), heat the fabric (Qf), and maintain the bath temperature (Qm).

Natural: Q (pre-scour) = Qw+Qf+Qm = 4,022.4 + 62.9 + 387.2 = 4,472.4

Natural: Q (mordant 1) = Qw+Qf+Qm = 4,928.4 + 123.3 + 2,240 = 7,291.6

Natural: Q (mordant 2) = Qw+Qf+Qm = 4,690 + 117.3 + 2,240 = 7,047.3

Natural: Q (coloration) = Qw+Qf+Qm = 5,596.7 + 117.3 + 3,393.9 = 9,107.9

Natural: Q (post rinse) = Qw+Qf+Qm = 4,521.4 + 113.2 + 282.8 = 4,917.4

Natural coloration total energy = 32,836.7 kJ to process 1.6 kg = 20,522.9 kJ/kg cotton processed.

Raw data and details of steam consumption calculations for natural colorants are in Appendix 5.

Petroleum based synthetic dyes required steam to set and hold the temperature for 3 different baths.

95°C Dyes: Q (pre-scour) = Qw+Qf+Qm = 4,022.4 + 62.9 + 387.2 = 4,472.4
95°C Dyes: Q (coloration) = Qw+Qf+Qm = 5,347.4 + 133.7 + 6,618.1 = 12,099.2
95°C Dyes: Q (post rinse) = Qw+Qf+Qm = 5,386.7 + 112.9 + 282.8 = 5,782.5
95°C dyes coloration total energy = 22,354.1 kJ to process 1.6 kg = 13,971.3 kJ/kg cotton processed.

Raw data and details of steam consumption calculations for synthetic dyeings at 95°C are in Appendix 6.

60°C Dyes: Q (pre-scour) = Qw+Qf+Qm = 4,022.4 + 62.9 + 387.2 = 4,472.4
60°C Dyes: Q (coloration) = Qw+Qf+Qm = 2,414.4 + 60.4 + 1,866.6 = 4,341.4
60°C Dyes: Q (post rinse) = Qw+Qf+Qm = 5,449.8 + 114.2 + 282.8 = 5,846.8
60°C dyes coloration total energy = 14,660.7 kJ to process 1.6 kg = 9,162.9 kJ/kg cotton processed.

Raw data and details of steam consumption calculations for synthetic dyeings at 60°C are in Appendix 7.

Comparison of total steam energy consumption for the various means of coloration:

Natural coloration: 20,522.9 kJ/kg cotton processed

Petroleum based synthetic dyes:

Direct and Hot Reactives (95°C): 13,971.3 kJ/kg cotton processed.

Cold Reactives (60°C): 9,162.9 kJ/kg cotton processed.

Petroleum based synthetic dyes require less energy than natural colorants to produce a similar shade. Synthetic dyes at 95°C use 31.9% less energy than natural colorants. Synthetic dyes at 60°C use 55.4% less energy than natural colorants.

Synthetic dyes at 60°C use 34.4% less energy than synthetic dyes at 95°C to produce a similar shade.

In commercial applications, the clean-up procedure for poly-functional and bi-functional fiber reactive dyes can be performed at temperatures lower than 85°C, allowing for further reduction in steam (energy) consumption (Table 13).

Table 13. Assigned Values and Ranking for Steam Consumption

Dye Class	Assigned Value
Poly-Functional and Bi-Functional	5
DFMCP and VS	4
MCT and Direct Dyes	3
Natural Colorants	2

5 = Excellent (Lowest usage) and 1 = Poor (highest usage)

6.4 Cycle Time

Total cycle time was measured for all natural colorants and synthetic dyes. As discussed in water usage and steam consumption, the standardized procedures used for this study were based on successful commercial dyeing procedures. The coloration step for each dyeing was maintained for 60 minutes for consistency. In a production environment, the coloration step could be optimized for each type of colorant and depth of shade to maximize equipment utilization.

The standardized pre-scour segment of the procedure ran for 32.5 minutes for all colorants and dyes. The standardized post rinse segment of the procedure ran for 50.5 minutes for all colorants and dyes.

The double mordant process used for natural colorants ran for 112 minutes and the actual natural coloration step ran for 96.5 minutes. The total time in the machine for natural colorants was 291.5 minutes. (See Appendix 1)

The coloration process for direct dyes at 95°C required 123.5 minutes. The total time for synthetic direct dyes at 95°C is 206.5 minutes. (See Appendix 2)

The coloration process for synthetic fiber reactive dyes at 95°C required 128.5 minutes. The total time in the machine for petroleum based synthetic dyes at 95°C is 211.5 minutes. (See Appendix 3)

The coloration process for synthetic fiber reactive dyes at 60°C required 119.5 minutes. The total time in the machine for petroleum based synthetic dyes at 60°C is 202.5 minutes. (See Appendix 4)

While the actual cycle times for small sample machine runs will not directly transfer to full production machine cycles, they will serve as a relative guide for larger scale production volumes. Water fills and drains, chemical additions, and heating steps are relatively quick with the small volume and high efficiency sample dye unit.

The petroleum based synthetic dyes all required less than 212 minutes while the natural colorants ran for 291 minutes. In this study, the synthetic dyes require 27% less machine time than the natural colorants.

In commercial applications, the clean-up procedure for poly-functional and bi-functional fiber reactive dyes can be performed at temperatures lower than 85°C, allowing for further reduction in cycle times (Table 14).

Table 14. Assigned Values and Ranking for Cycle Time

Dye Class	Assigned Value
Poly-Functional and Bi-Functional	5
DFMCP and VS	4
MCT and Direct Dyes	3
Natural Colorants	1

5 = Excellent (shortest cycle) and 1 = Poor (longest cycle)

6.5 Impact of Effluent

The textile industry consumes large amounts of fresh water, which needs to be treated before final discharge. The amounts and types of dyes used in a textile mill vary dramatically based upon the substrates being processed as well as the colors being dyed. Changes in dyestuff result in variations in the wastewater characteristics (COD, TDS, pH, and color). Large pH swings in the effluent are problematic since the pH tolerance of typical biological treatment systems is limited (69).

A 200 ml aliquot was collected just before every drain during all dyeings. These individual aliquots were used for both color analysis of the effluent as well as determining the relative impact on the waste stream. The individual aliquots for the natural colorants and selected petroleum based synthetic dyes were combined to build a representative waste stream of each type of dye and dyeing for wastewater testing. Due to the limited quantity of collected effluent, the test results will serve only as a guide to the environmental impact of the effluent streams.

The wastewater tests conducted were:
Total Organic Carbon (TOC, mg/L) is the amount of carbon found in an organic compound and is often used as a non-specific indicator of water cleanliness of manufacturing effluent. The organic carbon in the effluent is converted to carbon dioxide and measured using an infrared analyzer (70, 71, 72).

Chemical Oxygen Demand (COD, mg O2/L) is a basic test used for establishing the concentration of organic matter in wastewater. COD uses a solution of potassium dichromate in 50% sulfuric acid to ‘oxidize’ the organic substances. A colorimeter is used to measure the relative color change (70, 71, 72).

Total Dissolved Solids (TDS, mg/L) refers to any minerals, salts, metals, cations or anions dissolved in water (71).

pH is defined as the negative logarithm of the hydrogen ion concentration. The pH of a solution is measured on a scale of 1 to 14, with pH of 1 (strongly acidic) having a high concentration of hydrogen ions and pH of 14 (strongly alkaline) having a low concentration of hydrogen ions. The pH of the effluent stream is critical since both high and low pH values have detrimental impacts on biological treatment.

Table 15 provides the average data for the effluent streams of the tested natural colorants and synthetic dyes.

Table 15. Averaged Data from Effluent Testing

Units	Test	Natural Colorants	Synthetic Dyes
mg/L	TOC	647.00	116.00
mgO_2/L	COD	1997.00	226.17
mg/L	TDS	2595.33	8265.00
	pH	4.11	9.64

Raw Data for all effluent testing is in Appendix 8

The average waste streams for petroleum-based synthetic dyes have significantly lower TOC and COD than the waste streams of natural colorants.

Natural colorants have significantly lower TDS in their waste stream than synthetic dyes.

The average pH of the total waste stream of synthetic dyes is 9.64 and the average pH of the total waste stream of the natural colorants is 4.11.

TOC

The TOC for synthetic fiber reactive dyes (21-35 mg/L) are much lower than direct dyes (253 mg/L). Both fiber reactive and direct dyes have significantly lower TOC than natural colorants (484-950 mg/L), indicating that the effluent from synthetic dye cycles generates much lower levels of organic content than natural colorants.

COD

The COD for synthetic direct dyes (<100 mgO2/L) is lower than fiber reactive dyes (133-215 mgO2/L). All synthetic dyes in the study have significantly lower COD values than natural colorants (1,550-2,796 mgO2/L).

TDS

The natural colorants (2,308-3,112 mg/L) and synthetic direct dyes (2,360 mg/L) both have significantly lower TDS than the fiber reactive dyes (8,880-15,900 mg/L). The high levels of TDS in fiber reactive dyes can be attributed to the required amounts of electrolyte added to promote level exhaustion. There is a direct correlation between the TDS and the depth of shade processed using fiber reactive dyes. Darker shades (high amounts of dye) require larger quantities of sodium sulfate to produce level dyeings.

pH

The natural colorants all had pH on the acid side (3.21-4.94) and the synthetic fiber reactive dyes had pH on the alkaline side (9.48-10.62). There is a direct correlation between the pH and the depth of shade processed using fiber reactive dyes. Darker shades (high amounts of dye) require larger quantities of sodium carbonate to produce level dyeings. The total waste stream for direct dyes had a pH of 8.25.

Table 16 provides the assigned values for the effluent testing per dye class.

Table 16. Assigned Values for Effluent Testing of Each Dye Class

	Natural	Direct	VS	MCT	DFMCP	Bi-Func	Poly-Func
TOC	2	3	5	4	5	5	4
COD	2	5	5	3	4	4	4
TDS	5	5	1	2	2	1	1
pH	4	5	2	2	3	1	1

5 = Excellent and 1 = Poor

Working with wastewater treatment professionals, a default rating system was developed for determining the Impact of Effluent (73). Using a total of 100, TOC is assigned a value of 40%, COD accounts for 30%, TDS accounts for 20%, and pH accounts for 10% of the total Impact of Effluent (Table 17). The spreadsheet is designed to allow the end-user to rank the relative importance of each wastewater test performed based on their local conditions and have the data transferred directly to the overall ranking system.

Table 17. Weighted Parameter Spreadsheet for Effluent Testing

		Weighting of Factors Affecting Effluent							
	WEIGHT		Natural	Direct	MCT	DFMCP	VS	Bi-Func	Poly-Func
	40	TOC	0.8	1.2	1.6	2	2	2	1.6
	30	COD	0.6	1.5	0.9	1.2	1.5	1.2	1.2
	20	TDS	1	1	0.4	0.4	0.2	0.2	0.2
	10	pH	0.4	0.5	0.2	0.3	0.2	0.1	0.2
Total	100		2.8	4.2	3.1	3.9	3.9	3.5	3.2

The assigned values and rankings of each dye class for Impact of Effluent are shown in Table 18.

Table 18. Impact of Effluent using Default Rankings (73)

Dye Class	Default Value
Direct Dyes	4.2
DFMCP and VS	3.9
Bi-Functional	3.5
Poly-Functional	3.2
MCT	3.1
Natural Colorants	2.8

5 = Excellent (lowest impact) and 1 = Poor (highest impact)

6.6 Dyestuff Efficiency

Dyers are faced with the negative image of color in the waste stream, even if it can easily be removed with normal wastewater treatments.

Instead of working to remove the color from the effluent, one of our objectives was to evaluate dyes and dyeing systems to identify ways to minimize the amount of color discharged in the effluent. Reducing the discharged color can be approached through process modification and / or improvements in dyestuff chemistry. With 6 petroleum-based synthetic dyeing systems (18 separate dyes) and 3 natural colorants in the study, managing the individual procedures became an overwhelming task, therefore all of the procedures were standardized to allow a direct comparison of the various chemistries.

The original research plan called for a HueMetrix unit to be connected to the Tupesa sample dye machine located at Tumbling Colors, Raleigh NC, however issues with maintaining consistent pump flow and communication between devices forced us to shift to a bench top HueMetrix unit for single injection analysis instead of constant flow analysis.

After establishing a benchmark palette of 3 colors using natural colorants, the 3 benchmark colors were matched and dyed using 6 different types of synthetic dyes. The synthetic dyes were direct dyes and 5 types of fiber reactive dyes for a total of 18 unique dyeings.

Most plant based natural colorants have large particle sizes and are insoluble in water. The combination of particle size and insolubility prevented us from measuring the color content of the drain baths from each of the natural colorants using the HueMetrix Color Analyzer. Visual assessments were made for comparisons (see Figure 28).

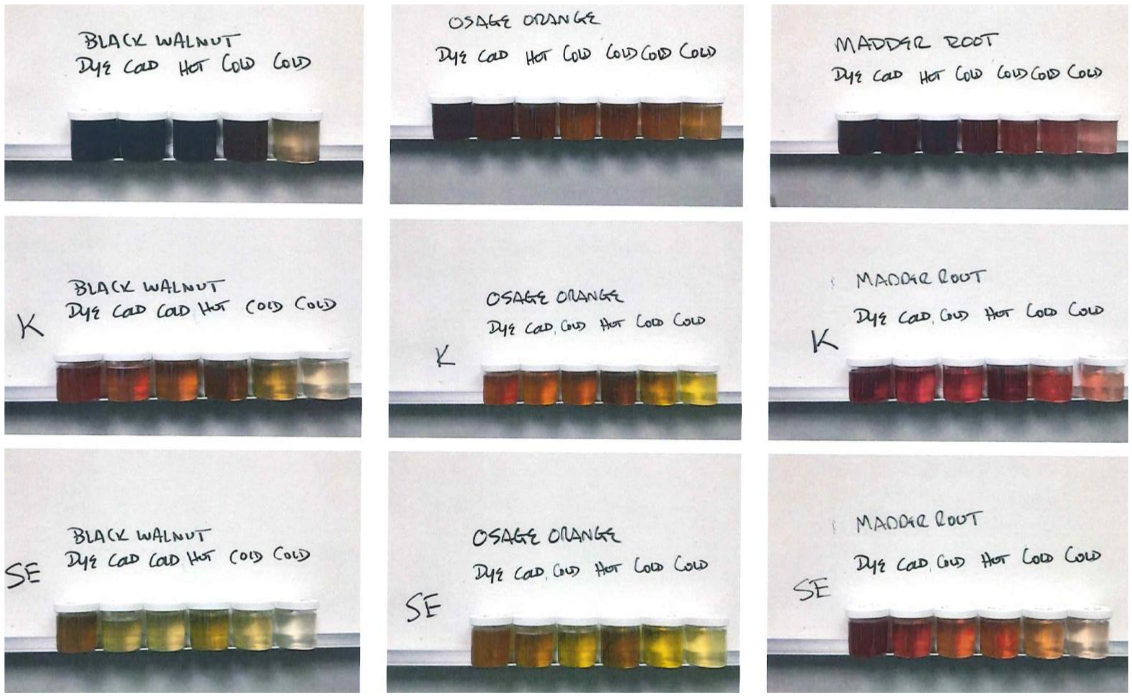


Figure 28. Photograph of Drains

Before an aliquot can be analyzed for color content by the HueMetrix unit, calibration data for each dyestuff must be created and stored. Individual solutions of each dye were prepared at 0.05 g/L, 0.1 g/L, 0.2g/L, 0.5 g/L, 1.0 g/L, and 2.0 g/L. Each concentration was repeatedly injected into the HueMetrix unit to build a validated calibration plot using concentration vs. absorbance. Calibration curves were built for each of the 18 different dyes sourced for the study (80).

The dyestuff manufacturers' recommendations for dyeing temperature, electrolyte and alkali dosage were followed for each type and class (49, 74, 75, 76).

Dyestuff manufacturers continue to manipulate (optimize) the suggested amounts of electrolyte and alkali for dyeing. Commercial dyers must remain vigilant of the electrolyte and alkali dosage levels, as well as time temperature profiles to generate consistent colors.

All selected synthetic dye classes followed the same fill/drain and cycle time sequence. The sample dye machine was manually paused seconds prior to each drain and a 200 ml aliquot was collected and labeled. Aliquots were collected at the conclusion of the exhaustion/fixation step, after each of first 2 cold rinses, after the hot soap, and after each of the final 2 cold rinses for a total of 6 aliquots per dyeing. Aliquots captured following pre-scour baths were not included in color analysis.

Before measuring the color in each captured aliquot, the HueMetrix unit was flushed with copious amounts of distilled water. The Solution Check tool was selected and the specific dyes involved in the dyeing being measured were loaded. To minimize cross staining and contamination, the aliquot with the smallest amount of dye was measured first. A minimum of 3 readings was taken for each aliquot. Between aliquots, the unit was flushed with distilled water to insure the tubing was free of color from the previous sample. Measurements were also recorded for the distilled water flushes.

After review of the total HueMetrix data set, it was determined that a measurable amount of Drimarene™ Rubine CL-3BL remained in the system between aliquot measurements of colors built using Drimarene™ HF-CL dyes (bi-functional). Based on this finding, an adjustment was made to the mathematical model of all samples to subtract the value of the previous flush from the value of the actual color measurement.

The HueMetrix software was designed to separate and quantify the amount of each individual dyes from the captured effluent stream based on the calibration data.
The measured values for the individual dyes were summed to create a total amount of raw color in each captured aliquot. The distilled water flushes were also measured to establish the amount of color 'hidden' in the HueMetrix system of tubes, mixing cell, and cuvette.

After each step, the amount of dye is first separated into 2 categories: dye discharged down the drain and dye remaining in machine. The amount of dye remaining in the machine can then be separated into 2 categories: dye on the fabric and dye in the retained liquor in the machine.

Using the HueMetrix system and a series of sequential calculations, the total amount of color discharged with each drain can be determined. Upon completion of the analysis, the amount of color that was discharged and the amount of color that is on the fabric can be derived from the collected HueMetrix measurements. The total of these 2 calculations equals the original weight of dyes added to the machine.

EXAMPLE: Avitera™ SE dyes used to match natural red created using madder root (SE_MR_439)

Sample 1, Drain following the dye bath

<u>Calculation 1</u>: Amount of color (g/L) discharged following dye bath

(Hue Raw 1) - (Hue Flush 1) = (Hue Adjusted 1)

(0.0607 g/L) – (0.0033 g/L) = 0.574 g/L

<u>Calculation 2</u>: Total weight of color (g) discharged after dye bath

(Calculation 1) x (Volume of discharge) = (Weight of dye in discharge following dye bath)

(0.574 g/L) x (16 L) = 0.9184 g

<u>Calculation 3</u>: Total amount of dye (g) left in the machine after dye bath

(Initial weight of dye added to machine) – (Calculation 2) = (Weight of dye left in the machine following dye bath)

(13.15 g) – (0.9184 g) = 12.2316 g

<u>Calculation 4</u>: Amount of dye (g) in retained water in machine following dye bath

(Calculation 1) x (Volume of retained water) = (Weight of dye in retained water in machine following dye bath)

(0.0574 g/L) x (4 L) = 0.2296 g

<u>Calculation 5</u>: Amount of dye (g) retained on fabric in machine following dye bath

(Calculation 3) – (Calculation 4) = (Weight of dye retained on fabric following dye bath)

(12.2316 g) – (0.2296 g) = 12.0020 g

Sample 2, drain following the first cold rinse

Calculation 6: Amount of color (g/L) in discharge following cold rinse 1

(Hue Raw 2) - (Hue Flush 2) = (Hue Adjusted 2)

(0.0267 g/L) – (0.0030 g/L) = 0.0237 g/L

Calculation 7: Total weight of color (g) in discharge following cold rinse 1

(Calculation 6) x (Volume of discharge) = (Weight of dye in discharge following cold rinse 1)

(0.0237 g/L) x (16 L) = 0.0218 g

Calculation 8: Total amount of dye (g) left in the machine following cold rinse 1.

(Calculation 3) – (Calculation 7) = (Weight of dye left in the machine following cold rinse 1)

(12.2316 g) – (0.0218 g) = 12.2098 g

Calculation 9: Amount of dye (g) in retained water in machine following cold rinse 1.

(Calculation 6) x (Volume of retained water) = (Weight of dye in retained water in machine following cold rinse 1)

(0.0237 g/L) x (4 L) = 0.0054 g

Calculation 10: Amount of dye (g) retained on fabric in machine following cold rinse 1.

(Calculation 8) – (Calculation 9) = (Weight of dye retained on fabric following cold rinse 1)

(12.2098 g) – (0.0054 g) = 12.2044 g

Sample 3, drain following second cold rinse

Calculation 11: Amount of color (g/L) discharged following cold rinse 2

(Hue Raw 3) - (Hue Flush 3) = (Hue Adjusted 3)

(0.0203 g/L) – (0.0023 g/L) = 0.0180 g/L

Calculation 12: Total weight of color (g) discharged following cold rinse 2

(Calculation 11) x (Volume of discharge) = (Weight of dye in discharge following cold rinse 2)

(0.0180 g/L) x (16 L) = 0.2880 g

Calculation 13: Total amount of dye (g) left in the machine following cold rinse 2

(Calculation 8) – (Calculation 12) = (Weight of dye left in the machine following cold rinse 2)

(12.2098 g) – (0.2880 g) = 11.9218 g

Calculation 14: Amount of dye (g) in retained water in machine following cold rinse 2

(Calculation 11) x (Volume of retained water) = (Weight of dye in retained water in machine following cold rinse 2)

(0.0180 g/L) x (4 L) = 0.0720 g

Calculation 15: Amount of dye (g) retained on fabric in machine following cold rinse 2.

(Calculation 13) – (Calculation 14) = (Weight of dye retained on fabric following cold rinse 2)

(11.9218 g) – (0.0720 g) = 11.8498 g

Sample 4, drain following hot soap

Calculation 16: Amount of color (g/L) discharged following hot soap.

(Hue Raw 4) - (Hue Flush 4) = (Hue Adjusted 4)

(0.0247 g/L) – (0.0023 g/L) = 0.0224 g/L

Calculation 17: Total weight of color (g) discharged following hot soap.

(Calculation 16) x (Volume of discharge) = (Weight of dye in discharge following hot soap)

(0.0224 g/L) x (16 L) = 0.3584 g

Calculation 18: Total amount of dye (g) left in the machine following hot soap.

(Calculation 13) – (Calculation 17) = (Weight of dye left in the machine following hot soap)

(11.9218 g) – (0.3584 g) = 11.5634 g

Calculation 19: Amount of dye (g) in retained water in machine following hot soap.

(Calculation 16) x (Volume of retained water) = (Weight of dye in retained water in machine following hot soap)

(0.0224 g/L) x (4 L) = 0.0896 g

Calculation 20: Amount of dye (g) retained on fabric in machine following hot soap.

(Calculation 18) – (Calculation 19) = (Weight of dye retained on fabric following hot soap)

(11.5634 g) – (0.0896 g) = 11.4738 g

Sample 5, drain following the third cold rinse

Calculation 21: Amount of color (g/L) discharged following cold rinse 3

(Hue Raw 5) - (Hue Flush 5) = (Hue Adjusted 5)

(0.0147 g/L) – (0.0037 g/L) = 0.0110 g/L

Calculation 22: Total weight of color (g) discharged following cold rinse 3.

(Calculation 21) x (Volume of discharge) = (Weight of dye in discharge following cold rinse 3)

(0.0110 g/L) x (16 L) = 0.1760 g

Calculation 23: Total amount of dye (g) left in the machine following cold rinse 3.

(Calculation 18) – (Calculation 22) = (Weight of dye left in the machine following cold rinse 3)

(11.5634 g) – (0.1760 g) = 11.3874 g

Calculation 24: Amount of dye (g) in retained water in machine following cold rinse 3.

(Calculation 21) x (Volume of retained water) = (Weight of dye in retained water in machine following cold rinse 3)

(0.0110 g/L) x (4 L) = 0.0440 g

Calculation 25: Amount of dye (g) retained on fabric in machine after cold rinse 3.

(Calculation 23) – (Calculation 24) = (Weight of dye retained on fabric following cold rinse 3)

(11.3874 g) – (0.0440 g) = 11.3434 g

Sample 6, drain and extract following fourth and final cold rinse

Calculation 26: Amount of color (g/L) discharged following cold rinse 4.

(Hue Raw 6) - (Hue Flush 6) = (Hue Adjusted 6)

(0.0083 g/L) – (0.0027 g/L) = 0.0056 g/L

Calculation 27: Total weight of color (g) discharged following cold rinse 4.

(Calculation 26) x (Volume of extract) = (Weight of dye following cold rinse 4)

(0.0056 g/L) x (18 L) = 0.1008 g

Calculation 28: Total amount of dye (g) left in the machine following extract of cold rinse 4

(Calculation 23) – (Calculation 27) = (Weight of dye left in the machine following extract of cold rinse 4)

(11.3874 g) – (0.1008 g) = 11.2866 g

Calculation 29: Amount of dye (g) in retained water in machine following extract of cold rinse 4.

(Calculation 26) x (Volume of retained water) = (Weight of dye in retained water in machine following extract of cold rinse 4)

(0.0056 g/L) x (2 L) = 0.0112 g

Calculation 30: Amount of dye (g) retained on fabric in machine following extract of cold rinse 4.

(Calculation 28) - (Calculation 29) = (Weight of dye retained on fabric following extract of cold rinse 4)

(11.2866 g) - (0.0112 g) = 11.2574 g

Each class of petroleum based synthetic dyes was used to match the baseline palette established with natural colorants. The percentage of color exhausted onto the fabric and the percentage of color discharged in the effluent stream are detailed below (Table 19, p. 79).

Table 19. Percentage of Synthetic Dye Exhausted versus Discharged

Sample Dyeing	% Exhausted	% Discharged	Raw Data (Appendix)	Calculations (Appendix)
Direct Dye (98°C)				
yellow/orange shade	59.02	40.98	9	10
red shade	68.73	31.27	11	12
brown shade	72.19	27.81	13	14
Average	66.65	33.35		
MCT (98°C)				
yellow/orange shade	79.44	20.56	15	16
red shade	73.93	26.07	17	18
brown shade *	67.88	32.12	19	20
Average	73.75	26.25		
Vinyl Sulfone (60°C)				
yellow/orange shade	59.41	40.59	21	22
red shade	63.41	36.59	23	24
brown shade	63.04	36.96	25	26
Average	61.95	38.05		
DFMCP (60°C)				
yellow / orange shade	65.53	34.46	27	28
red shade	69.06	30.94	29	30
brown shade	52.25	47.45	31	32
Average	62.28	37.62		
Bi-Functional (60°C)				
yellow / orange shade	72.36	27.64	33	34
red shade	76.34	23.66	35	36
brown shade	63.20	36.80	37	38
Average	70.63	29.37		
Poly-Functional (60°C)				
yellow/orange shade	74.86	25.14	39	40
red shade	85.83	14.17	41	42
brown shade	72.04	27.96	43	44
Average	77.58	22.42		

The standardized dyeing procedure allows for comparison of the color removed and discharged in each step. At the conclusion of the dyebath, the average amount of color discharged for the petroleum based synthetic dyes was 0.09 g/L. After the first and second cold rinses, the amounts discharged were 0.04 g/L and 0.03 g/L. The hot soap removed an increased amount of color and averaged 0.07 g/L. The final 2 cold rinses at the end of the standardized cycle have average discharges of 0.02 g/L and 0.01 g/L.

Advances in product development for reactive dyes are obvious in the amount of color discharged versus the amount of color on the fabric. The latest derivation, poly-functional fiber reactive dyes applied at 60°C, have the highest level of exhaustion / fixation and thus the lowest amount of color discharged into the effluent stream.

Bi-functional fiber reactive dyes (applied at 60°C) displayed the next highest efficiency, followed by MCT and direct dyes, applied at 98°C. The early forms of 60°C fiber reactive dyes (DFMCP and VS) had the lowest efficiency of the petroleum based dyes tested.

Based on the visual assessment and comparison of all captured aliquots, the petroleum based synthetic dyes consistently had less visible color in the effluent than the natural colorants. Table 20 details the assigned values and rankings based on both spectrophotometric and visual assessments.

Table 20. Assigned Values and Ranking for Dyestuff Efficiency

Dye Class	Assigned Value
Poly-Functional	5
Bi-Fucntional and MCT	4
Direct Dyes	3
DFMCP and VS	2
Natural Colorants	1

5 = Excellent and 1 = Poor

6.7 Fastness

Cotton fabrics must have a minimum level of color and wash fastness to satisfy commercial standards. Color fastness is not directly related to the environmental impact of the dyeing system, however dyers must balance the amount of water and energy used for rinsing hydrolyzed, unfixed, and surface deposited colors from the fabric against the fastness requirements for washing and water. Light fastness is more dependent upon the molecular structure of the colorant than the amount of rinsing detailed in the procedure. The standardized procedures used for this study were based on successful commercial dyeing procedures and include additional rinses for improved fastness to washing and water.

A series of color fastness tests were conducted by a certified third part testing facility on fabrics representing all colorants used in the study. The color fastness tests conducted are detailed in Table 21 (p. 82).

Table 21. Fastness Testing Conducted on Selected Dyed Samples

Colorfastness to:	AATCC	Additional Information
Washing	61-2013, #2A	45 minutes at 40°C with 50 steel balls
Crocking	8-2013	Wet and Dry
Perspiration	15-2013	
Water	107-2013	
Light	16.3, Option 3	Xenon Arc, 20 AFU exposure

Unless otherwise noted, all test results were 4 or better.

Colorfastness to Washing

Shade change: natural osage orange (2), natural madder root (3), natural black walnut (3)

Multi fiber: osage orange stained nylon (3.5)

Colorfastness to Crocking

Dry: natural osage orange (2.5), natural madder root (2.5), natural black walnut (3)

Colorfastness to Perspiration

Multi fiber: natural osage orange stained nylon (3) and wool (3.5), natural madder root stained nylon (3.5)

Colorfastness to Water

Multi fiber: natural osage orange stained cotton (3.5), nylon (2.5) and wool (3.5)

Colorfastness to Light

20 AFU exposure: natural osage orange (3.5), natural madder root (2.5), direct dye (3.5), fiber reactive 95°C (3), fiber reactive 60°C (2.5-3.5)

With the exception of natural colorant osage orange, the overall fastness of the natural madder root and natural black walnut colorants and petroleum based synthetic dyes were acceptable. The extended procedures with additional rinses utilized in the study contributed to the satisfactory fastness ratings.

Total results from Fastness Testing is provided in Appendix 9.

7. WEIGHTED PARAMETER COMPARISON

The final aspect of the project involved building an interactive spreadsheet for Weighted Parameter Comparisons using the compiled data and rankings from each of the 5 separate studies: water usage, steam consumption, cycle time, impact of effluent, and dyestuff efficiency (Table 22). The rankings for the individual studies (except Impact of Effluent) were built on a scale of 5 for excellent and 1 for poor.

Since the Impact of Effluent provided for the ability to rank various individual impacts of the effluent stream, a separate weighting is allowed (Table 17, p.68). A default weighting was established by wastewater professionals (73) and can be used in place of personal weighting for Impact of Effluent (Table 18). The default weightings are TOC 40%, COD 30%, TDS 20%, and pH 10%. Once the weighting is done for Impact of Effluent, the results can be automatically transferred to the Weighted Parameter Spreadsheet.

Table 22. Parameters Used for Comparing Various Colorants and Dyes

Parameter Measured	5 =	1 =
Water Usage	lowest usage	highest usage
Steam Consumption	lowest consumption	highest consumption
Cycle Time	shortest cycle	longest cycle
Impact of Effluent	lowest impact	highest impact
Dyestuff Efficiency	most efficient	least efficient

Figure 29 contains the individually assigned values for each measured parameter by dye class. The Impact of Effluent values shown in Figure 29 are based on the default ranking system developed by a wastewater professional (73).

Metrics							
	Natural	**Direct**	**MCT**	**DFMCP**	**VS**	**Bi-Func**	**Poly-Func**
Water	1	2	3	2	2	4	5
Steam	1	3	3	4	4	5	5
Time	1	3	2	4	4	5	5
Effluent	2.8	4.2	3.1	3.9	3.9	3.5	3.2
Efficiency	1	3	4	2	2	4	5

Figure 29. Assigned Values for Dyeings for Each Parameter Tested

The Weighted Parameter Spreadsheet (Figure 30) allows the user to assign a specific value (percentages with total of 100). The specific values are used as multipliers to calculate a total impact of the dyeing system based on all parameters tested in the study.

	Weighting of Metrics							
WEIGHT		**Natural**	**Direct**	**MCT**	**DFMCP**	**VS**	**Bi-Func**	**Poly-Func**
10	**Water**	10	20	30	20	20	40	50
15	**Steam**	15	45	45	60	60	75	75
5	**Time**	5	15	10	20	20	25	25
35	**Effluent**	98	147	108.5	136.5	136.5	122.5	112
35	**Efficiency**	35	105	140	70	70	140	175
100		**163**	**332**	**333.5**	**306.5**	**306.5**	**402.5**	**437**

Figure 30. Weighted Parameter Spreadsheet Using Default Rated Impact of Effluent

Once the calculations are completed, the different dye classes can be ranked for their overall impact on the environment. A score of 500 is excellent (perfect in all categories) and a score of 100 is poor. Figure 30 displays the overall ranking (using the default ranking for impact of effluent) of the different dyes evaluated in the study. Poly-functional fiber reactive dyes applied at 60°C have the highest score (437), followed by bi-functional fiber reactive dyes (402.5), MCT fiber reactive dyes (333.5), Direct dyes (332), DFMCP and Vinyl Sulfone fiber reactive dyes (306.5), and Natural Colorants (163).

8. CONCLUSIONS

By working within the research boundaries established at the beginning of the project (the dye house walls), we have demonstrated that:

8.1 Response to Original Hypothesis

Petroleum based synthetic dyestuffs (direct and fiber reactive dyes) have higher color yields and lower environmental impacts than natural colors when applied to cotton using standardized procedures. Poly-functional and bi-functional fiber reactive dyes have the highest total scores and thus, the lowest overall environmental impact.

The parameters selected to address the original hypothesis were chosen based on the ability to control and measure the individual results. Water usage, steam consumption, cycle time, impact of effluent, and dyestuff efficiency were documented for 24 large sample dyeings carried out on 5 meter lengths of greige cotton knit.

8.2 Water Usage

Natural colorants allow for a unique marketing story, however their processing conditions do not support the story. Natural colorants require higher amounts of water, steam, and cycle time for processing when compared to petroleum based synthetic dyes.

Many marketing campaigns greatly exaggerate the amount of water used is processing cotton without defining the boundaries or parameters of their findings. Building upon 17 years of commercial dyeing success at Tumbling Colors, we were able to construct standard procedures that allowed us to measure the exact amount of water needed for preparation, dyeing, and rinsing for each group of dyes and dyeing systems evaluated.

To produce the selected palette of colors on greige cotton knit for the study, natural colorants used 140 liters per kg of cotton processed. Petroleum based synthetic dyes used 100 liters per kg of cotton processed. Depending upon the yarn size, construction, and shirt size, 5-7 cotton t-shirts can be made from 1 kg of fabric. Assuming 6 cotton t-shirts/kg of fabric, natural colorants consume 23 liters/shirt prepared, dyed, and rinsed. If the same 6 cotton t-shirts were dyed using petroleum based synthetic dyes, the amount of water needed per shirt is reduced to 17 liters/shirt.

Natural colorants require about 30% more water than petroleum based dyes to produce similar shades on cotton. The added water is due to the extra steps required for applying the mordants during the coloration phase of the process.

Within the range of petroleum based synthetic dyes, the bi-functional and poly-functional fiber reactive dyes will consume the lowest amount of water due to their higher levels of fixation.

8.3 Steam Consumption

Dyes and dyeing systems that run at 60°C require less energy than dyes and dyeing systems that require 98°C. Natural colorants require multiple baths at 90°C to apply the mordant prior to the colorant. Natural colorants consume 20,523 kJ/kg while dyeings at 98°C (direct and

MCT) consume 13,971 kJ/kg and dyeings at 60°C (VS, DFMCP, bi-functional, and poly-functional) required 9,163 kJ/kg cotton processed.

The bi-functional and poly-functional fiber reactive dyes can be rinsed easier and soaped cooler than other reactive dyes resulting in even lower steam consumption for processing cotton.

8.4 Cycle Time

As with previous discussions regarding increased consumption of water and steam, natural colorants require longer cycle times due to the extra steps necessary to apply the mordant prior to the application of color. As with water and steam, natural colorants require 30-40% longer cycle times when compared to petroleum based synthetic dyes.

8.5 Impact of Effluent

Natural colorants have very low Total Dissolved Solids (TDS) in their effluent stream when compared to petroleum based synthetic dyes. When using the default weighting system for Impact of Effluent developed by a wastewater professional (73), Direct dyes, VS, and DFMCP have the lowest overall environmental impact on the total effluent stream based on TOC, COD, TDS, and pH. Natural colorants have similar TOTAL impacts as MCT and Poly-functional reactive dyes.

The separate weighting system for Impact of Effluent allows user to customize their findings to the local regulations.

8.6 Dyestuff Efficiency

The natural colorants selected for this research have large particle size and limited to no solubility in water. A combination of particle size and poor solubility prevented these colorants from being characterized and evaluated using the HueMetrix Color Analyzer. Visual assessments and comparisons were used to determine the relative amount of color discharged following each step during the coloration process. Natural colorants discharge a large amount of visual color following the dye cycle, first cold rinse, and hot soap. The amount of visual color drops with each subsequent cold rinse. The final cold rinse is relatively clear and comparable to the less efficient petroleum based synthetic dyes.

Based on the data acquired from the HueMetrix Color Analyzer, the poly-functional fiber reactive dyes discharge the lowest amount of color in their effluent stream, which translates to having the highest level of exhaustion/fixation of all dyes and dyeing systems tested.

8.7 Fastness

While color fastness is not directly related to the environmental impact of dyeing systems, each of the samples was submitted for a panel of apparel fastness tests for comparison. With the exception of lightfastness, the fastness of all dyes tested was satisfactory. The additional rinses built into the standardized procedures contributed to the overall fastness levels of natural colorants, direct dyes, and fiber reactive dyes.

8.8 Costs

When selecting the metrics to measure and compare, costs were intentionally omitted. The environmental impact of dyes and dyeing systems is independent of the cost to purchase dye and reproduce a color. Costs are totally dependent upon local conditions, infra-structure (water and energy), and availability of required dyes. The metrics of water, steam, and time are constant and provide a solid basis for the comparison of dyes and dyeing systems.

9. FUTURE ACTIONS

The natural colorants and petroleum based synthetic dyes used for this study were selected based on the combination of commercial successes at Tumbling Colors and the recommendations of numerous technical colleagues. The study involved 3 different natural colorants, 18 different synthetic dyes and 7 different sets of application parameters. The original experimental plan called for using optimized application techniques for each colorant and class of dye. Soon after starting the study, the challenge of process optimization by dye class was overwhelming. A standardized application procedure, patterned after Tumbling Colors' production dyeings was adopted to evaluate the selected metrics of water usage, steam consumption, cycle time, impact of effluent, and dyestuff efficiency.

The findings demonstrate the industrial evolution of petroleum based synthetic dyes from direct dyes to poly-functional fiber reactive dyes. In each of the major metrics evaluated, the synthetic colors performed better than the natural colorants.

Due to the large particle size and lack of solubility in water of the natural colorants, the amount of color in the drain baths of natural colorations was not quantified in our study. Additional studies are necessary to identify a suitable solvent for dissolving the natural colorants without altering their color profiles. The data obtained from this additional study will allow for a numerical comparison of natural colors and synthetic dyes instead of a visual assessment.

Further studies can be designed to explore and compare the aquatic toxicity of the effluent streams for natural colorants and poly-functional fiber reactive dyes. With only natural colorants and poly-functional fiber reactive dyes in the study, the fabric weights can be increased to small batch production load sizes and process optimization can be implemented to validate the original findings for water usage, steam consumption, and cycle time.

Using the data from this study as a benchmark, additional dyeing systems for cotton can be evaluated for water usage, steam consumption, cycle time, impact of effluent, and dyestuff efficiency. An example of a dyeing system to evaluate is anionic dyes applied to cationic cotton.

Having identified the efficiency of the various synthetic dyestuffs in the original study, combined with the ability of the HueMetrix Color Analyzer to identify and quantify the individual components of an aquatic dye bath, a series of experiments can be conducted to explore predicting of the final shade based on an aqueous solution of known dyes. Being able to predict final shades using only a solution of dyes has the potential to reduce the amount of time and number of lab dips required to match a target.

There are numerous assumptions and variables that need to be identified before using transmission values for shade prediction. A precise series of single component solutions must be measured using the HueMetrix to establish the exact amount of dye in solution. A piece of fabric will be dyed using the original single component solutions and the reflectance measured using a spectrophotometer. A correlation can be established between the transmission and reflectance measurements of the single component color. By knowing the exhaustion efficiency of the specific dye class (from the original research), a simple mathematical formula can be written to predict the amount of dye needed to achieve a specific shade. Once several single component colors have been qualified, combinations of dye can be made up, measured for transmission, dyed, and then measured for reflectance. The ability of the HueMetrix Color Analyzer to recognize different dyes in a solution, combined with the knowledge of dyestuff efficiencies will allow the user to predict the final shade prior to dyeing. Time savings will be recognized in shade development labs and in the plant to avoid running an incorrect formula.

The mathematical models written for this study have already been applied to other dyeing systems for comparisons of different dyes and dyeing systems based on water usage, steam consumption, and cycle time. Based on the early success of the comparison models, a new program needs to be written with an easy user interface. The model should allow us to compare the water, energy, and time for any dyeing systems.

Information regarding the formulas used to build the mathematical models and spreadsheets can be requested from the author.

APPENDIX

10. APPENDIX

1. Natural Colorant Procedure
2. Direct Dye Procedure
3. Fiber Reactive (95°C) Procedure
4. Fiber Reactive (60°C) Procedure
5. Raw Data and Details for Calculation of Steam Consumption for Natural Colorants
6. Raw Data and Details for Calculation of Steam Consumption for Dyeings at 95°C
7. Raw Data and Details for Calculation of Steam Consumption for Dyeings at 60°C
8. Raw Data for Effluent Testing
9. Raw Data from HueMetrix for Direct Dye, Osage Orange
10. Calculations for % Exhaustion for Direct Dye, Osage Orange
11. Raw Data from HueMetrix for Direct Dye, Madder Root
12. Calculations for % Exhaustion for Direct Dye, Madder Root
13. Raw Data from HueMetrix for Direct Dye, Black Walnut
14. Calculations for % Exhaustion for Direct Dye, Black Walnut
15. Raw Data from HueMetrix for MCT 95°C, Osage Orange
16. Calculations for % Exhaustion for MCT 95°C, Osage Orange
17. Raw Data from HueMetrix for MCT 95°C, Madder Root
18. Calculations for % Exhaustion for MCT 95°C, Madder Root
19. Raw Data from HueMetrix for MCT 95°C, Black Walnut
20. Calculations for % Exhaustion for MCT 95°C, Black Walnut
21. Raw Data from HueMetrix for VS 60°C, Osage Orange
22. Calculations for % Exhaustion for VS 60°C, Osage Orange

Appendix 1. Natural Colorant Procedure

NATURAL COLOR ACTION	PRODUCT	AMOUNT (Liquor Ratio)	AMOUNT (% owg)	AMOUNT (g/l)	WEIGHT (grams)	VOLUME (liters)	RATE OF RISE °C/minute	TEMP (°C)	TIME (minutes)
Load fabric	cotton knit				1600				2
Add water		20				32		30	0.5
Add surfacatant	Rucowet FIN Conc		0.25		1.5			30	1
Heat							5.0	60	6
Hold								60	10
Sample bath									
Drain									1
Add water		20				32		30	0.5
Hold								30	5
Sample bath									
Drain									1
Extract (250 rpm)									3
Unload fabric									1
Fluff									0.5
Load fabric									1
Add water		10				16		30	0.5
Add tannins	Myroboloan Pdr		10		160.0			30	1
Hold								30	5
Heat							5.0	90	12
Hold								90	30
Sample bath									
Drain									
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Add mordant	Potassium Aluminum Sulfate		20		320.0			30	1
Hold								30	5
Heat							5.0	90	12
Hold								90	30
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Add Colorant	Natural Color		X					30	10
Hold								30	5
Heat							3.0	90	20
Hold								90	60
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Add scouring agent	Verolan NBO		0.5		8.0			30	1
Heat							5.0	85	11
Hold								85	5
Sample Bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Extract (250 rpm)									5
Unload fabric									1
TOTAL						224	Liters		290.5

Appendix 2. Direct Dye Procedure

DIRECT actual FINAL

ACTION	PRODUCT	AMOUNT (Liquor Ratio)	AMOUNT (% owg)	AMOUNT (g/l)	WEIGHED (grams)	VOLUME (liters)	RATE OF RISE (°C/minute)	TEMP (°C)	TIME (minutes
Load fabric	cotton knit				1600				2
Add water		20				32		30	0.5
Add surfacatant	Rucowet FIN Conc		0.25		1.5			30	1
Heat							5	60	6
Hold								60	10
Sample bath									
Drain									1
Add water		20				32		30	0.5
Hold								30	5
Sample bath									
Drain									1
Extract (250 rpm)									3
Unload fabric									1
Fluff									0.5
Load fabric									1
Add water		10				16		30	0.5
Add water treatment	Verolan NBO			0.5	10.0			30	1
Hold								30	3
Add DYE	Direct Dye		X					30	10
Hold								30	10
Heat							3	95	19
Hold								95	3
Add electrolyte	Sodium Sulfate			1/10 total				95	2
Hold								95	5
Add electrolyte	Sodium Sulfate			3/10 total				95	2
Hold								95	5
Add electrolyte	Sodium Sulfate			6/10 total				95	2
Hold								95	60
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Add scouring agent	NBO		0.5		8.0			30	1
Heat							5	85	11
Hold								85	5
Sample Bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Extract (250 rpm)									5
Unload fabric									1
TOTAL						160	Liters		206.5

Appendix 3. Fiber Reactive Dye (95°C) Procedure

95°C reactive final

ACTION	PRODUCT	AMOUNT (Liquor Ratio)	AMOUNT (% owg)	AMOUNT (g/l)	WEIGHED (grams)	VOLUME (liters)	RATE OF RISE (°C/minute)	TEMP (°C)	TIME (minutes)
Load fabric	cotton knit				1600				2
Add water		20				32		30	0.5
Add surfacatant	Rucowet FIN Conc		0.25		1.5			30	1
Heat							5	60	6
Hold								60	10
Sample bath									
Drain									1
Add water		20				32		30	0.5
Hold								30	5
Sample bath									
Drain									1
Extract (250 rpm)									3
Unload fabric									1
Fluff									0.5
Load fabric									1
Add water		10				16		30	0.5
Add water treatment	Verolan NBO			0.5	10.0			30	1
Add electrolyte	Sodium Sulfate			x					5
Hold								30	3
Add DYE	60°C reactive		X					30	10
Hold								30	10
Heat							3	95	19
Hold								95	3
Add alkali	Soda Ash			1/10 total				95	2
Hold								95	5
Add alkali	Soda Ash			3/10 total				95	2
Hold								95	5
Add alkali	Soda Ash			6/10 total				95	2
Hold								95	60
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Add scouring agent	NBO		0.5		8.0			30	1
Heat							5	85	11
Hold								85	5
Sample Bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Extract (250 rpm)									5
Unload fabric									1
TOTAL						160	Liters		211.5

Appendix 4. Fiber Reactive Dye (60°C) Procedure

60°C reactive actual FINAL

ACTION	PRODUCT	AMOUNT (Liquor Ratio)	AMOUNT (% owg)	AMOUNT (g/l)	WEIGHED (grams)	VOLUME (liters)	RATE OF RISE (°C/minute)	TEMP (°C)	TIME (minutes)
Load fabric	cotton knit				1600				2
Add water		20				32		30	0.5
Add surfacatant	Rucowet FIN Conc		0.25		1.5			30	1
Heat							5	60	6
Hold								60	10
Sample bath									
Drain									1
Add water		20				32		30	0.5
Hold								30	5
Sample bath									
Drain									1
Extract (250 rpm)									3
Unload fabric									1
Fluff									0.5
Load fabric									1
Add water		10				16		30	0.5
Add water treatment	Verolan NBO			0.5	10.0			30	1
Add electrolyte	Sodium Sulfate			x					5
Hold								30	3
Add DYE	60°C reactive		X					30	10
Hold								30	10
Heat							3	60	10
Hold								60	3
Add alkali	Soda Ash			1/10 total				60	2
Hold								60	5
Add alkali	Soda Ash			3/10 total				60	2
Hold								60	5
Add alkali	Soda Ash			6/10 total				60	2
Hold								60	60
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Add scouring agent	NBO		0.5		8.0			30	1
Heat							5	85	11
Hold								85	5
Sample Bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Add water		10				16		30	0.5
Hold								30	5
Sample bath									
Drain									1
Extract (250 rpm)									5
Unload fabric									1
TOTAL						160	Liters		202.5

Appendix 5. Data and Calculations for Steam Consumption for Natural Colorants.

	Cp	Loss @ (°C/min)	30C	40C	60C	85C	90C	95C
water	4.19							
fabric	1.31		0	0.05	0.275	0.625	0.825	0.975

	Time (min)	Fresh Water kg	Fresh Water Temp	Fabric kg	C	Previous Water kg	C	T final			kJ
Bath 1	10	32	30	1.6	30.0	0		60.0	Qw	4022.4	
									Qf	62.9	
									Qm	387.2	
										Bath 1	4472.4
Bath 2	5	32	30	1.6	60.0	4	60.0	34.5			
Bath 2-3		16	30	1.6	34.5	4	34.5	31.2			
Bath 3	30	16	30	1.6	31.2	4	31.2	90.0	Qw	4928.4	
									Qf	123.3	
									Qm	2240.0	
										Bath 3	7291.6
Bath 4	5	16	30	1.6	90.0	4	90.0	45.6			
Bath 4-5		16	30	1.6	45.6	4	45.6	34.0			
Bath 5	30	16	30	1.6	34.0	4	34.0	90.0	Qw	4690.0	
									Qf	117.3	
									Qm	2240.0	
										Bath 5	7047.3
Bath 6	5	16	30	1.6	90.0	4	90.0	45.6			
Bath 6-7		16	30	1.6	45.6	4	45.6	34.0			
Bath 7	60	16	30	1.6	34.0	4	34.0	90.0	Qw	5596.7	
									Qf	117.3	
									Qm	3393.9	
										Bath 7	9107.9
Bath 8	5	16	30	1.6	90.0	4	90.0	45.6			
Bath 9	5	16	30	1.6	45.6	4	45.6	34.0			
Bath 9-10		16	30	1.6	34.0	4	34.0	31.0			
Bath 10	5	16	30	1.6	31.0	4	31.0	85.0	Qw	4521.4	
									Qf	113.2	
									Qm	282.8	
										Bath 10	4917.4
Bath 11	5	16	30	1.6	85.0	4	85.0	44.3			
Bath 12	5	16	30	1.6	44.3	4	44.3	33.7			
										Total kJ	32836.7

Appendix 6. Data and Calculations for Steam Consumption for Dyeings at 95°C.

	Cp	Loss @ (°C/min)	30C	40C	60C	85C	90C	95C
water	4.19		0	0.05	0.275	0.625	0.825	0.975
fabric	1.31							

	Time (min)	Fresh Water kg	Fresh Water Temp	Fabric kg	C	Previous Water kg	C	T final			kJ
Bath 1	10	32	30	1.6	30.0	0		60.0	Qw	4022.4	
									Qf	62.9	
									Qm	387.2	
										Bath 1	4472.4
Bath 2	5	32	30	1.6	60.0	4	60.0	34.5			
Bath 2-3		16	30	1.6	34.5	4	34.5	31.2			
Bath 3	75	16	30	1.6	31.2	4	31.2	95.0	Qw	5347.4	
									Qf	133.7	
									Qm	6618.1	
										Bath 3	12099.2
Bath 4		16	30	1.6	95.0	4	95.0	46.9			
Bath 5		16	30	1.6	46.9	4	46.9	34.4			
Bath 5-6		16	30	1.6	34.4	4	34.4	31.1			
Bath 6	5	16	30	1.6	31.1	4	31.1	85.0	Qw	5386.7	
									Qf	112.9	
									Qr	282.8	
										Bath 6	5782.5
Bath 7		16	30	1.6	85.0	4	85.0	44.3			
Bath 8		16	30	1.6	44.3	4	44.3	33.7			
										Total kJ	22354.1

Appendix 7. Data and Calculations for Steam Consumption for Dyeings at 60°C.

	Cp
water	4.19
fabric	1.31

Loss @ (°C/min)	30C	40C	60C	85C	90C	95C
	0	0.05	0.275	0.625	0.825	0.975

	Time (min)	Fresh Water kg	Fresh Water Temp	Fabric kg	C	Previous Water kg	C	T final			kJ
Bath 1	10	32	30	1.6	30.0	0		60.0	Qw	4022.4	
									Qf	62.9	
									Qm	387.2	
										Bath 1	4472.4
Bath 2	5	32	30	1.6	60.0	4	60.0	34.5			
Bath 2-3		16	30	1.6	34.5	4	34.5	31.2			
Bath 3	75	16	30	1.6	31.2	4	31.2	60.0	Qw	2414.4	
									Qf	60.4	
									Qm	1866.6	
										Bath 3	4341.4
Bath 4		16	30	1.6	60.0	4	60.0	37.8			
Bath 5		16	30	1.6	37.8	4	37.8	32.0			
Bath 5-6		16	30	1.6	32.0	4	32.0	30.5			
Bath 6	5	16	30	1.6	30.5	4	30.5	85.0	Qw	5449.8	
									Qf	114.2	
									Qr	282.8	
										Bath 6	5846.8
Bath 7		16	30	1.6	85.0	4	85.0	44.3			
Bath 8		16	30	1.6	44.1	4	44.1	33.6			
										Total kJ	14660.7

Appendix 8. Raw Data from Effluent Testing

		NAT.OO	NAT.MR	NAT.BW	DFMCP.BW.428	MCT.BW.430
mg/L	**TOC**	507	484	950	21	70
mgO2/L	**COD**	1645	1550	2796	210	390
mg/L	**TDS**	2366	2308	3112	8880	9640
	pH	3.21	4.94	4.17	9.48	10.46
		Direct.BW.444	**Poly.BW.427**	**VS.BW.441**	**Bi.BW.429**	
mg/L	**TOC**	253	35	21	23	
mgO2/L	**COD**	<100	200	133	215	
mg/L	**TDS**	2360	15900	13700	12700	
	pH	8.25	10.21	10.48	10.62	

Appendix 9. Raw Data from HueMetrix for Direct Dye, Osage Orange

RAW DATA (g/L) D.OO.446

	Solophenyl Yellow SE		Solophenyl Red 3BL		Dyrite Blue FG 400%				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	-0.0010		0.0010		0.0020				
water	-0.0010	-0.0010	0.0010	0.0010	0.0020	0.0020		0.0020	
	-0.0010		0.0010		0.0020				
	0.0100		0.0020		0.0020				
final cold rinse	0.0100	0.0100	0.0020	0.0017	0.0030	0.0027	0.0143		0.0123
	0.0100		0.0010		0.0030				
	0.0000		0.0000		0.0030				
water	0.0000	0.0000	0.0020	0.0010	0.0030	0.0030		0.0040	
	0.0000		0.0010		0.0030				
	0.0350		0.0030		0.0030				
third cold rinse	0.0410	0.0377	0.0020	0.0023	0.0040	0.0037	0.0437		0.0397
	0.0370		0.0020		0.0040				
	-0.0010		0.0010		0.0020				
water	0.0000	-0.0003	0.0020	0.0013	0.0030	0.0023		0.0033	
	0.0000		0.0010		0.0020				
	0.1190		0.0040		0.0060				
hot soap	0.1080	0.1100	0.0050	0.0043	0.0050	0.0053	0.1197		0.1163
	0.1030		0.0040		0.0050				
	0.0000		0.0010		0.0030				
water	0.0000	0.0007	0.0010	0.0013	0.0020	0.0027		0.0047	
	0.0020		0.0020		0.0030				
	0.0460		0.0030		0.0040				
second cold rinse	0.0430	0.0457	0.0030	0.0030	0.0030	0.0037	0.0523		0.0477
	0.0480		0.0030		0.0040				
	-0.0010		0.0010		0.0020				
water	0.0000	-0.0010	0.0010	0.0010	0.0030	0.0023		0.0023	
	-0.0020		0.0010		0.0020				
	0.0630		0.0040		0.0040				
first cold rinse	0.0610	0.0640	0.0040	0.0037	0.0040	0.0043	0.0720		0.0697
	0.0680		0.0030		0.0050				
	0.0010		0.0010		0.0030				
water	-0.0020	-0.0007	0.0020	0.0013	0.0030	0.0030		0.0037	
	-0.0010		0.0010		0.0030				
	0.0950		0.0090		0.0070				
dyebath drain	0.0820	0.0883	0.0080	0.0087	0.0070	0.0067	0.1037		0.1000
	0.0880		0.0090		0.0060				
	0.0010		0.0010		0.0020				
water	0.0010	0.0007	0.0010	0.0013	0.0030	0.0027		0.0047	
	0.0000		0.0020		0.0030				

Appendix 10. Calculations for % Exhaustion for Direct Dye, Osage Orange

DIRECT_OO_446

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	1.6	10.67	0.4	0	12.67
Cold Rinse 1	0.1115	10.9306	0.0279	1.6	12.67
Cold Rinse 2	0.7616	10.0065	0.1904	1.7115	12.67
Hot Soap	1.8624	7.8696	0.4656	2.4731	12.67
Cold Rinse 3	0.6352	7.5405	0.1588	4.3355	12.67
Cold Rinse 4	0.2214	7.4533	0.0246	4.9707	12.67

Dye on fabric (g)	7.4779	59.02	% of total dye
Dye discharged (g)	5.1921	40.98	% of total dye

Appendix 11. Raw Data from HueMetrix for Direct Dye, Madder Root

RAW DATA (g/L) D.MR.445

	Solophenyl Yellow SE		Solophenyl Red 3BL		Dyrite Blue FG 400%				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	-0.0020		0.0000		0.0010				
water	-0.0010	-0.0010	0.0010	0.0007	0.0020	0.0017		0.0013	
	0.0000		0.0010		0.0020				
	0.0020		0.0040		0.0020				
final cold rinse	0.0030	0.0027	0.0050	0.0047	0.0020	0.0023	0.0097		0.0083
	0.0030		0.0050		0.0030				
	0.0000		0.0010		0.0030				
water	0.0010	0.0007	0.0010	0.0010	0.0020	0.0023		0.0040	
	0.0010		0.0010		0.0020				
	0.0110		0.0140		0.0030				
third cold rinse	0.0100	0.0113	0.0120	0.0140	0.0030	0.0030	0.0283		0.0243
	0.0130		0.0160		0.0030				
	0.0010		0.0010		0.0020				
water	-0.0010	0.0003	0.0010	0.0010	0.0020	0.0020		0.0033	
	0.0010		0.0010		0.0020				
	0.0380		0.0440		0.0050				
hot soap	0.0410	0.0413	0.0490	0.0483	0.0050	0.0053	0.0950		0.0917
	0.0450		0.0520		0.0060				
	0.0000		0.0010		0.0020				
water	-0.0010	-0.0003	0.0010	0.0010	0.0020	0.0020		0.0027	
	0.0000		0.0010		0.0020				
	0.0100		0.0120		0.0030				
second cold rinse	0.0100	0.0103	0.0120	0.0120	0.0030	0.0030	0.0253		0.0227
	0.0110		0.0120		0.0030				
	0.0000		0.0010		0.0020				
water	-0.0010	0.0003	0.0010	0.0007	0.0020	0.0023		0.0033	
	0.0020		0.0000		0.0030				
	0.0110		0.0130		0.0040				
first cold rinse	0.0090	0.0103	0.0140	0.0133	0.0040	0.0037	0.0273		0.0240
	0.0110		0.0130		0.0030				
	-0.0010		0.0010		0.0020				
water	-0.0010	-0.0007	0.0010	0.0010	0.0020	0.0020		0.0023	
	0.0000		0.0010		0.0020				
	0.0150		0.0210		0.0050				
dyebath drain	0.0150	0.0143	0.0230	0.0213	0.0060	0.0057	0.0413		0.0390
	0.0130		0.0200		0.0060				
	0.0000		0.0010		0.0030				
water	-0.0010	-0.0003	0.0010	0.0010	0.0020	0.0027		0.0033	
	0.0000		0.0010		0.0030				

Appendix 12. Calculations for % Exhaustion for Direct Dye, Madder Root

DIRECT_MR_445

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	0.624	8.84	0.156	0	9.62
Cold Rinse 1	0.015	8.9773	0.0037	0.624	9.62
Cold Rinse 2	0.3616	8.529	0.0904	0.639	9.62
Hot Soap	1.4672	6.7854	0.3668	1.0006	9.62
Cold Rinse 3	0.3888	6.6662	0.0972	2.4678	9.62
Cold Rinse 4	0.1512	6.5954	0.0168	2.8566	9.62

Dye on fabric (g)	6.6122	68.73	% of total dye
Dye discharged (g)	3.0078	31.27	% of total dye

Appendix 13. Raw Data from HueMetrix for Direct Dye, Black Walnut

RAW DATA (g/L) D.BW.444

	Solophenyl Yellow SE		Solophenyl Red 3BL		Dyrite Blue FG 400%				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	0.0000		0.0010		0.0020				
water	-0.0010	-0.0003	0.0010	0.0010	0.0020	0.0020		0.0027	
	0.0000		0.0010		0.0020				
	0.0020		0.0010		0.0030				
final cold rinse	0.0010	0.0010	0.0010	0.0010	0.0020	0.0023	0.0043		0.0017
	0.0000		0.0010		0.0020				
	0.0000		0.0010		0.0020				
water	0.0000	-0.0003	0.0010	0.0010	0.0020	0.0020		0.0027	
	-0.0010		0.0010		0.0020				
	0.0030		0.0030		0.0030				
third cold rinse	0.0060	0.0047	0.0030	0.0030	0.0030	0.0030	0.0107		0.0080
	0.0050		0.0030		0.0030				
	0.0010		0.0000		0.0020				
water	-0.0010	-0.0003	0.0010	0.0007	0.0020	0.0020		0.0023	
	-0.0010		0.0010		0.0020				
	0.0120		0.0060		0.0050				
hot soap	0.0110	0.0117	0.0050	0.0057	0.0050	0.0050	0.0223		0.0200
	0.0120		0.0060		0.0050				
	-0.0010		0.0010		0.0030				
water	0.0000	-0.0003	0.0010	0.0010	0.0020	0.0027		0.0033	
	0.0000		0.0010		0.0030				
	0.0040		0.0030		0.0030				
second cold rinse	0.0030	0.0030	0.0030	0.0027	0.0030	0.0030	0.0087		0.0053
	0.0020		0.0020		0.0030				
	0.0010		0.0000		0.0020				
water	0.0010	0.0010	0.0010	0.0007	0.0020	0.0020		0.0037	
	0.0010		0.0010		0.0020				
	0.0030		0.0030		0.0040				
first cold rinse	0.0020	0.0023	0.0030	0.0030	0.0030	0.0037	0.0090		0.0053
	0.0020		0.0030		0.0040				
	0.0010		0.0010		0.0020				
water	0.0010	0.0010	0.0010	0.0010	0.0020	0.0020		0.0040	
	0.0010		0.0010		0.0020				
	0.0060		0.0060		0.0060				
dyebath drain	0.0080	0.0070	0.0060	0.0063	0.0060	0.0060	0.0193		0.0153
	0.0070		0.0070		0.0060				
	0.0010		0.0010		0.0030				
water	0.0000	0.0000	0.0010	0.0010	0.0020	0.0023		0.0033	
	-0.0010		0.0010		0.0020				

Appendix 14. Calculations for % Exhaustion for Direct Dye, Black Walnut

DIRECT_BW_444

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	0.2448	2.604	0.0612	0	2.91
Cold Rinse 1	0.0013	2.6636	0.0003	0.2448	2.91
Cold Rinse 2	0.0864	2.5559	0.0216	0.2461	2.91
Hot Soap	0.32	2.1775	0.08	0.3325	2.91
Cold Rinse 3	0.128	2.0975	0.032	0.6525	2.91
Cold Rinse 4	0.0288	2.0975	0.0032	0.7805	2.91

Dye on fabric (g)	2.1007	72.19	% of total dye
Dye discharged (g)	0.8093	27.81	% of total dye

Appendix 15. Raw Data from HueMetrix for MCT 95°C, Osage Orange

RAW DATA (g/L) X.OO.431

	Drimarene Yellow X-4RN		Drimarene Red X-6BN		Permabril Navy H-ER 150				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	-0.0060		0.0020		0.0010				
water	-0.0020	-0.0040	0.0020	0.0020	0.0020	0.0017		-0.0003	
	-0.0040		0.0020		0.0020				
	0.0040		0.0030		0.0030				
final cold rinse	0.0050	0.0040	0.0020	0.0030	0.0030	0.0027	0.0097		0.0100
	0.0030		0.0040		0.0020				
	-0.0020		0.0020		0.0020				
water	-0.0060	-0.0037	0.0020	0.0023	0.0010	0.0017		0.0003	
	-0.0030		0.0030		0.0020				
	0.0130		0.0040		0.0040				
third cold rinse	0.0150	0.0137	0.0030	0.0037	0.0040	0.0043	0.0217		0.0213
	0.0130		0.0040		0.0050				
	-0.0030		0.0020		0.0020				
water	-0.0020	-0.0030	0.0020	0.0023	0.0010	0.0017		0.0010	
	-0.0040		0.0030		0.0020				
	0.0500		0.0040		0.0080				
hot soap	0.0490	0.0497	0.0040	0.0040	0.0080	0.0080	0.0617		0.0607
	0.0500		0.0040		0.0080				
	-0.0040		0.0030		0.0020				
water	-0.0030	-0.0030	0.0020	0.0023	0.0020	0.0020		0.0013	
	-0.0020		0.0020		0.0020				
	0.0100		0.0050		0.0050				
second cold rinse	0.0070	0.0100	0.0040	0.0043	0.0050	0.0053	0.0197		0.0183
	0.0130		0.0040		0.0060				
	-0.0040		0.0020		0.0010				
water	-0.0040	-0.0040	0.0030	0.0023	0.0020	0.0017		0.0000	
	-0.0040		0.0020		0.0020				
	0.0180		0.0050		0.0050				
first cold rinse	0.0180	0.0187	0.0050	0.0050	0.0060	0.0053	0.0290		0.0290
	0.0200		0.0050		0.0050				
	-0.0020		0.0020		0.0020				
water	-0.0050	-0.0037	0.0020	0.0023	0.0000	0.0013		0.0000	
	-0.0040		0.0030		0.0020				
	0.0600		0.0120		0.0090				
dyebath drain	0.0590	0.0583	0.0120	0.0120	0.0090	0.0090	0.0793		0.0793
	0.0560		0.0120		0.0090				
	-0.0040		0.0020		0.0020				
water	-0.0040	-0.0047	0.0020	0.0023	0.0020	0.0017		-0.0007	
	-0.0060		0.0030		0.0010				

Appendix 16. Calculations for % Exhaustion for MCT 95°C, Osage Orange

X_OO_431

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	1.2688	13.464	0.3172	0	15.05
Cold Rinse 1	0.0368	13.7352	0.0092	1.2688	15.05
Cold Rinse 2	0.2944	13.3764	0.0736	1.3056	15.05
Hot Soap	0.9712	12.236	0.2428	1.6	15.05
Cold Rinse 3	0.3424	12.0508	0.0856	2.5712	15.05
Cold Rinse 4	0.18	11.9318	0.0246	2.9136	15.05

Dye on fabric (g)	11.9564	79.44	% of total dye
Dye discharged (g)	3.0936	20.56	% of total dye

Appendix 17. Raw Data from HueMetrix for MCT 95°C, Madder Root

RAW DATA (g/L) X.MR.432

	Drimarene Yellow X-4RN		Drimarene Red X-6BN		Permabril Navy H-ER 150				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	-0.0050		0.0020		0.0010				
water	-0.0060	-0.0047	0.0020	0.0020	0.0010	0.0010		-0.0017	
	-0.0030		0.0020		0.0010				
	0.0010		0.0030		0.0020				
final cold rinse	-0.0010	0.0007	0.0040	0.0040	0.0020	0.0030	0.0077		0.0093
	0.0020		0.0050		0.0050				
	-0.0010		0.0020		0.0020				
water	-0.0040	-0.0030	0.0030	0.0023	0.0020	0.0020		0.0013	
	-0.0040		0.0020		0.0020				
	0.0060		0.0070		0.0040				
third cold rinse	0.0060	0.0063	0.0070	0.0073	0.0040	0.0043	0.0180		0.0167
	0.0070		0.0080		0.0050				
	-0.0010		0.0030		0.0030				
water	-0.0030	-0.0023	0.0030	0.0030	0.0030	0.0027		0.0033	
	-0.0030		0.0030		0.0020				
	0.0250		0.0210		0.0080				
hot soap	0.0250	0.0253	0.0210	0.0210	0.0080	0.0080	0.0543		0.0510
	0.0260		0.0210		0.0080				
	-0.0010		0.0020		0.0020				
water	-0.0030	-0.0033	0.0020	0.0023	0.0010	0.0013		0.0003	
	-0.0060		0.0030		0.0010				
	0.0040		0.0110		0.0040				
second cold rinse	0.0070	0.0060	0.0110	0.0110	0.0050	0.0047	0.0217		0.0213
	0.0070		0.0110		0.0050				
	-0.0020		0.0020		0.0020				
water	-0.0040	-0.0027	0.0010	0.0020	0.0010	0.0017		0.0010	
	-0.0020		0.0030		0.0020				
	0.0100		0.0170		0.0050				
first cold rinse	0.0080	0.0083	0.0170	0.0170	0.0050	0.0047	0.0300		0.0290
	0.0070		0.0170		0.0040				
	-0.0040		0.0020		0.0010				
water	-0.0040	-0.0043	0.0030	0.0027	0.0010	0.0010		-0.0007	
	-0.0050		0.0030		0.0010				
	0.0280		0.0420		0.0080				
dyebath drain	0.0290	0.0300	0.0430	0.0427	0.0100	0.0093	0.0820		0.0827
	0.0330		0.0430		0.0100				
	-0.0030		0.0030		0.0010				
water	-0.0020	-0.0023	0.0020	0.0023	0.0020	0.0013		0.0013	
	-0.0020		0.0020		0.0010				

Appendix 18. Calculations for % Exhaustion for MCT 95°C, Madder Root

X_MR_432

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	1.3232	9.686	0.3308	0	11.34
Cold Rinse 1	0.0384	9.9688	0.0096	1.3232	11.34
Cold Rinse 2	0.3424	9.5504	0.0856	1.3616	11.34
Hot Soap	0.816	8.616	0.204	1.704	11.34
Cold Rinse 3	0.2672	8.486	0.0668	2.52	11.34
Cold Rinse 4	0.1692	8.3648	0.0188	2.7872	11.34

Dye on fabric (g)	8.3836	73.93	% of total dye
Dye discharged (g)	2.9564	26.07	% of total dye

Appendix 19. Raw Data from HueMetrix for MCT 95°C, Black Walnut

RAW DATA (g/L) X.BW.430

	Drimarene Yellow X-4RN		Drimarene Red X-6BN		Permabril Navy H-ER 150				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	0.0000		0.0010		0.0020				
water	-0.0030	-0.0017	0.0020	0.0017	0.0020	0.0020		0.0020	
	-0.0020		0.0020		0.0020				
	0.0010		0.0030		0.0020				
final cold rinse	0.0000	0.0010	0.0040	0.0033	0.0030	0.0027	0.0070		0.0050
	0.0020		0.0030		0.0030				
	-0.0020		0.0020		0.0020				
water	-0.0020	-0.0027	0.0020	0.0023	0.0020	0.0020		0.0017	
	-0.0040		0.0030		0.0020				
	0.0040		0.0040		0.0040				
third cold rinse	0.0070	0.0057	0.0040	0.0040	0.0050	0.0043	0.0140		0.0123
	0.0060		0.0040		0.0040				
	-0.0020		0.0020		0.0020				
water	-0.0050	-0.0030	0.0020	0.0020	0.0010	0.0013		0.0003	
	-0.0020		0.0020		0.0010				
	0.0190		0.0050		0.0070				
hot soap	0.0170	0.0177	0.0060	0.0057	0.0070	0.0067	0.0300		0.0297
	0.0170		0.0060		0.0060				
	-0.0050		0.0020		0.0000				
water	-0.0040	-0.0043	0.0030	0.0027	0.0020	0.0013		-0.0003	
	-0.0040		0.0030		0.0020				
	0.0060		0.0050		0.0050				
second cold rinse	0.0030	0.0047	0.0050	0.0047	0.0050	0.0047	0.0140		0.0143
	0.0050		0.0040		0.0040				
	-0.0050		0.0030		0.0010				
water	-0.0020	-0.0040	0.0020	0.0027	0.0020	0.0017		0.0003	
	-0.0050		0.0030		0.0020				
	0.0110		0.0060		0.0060				
first cold rinse	0.0100	0.0100	0.0060	0.0060	0.0060	0.0060	0.0220		0.0217
	0.0090		0.0060		0.0060				
	-0.0050		0.0030		0.0010				
water	-0.0010	-0.0023	0.0020	0.0027	0.0030	0.0020		0.0023	
	-0.0010		0.0030		0.0020				
	0.0690		0.0200		0.0300				
dyebath drain	0.0600	0.0640	0.0190	0.0193	0.0240	0.0267	0.1100		0.1077
	0.0630		0.0190		0.0260				
	-0.0030		0.0020		0.0020				
water	-0.0030	-0.0030	0.0020	0.0020	0.0010	0.0017		0.0007	
	-0.0030		0.0020		0.0020				

Appendix 20. Calculations for % Exhaustion for MCT 95°C, Black Walnut

X_BW_430ADJ

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	0.58	4.2052	0.1448	0	4.93
Cold Rinse 1	0.0126	4.3343	0.0031	0.58	4.93
Cold Rinse 2	0.2288	4.0514	0.0572	0.5926	4.93
Hot Soap	0.4752	3.5146	0.1188	0.8214	4.93
Cold Rinse 3	0.1968	3.3874	0.0492	1.2966	4.93
Cold Rinse 4	0.09	3.3366	0.01	1.4934	4.93

Dye on fabric (g)	3.3466	67.88	% of total dye
Dye discharged (g)	1.5834	32.12	% of total dye

Appendix 21. Raw Data from HueMetrix for VS 60°C, Osage Orange

RAW DATA (g/L) RGB.OO.440

	Remazol Gold. Yellow RGB		Remazol Red RGB		Remazol Navy RGB 150				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	-0.0010		0.0050		0.0000				
water	-0.0010	-0.0010	0.0050	0.0050	0.0000	0.0000		0.0040	
	-0.0010		0.0050		0.0000				
	0.0090		0.0060		0.0010				
final cold rinse	0.0120	0.0107	0.0060	0.0063	0.0010	0.0013	0.0183		0.0143
	0.0110		0.0070		0.0020				
	-0.0020		0.0040		0.0000				
water	0.0000	-0.0003	0.0050	0.0043	0.0000	0.0000		0.0040	
	0.0010		0.0040		0.0000				
	0.0260		0.0070		0.0010				
third cold rinse	0.0290	0.0277	0.0060	0.0067	0.0020	0.0013	0.0357		0.0317
	0.0280		0.0070		0.0010				
	0.0030		0.0050		0.0010				
water	0.0000	0.0013	0.0050	0.0050	0.0010	0.0007		0.0070	
	0.0010		0.0050		0.0000				
	0.0680		0.0080		0.0020				
hot soap	0.0730	0.0700	0.0090	0.0087	0.0020	0.0020	0.0807		0.0737
	0.0690		0.0090		0.0020				
	0.0020		0.0040		0.0000				
water	-0.0010	0.0010	0.0050	0.0047	0.0000	0.0000		0.0057	
	0.0020		0.0050		0.0000				
	0.0510		0.0060		0.0010				
second cold rinse	0.0570	0.0527	0.0060	0.0060	0.0010	0.0007	0.0593		0.0537
	0.0500		0.0060		0.0000				
	0.0010		0.0050		0.0000				
water	-0.0010	0.0007	0.0050	0.0047	0.0000	0.0003		0.0057	
	0.0020		0.0040		0.0010				
	0.1020		0.0050		0.0000				
first cold rinse	0.0980	0.1010	0.0050	0.0047	0.0000	0.0003	0.1060		0.1003
	0.1030		0.0040		0.0010				
	0.0010		0.0050		0.0010				
water	-0.0010	0.0003	0.0050	0.0047	0.0010	0.0007		0.0057	
	0.0010		0.0040		0.0000				
	0.2470		0.0050		0.0000				
dyebath drain	0.2680	0.2537	0.0050	0.0050	0.0010	0.0003	0.2590		0.2533
	0.2460		0.0050		0.0000				
	0.0030		0.0040		0.0000				
water	0.0010	0.0017	0.0050	0.0043	0.0000	0.0003		0.0063	
	0.0010		0.0040		0.0010				

Appendix 22. Calculations for % Exhaustion for VS 60°C, Osage Orange

VS_RGB_OO_440

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	4.0528	12.824	1.0132	0	17.89
Cold Rinse 1	0.4065	13.3291	0.1016	4.0528	17.89
Cold Rinse 2	0.8576	12.3587	0.2144	4.4593	17.89
Hot Soap	1.1792	11.0991	0.2948	5.3169	17.89
Cold Rinse 3	0.5072	10.7599	0.1268	6.4961	17.89
Cold Rinse 4	0.2574	10.6007	0.0286	7.0033	17.89

Dye on fabric (g)	10.6293	59.41	% of total dye
Dye discharged (g)	7.2607	40.59	% of total dye

Appendix 23. Raw Data from HueMetrix for VS 60°C, Madder Root

RAW DATA (g/L) RGB.MR.442

	Remazol Gold. Yellow RGB		Remazol Red RGB		Remazol Navy RGB 150				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	0.0000		0.0050		0.0000				
water	0.0000	0.0003	0.0050	0.0050	0.0010	0.0003		0.0057	
	0.0010		0.0050		0.0000				
	0.0080		0.0110		0.0010				
final cold rinse	0.0050	0.0067	0.0100	0.0103	0.0010	0.0010	0.0180		0.0123
	0.0070		0.0100		0.0010				
	0.0020		0.0050		0.0000				
water	0.0000	0.0003	0.0050	0.0050	0.0000	0.0003		0.0057	
	-0.0010		0.0050		0.0010				
	0.0180		0.0240		0.0020				
third cold rinse	0.0200	0.0190	0.0250	0.0247	0.0010	0.0017	0.0453		0.0397
	0.0190		0.0250		0.0020				
	0.0000		0.0050		0.0000				
water	0.0000	0.0003	0.0050	0.0047	0.0000	0.0000		0.0050	
	0.0010		0.0040		0.0000				
	0.0420		0.0580		0.0030				
hot soap	0.0390	0.0413	0.0570	0.0587	0.0030	0.0030	0.1030		0.0980
	0.0430		0.0610		0.0030				
	-0.0020		0.0060		0.0000				
water	-0.0020	-0.0020	0.0050	0.0057	0.0010	0.0003		0.0040	
	-0.0020		0.0060		0.0000				
	0.0280		0.0440		0.0020				
second cold rinse	0.0310	0.0290	0.0450	0.0437	0.0030	0.0023	0.0750		0.0710
	0.0280		0.0420		0.0020				
	0.0020		0.0040		0.0000				
water	-0.0010	0.0000	0.0050	0.0047	0.0010	0.0003		0.0050	
	-0.0010		0.0050		0.0000				
	0.0630		0.0680		0.0040				
first cold rinse	0.0640	0.0637	0.0700	0.0700	0.0040	0.0043	0.1380		0.1330
	0.0640		0.0720		0.0050				
	0.0010		0.0050		0.0010				
water	0.0000	0.0010	0.0050	0.0050	0.0000	0.0007		0.0067	
	0.0020		0.0050		0.0010				
	0.1320		0.1100		0.0080				
dyebath drain	0.1330	0.1290	0.1080	0.1067	0.0130	0.0087	0.2443		0.2377
	0.1220		0.1020		0.0050				
	0.0000		0.0050		0.0000				
water	0.0000	0.0007	0.0050	0.0047	0.0000	0.0000		0.0053	
	0.0020		0.0040		0.0000				

Appendix 24. Calculations for % Exhaustion for VS 60°C, Madder Root

VS_RGB_MR_442

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	3.8016	16.748	0.9504	0	21.50
Cold Rinse 1	0.5056	17.0664	0.1264	3.8016	21.50
Cold Rinse 2	1.136	15.7728	0.284	4.3072	21.50
Hot Soap	1.568	14.0968	0.392	5.4432	21.50
Cold Rinse 3	0.6336	13.6968	0.1584	7.0112	21.50
Cold Rinse 4	0.2214	13.6092	0.0246	7.6448	21.50

Dye on fabric (g)	13.6338	63.41	% of total dye
Dye discharged (g)	7.8662	36.59	% of total dye

Appendix 25. Raw Data from HueMetrix for VS 60°C, Black Walnut

RAW DATA (g/L) RGB.BW.441

	Remazol Gold. Yellow RGB		Remazol Red RGB		Remazol Navy RGB 150				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	0.0010		0.0040		0.0000				
water	0.0030	0.0013	0.0040	0.0043	0.0000	0.0000		0.0057	
	0.0000		0.0050		0.0000				
	0.0040		0.0060		0.0010				
final cold rinse	0.0040	0.0040	0.0050	0.0057	0.0010	0.0010	0.0107		0.0050
	0.0040		0.0060		0.0010				
	-0.0010		0.0050		0.0000				
water	0.0000	-0.0003	0.0050	0.0050	0.0000	0.0000		0.0047	
	0.0000		0.0050		0.0000				
	0.0090		0.0080		0.0010				
third cold rinse	0.0090	0.0090	0.0080	0.0080	0.0010	0.0010	0.0180		0.0133
	0.0090		0.0080		0.0010				
	0.0000		0.0050		0.0000				
water	0.0010	-0.0007	0.0050	0.0050	0.0000	0.0000		0.0043	
	-0.0030		0.0050		0.0000				
	0.0160		0.0110		0.0020				
hot soap	0.0150	0.0163	0.0130	0.0123	0.0020	0.0020	0.0307		0.0263
	0.0180		0.0130		0.0020				
	0.0010		0.0040		0.0000				
water	0.0000	0.0007	0.0050	0.0047	0.0010	0.0007		0.0060	
	0.0010		0.0050		0.0010				
	0.0110		0.0100		0.0010				
second cold rinse	0.0090	0.0103	0.0100	0.0097	0.0010	0.0010	0.0210		0.0150
	0.0110		0.0090		0.0010				
	0.0000		0.0050		0.0000				
water	0.0010	0.0000	0.0050	0.0047	0.0000	0.0000		0.0047	
	-0.0010		0.0040		0.0000				
	0.0190		0.0100		0.0010				
first cold rinse	0.0180	0.0193	0.0090	0.0100	0.0010	0.0010	0.0303		0.0257
	0.0210		0.0110		0.0010				
	0.0030		0.0040		0.0000				
water	0.0000	0.0013	0.0050	0.0047	0.0010	0.0003		0.0063	
	0.0010		0.0050		0.0000				
	0.0720		0.0200		0.0040				
dyebath drain	0.0770	0.0730	0.0190	0.0193	0.0030	0.0033	0.0957		0.0893
	0.0700		0.0190		0.0030				
	0.0000		0.0050		0.0000				
water	0.0010	0.0003	0.0050	0.0050	0.0010	0.0003		0.0057	
	0.0000		0.0050		0.0000				

Appendix 26. Calculations for % Exhaustion for VS 60°C, Black Walnut

VS_RGB_BW_441

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	1.4304	4.792	0.3576	0	6.58
Cold Rinse 1	0.0366	5.1038	0.0092	1.4304	6.58
Cold Rinse 2	0.24	4.813	0.06	1.467	6.58
Hot Soap	0.4224	4.345	0.1056	1.707	6.58
Cold Rinse 3	0.2128	4.1846	0.0532	2.1294	6.58
Cold Rinse 4	0.09	4.1378	0.01	2.3422	6.58

Dye on fabric (g)	4.1478	63.04	% of total dye
Dye discharged (g)	2.4322	36.96	% of total dye

Appendix 27. Raw Data from HueMetrix for DFMCP 60°C, Osage Orange

RAW DATA (g/L) K.OO.435

	Drimarene Yellow K-2R		Drimarene Red K-4BL		Drimarene Blue K-2RL				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	0.0000		0.0030		-0.0020				
water	0.0010	0.0007	0.0030	0.0030	0.0010	-0.0003		0.0033	
	0.0010		0.0030		0.0000				
	0.0120		0.0060		0.0020				
final cold rinse	0.0120	0.0113	0.0050	0.0057	0.0020	0.0020	0.0190		0.0113
	0.0100		0.0060		0.0020				
	0.0000		0.0030		0.0000				
water	0.0000	0.0000	0.0030	0.0030	0.0000	0.0003		0.0033	
	0.0000		0.0030		0.0010				
	0.0380		0.0100		0.0050				
third cold rinse	0.0400	0.0390	0.0100	0.0100	0.0050	0.0050	0.0540		0.0227
	0.0390		0.0100		0.0050				
	-0.0010		0.0030		0.0000				
water	-0.0010	0.0003	0.0030	0.0030	0.0000	0.0003		0.0037	
	0.0030		0.0030		0.0010				
	0.1130		0.0230		0.0100				
hot soap	0.1120	0.1127	0.0220	0.0220	0.0100	0.0100	0.1447		0.0583
	0.1130		0.0210		0.0100				
	0.0010		0.0030		-0.0010				
water	0.0020	0.0007	0.0030	0.0033	0.0010	0.0000		0.0040	
	-0.0010		0.0040		0.0000				
	0.0570		0.0190		0.0040				
second cold rinse	0.0580	0.0583	0.0150	0.0160	0.0040	0.0040	0.0783		0.0310
	0.0600		0.0140		0.0040				
	0.0030		0.0030		0.0000				
water	-0.0010	0.0010	0.0040	0.0033	0.0000	0.0000		0.0043	
	0.0010		0.0030		0.0000				
	0.0420		0.0150		0.0020				
first cold rinse	0.0420	0.0420	0.0130	0.0133	0.0020	0.0020	0.0573		0.0293
	0.0420		0.0120		0.0020				
	0.0010		0.0030		0.0000				
water	0.0020	0.0010	0.0030	0.0030	0.0010	0.0003		0.0043	
	0.0000		0.0030		0.0000				
	0.0720		0.0170		0.0010				
dyebath drain	0.0710	0.0720	0.0160	0.0163	0.0000	0.0003	0.0883		0.0697
	0.0730		0.0160		0.0000				
	0.0030		0.0030		0.0010				
water	0.0000	0.0013	0.0030	0.0030	0.0010	0.0007		0.0050	
	0.0010		0.0030		0.0000				

Appendix 28. Calculations for % Exhaustion for DFMCP 60°C, Osage Orange

K_OO_435

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	1.344	15.59	0.336	0	17.27
Cold Rinse 1	0.0712	15.837	0.0178	1.344	17.27
Cold Rinse 2	1.1888	14.3688	0.2972	1.4152	17.27
Hot Soap	2.256	11.846	0.564	2.604	17.27
Cold Rinse 3	0.8112	11.396	0.2028	4.86	17.27
Cold Rinse 4	0.2826	11.2916	0.0314	5.6712	17.28

Dye on fabric (g)	11.323	65.54	% of total dye
Dye discharged (g)	5.9538	34.46	% of total dye

Appendix 29. Raw Data from HueMetrix for DFMCP 60°C, Madder Root

RAW DATA (g/L) K.MR.436

	Drimarene Yellow K-2R		Drimarene Red K-4BL		Drimarene Blue K-2RL				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	0.0000		0.0030		-0.0010				
water	0.0000	0.0003	0.0040	0.0033	0.0010	0.0000		0.0037	
	0.0010		0.0030		0.0000				
	0.0060		0.0090		0.0020				
final cold rinse	0.0060	0.0063	0.0080	0.0083	0.0010	0.0013	0.0160		0.0123
	0.0070		0.0080		0.0010				
	0.0000		0.0020		0.0000				
water	-0.0010	-0.0003	0.0030	0.0030	0.0000	0.0003		0.0030	
	0.0000		0.0040		0.0010				
	0.0230		0.0220		0.0040				
third cold rinse	0.0210	0.0227	0.0220	0.0220	0.0040	0.0040	0.0487		0.0457
	0.0240		0.0220		0.0040				
	0.0010		0.0020		0.0000				
water	0.0010	0.0003	0.0030	0.0030	0.0000	0.0000		0.0033	
	-0.0010		0.0040		0.0000				
	0.0650		0.0600		0.0100				
hot soap	0.0660	0.0650	0.0600	0.0600	0.0080	0.0087	0.1337		0.1303
	0.0640		0.0600		0.0080				
	0.0000		0.0030		0.0000				
water	0.0000	0.0010	0.0030	0.0033	0.0000	0.0003		0.0047	
	0.0030		0.0040		0.0010				
	0.0210		0.0350		0.0010				
second cold rinse	0.0230	0.0223	0.0350	0.0350	0.0010	0.0017	0.0590		0.0543
	0.0230		0.0350		0.0030				
	-0.0020		0.0030		-0.0020				
water	0.0010	-0.0007	0.0030	0.0030	0.0000	-0.0013		0.0010	
	-0.0010		0.0030		-0.0020				
	0.0200		0.0450		0.0010				
first cold rinse	0.0220	0.0210	0.0450	0.0447	0.0020	0.0013	0.0670		0.0660
	0.0210		0.0440		0.0010				
	-0.0020		0.0030		0.0000				
water	0.0010	-0.0013	0.0030	0.0030	0.0000	0.0000		0.0017	
	-0.0030		0.0030		0.0000				
	0.0410		0.0690		0.0020				
dyebath drain	0.0420	0.0400	0.0690	0.0687	0.0020	0.0013	0.1100		0.1083
	0.0370		0.0680		0.0000				
	0.0030		0.0030		0.0010				
water	-0.0010	0.0007	0.0030	0.0030	0.0010	0.0007		0.0043	
	0.0000		0.0030		0.0000				

Appendix 30. Calculations for % Exhaustion for DFMCP 60°C, Madder Root

K_MR_436

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	1.7328	16.434	0.4332	0	18.60
Cold Rinse 1	0.1144	16.7242	0.0286	1.7328	18.60
Cold Rinse 2	0.8688	15.6686	0.2172	1.8472	18.60
Hot Soap	2.0864	13.276	0.5216	2.716	18.60
Cold Rinse 3	0.7312	12.8836	0.1828	4.8024	18.60
Cold Rinse 4	0.2214	12.8204	0.0246	5.5336	18.60

Dye on fabric (g)	12.845	69.06	% of total dye
Dye discharged (g)	5.755	30.94	% of total dye

Appendix 31. Raw Data from HueMetrix for DFMCP 60°C, Black Walnut

RAW DATA (g/L) K.BW.428

	Drimarene Yellow K-2R		Drimarene Red K-4BL		Drimarene Blue K-2RL				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	-0.0010		0.0030		-0.0020				
water	-0.0010	-0.0007	0.0030	0.0030	0.0000	-0.0007		0.0017	
	0.0000		0.0030		0.0000				
	0.0050		0.0050		0.0020				
final cold rinse	0.0060	0.0060	0.0050	0.0047	0.0030	0.0023	0.0130		0.0113
	0.0070		0.0040		0.0020				
	0.0000		0.0040		0.0010				
water	0.0020	0.0003	0.0040	0.0037	0.0010	0.0007		0.0047	
	-0.0010		0.0030		0.0000				
	0.0140		0.0080		0.0050				
third cold rinse	0.0140	0.0143	0.0080	0.0080	0.0050	0.0050	0.0273		0.0227
	0.0150		0.0080		0.0050				
	0.0000		0.0030		0.0000				
water	0.0020	0.0003	0.0030	0.0030	0.0010	0.0003		0.0037	
	-0.0010		0.0030		0.0000				
	0.0370		0.0150		0.0110				
hot soap	0.0370	0.0367	0.0140	0.0143	0.0110	0.0110	0.0620		0.0583
	0.0360		0.0140		0.0110				
	0.0000		0.0030		0.0000				
water	0.0020	0.0007	0.0030	0.0033	0.0010	0.0003		0.0043	
	0.0000		0.0040		0.0000				
	0.0170		0.0120		0.0060				
second cold rinse	0.0200	0.0177	0.0110	0.0117	0.0060	0.0060	0.0353		0.0310
	0.0160		0.0120		0.0060				
	0.0000		0.0030		0.0010				
water	0.0020	0.0017	0.0030	0.0030	0.0010	0.0013		0.0060	
	0.0030		0.0030		0.0020				
	0.0180		0.0130		0.0060				
first cold rinse	0.0170	0.0173	0.0130	0.0130	0.0050	0.0050	0.0353		0.0293
	0.0170		0.0130		0.0040				
	0.0000		0.0030		0.0010				
water	0.0000	0.0000	0.0040	0.0033	0.0010	0.0010		0.0043	
	0.0000		0.0030		0.0010				
	0.0370		0.0250		0.0110				
dyebath drain	0.0370	0.0373	0.0250	0.0253	0.0110	0.0113	0.0740		0.0697
	0.0380		0.0260		0.0120				
	-0.0010		0.0030		0.0000				
water	0.0010	-0.0007	0.0030	0.0033	0.0000	0.0000		0.0027	
	-0.0020		0.0040		0.0000				

Appendix 32. Calculations for % Exhaustion for DFMCP 60°C, Black Walnut

K_BW_428

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	1.1152	5.186	0.2788	0	6.58
Cold Rinse 1	0.0327	5.424	0.0082	1.1152	6.58
Cold Rinse 2	0.496	4.8121	0.124	1.1479	6.58
Hot Soap	0.9328	3.7701	0.2332	1.6439	6.58
Cold Rinse 3	0.3616	3.5513	0.0904	2.5767	6.58
Cold Rinse 4	0.2034	3.4157	0.0226	2.9383	6.58

Dye on fabric (g)	3.4383	52.25	% of total dye
Dye discharged (g)	3.1417	47.75	% of total dye

Appendix 33. Raw Data from HueMetrix for Bi-Functional 60°C, Osage Orange

RAW DATA (g/L) HFCL.OO.433

	Drimarene Yellow CL-2R		Drimarene Rubine CL-3BL		Drimarene Blue HF-RL				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	0.0070		0.0160		0.0020				
water	0.0070	0.0070	0.0150	0.0153	0.0020	0.0020		0.0243	
	0.0070		0.0150		0.0020				
	0.0170		0.0160		0.0050				
final cold rinse	0.0170	0.0163	0.0160	0.0163	0.0050	0.0050	0.0377		0.0133
	0.0150		0.0170		0.0050				
	0.0050		0.0160		0.0020				
water	0.0080	0.0067	0.0160	0.0157	0.0020	0.0023		0.0247	
	0.0070		0.0150		0.0030				
	0.0360		0.0190		0.0080				
third cold rinse	0.0370	0.0357	0.0180	0.0180	0.0100	0.0087	0.0623		0.0377
	0.0340		0.0170		0.0080				
	0.0070		0.0150		0.0020				
water	0.0070	0.0067	0.0160	0.0157	0.0020	0.0020		0.0243	
	0.0060		0.0160		0.0020				
	0.0890		0.0220		0.0220				
hot soap	0.0920	0.0897	0.0210	0.0213	0.0220	0.0217	0.1327		0.1083
	0.0880		0.0210		0.0210				
	0.0100		0.0150		0.0030				
water	0.0080	0.0090	0.0150	0.0150	0.0030	0.0030		0.0270	
	0.0090		0.0150		0.0030				
	0.0390		0.0180		0.0110				
second cold rinse	0.0410	0.0393	0.0170	0.0180	0.0110	0.0113	0.0687		0.0417
	0.0380		0.0190		0.0120				
	0.0050		0.0150		0.0020				
water	0.0060	0.0063	0.0150	0.0150	0.0030	0.0023		0.0237	
	0.0080		0.0150		0.0020				
	0.0400		0.0180		0.0080				
first cold rinse	0.0430	0.0403	0.0180	0.0183	0.0090	0.0083	0.0670		0.0433
	0.0380		0.0190		0.0080				
	0.0050		0.0160		0.0020				
water	0.0050	0.0063	0.0160	0.0160	0.0020	0.0023		0.0247	
	0.0090		0.0160		0.0030				
	0.0630		0.0210		0.0060				
dyebath drain	0.0670	0.0650	0.0210	0.0210	0.0070	0.0063	0.0923		0.0677
	0.0650		0.0210		0.0060				
	0.0050		0.0160		0.0020				
water	0.0070	0.0067	0.0160	0.0157	0.0020	0.0020		0.0243	
	0.0080		0.0150		0.0020				

Appendix 34. Calculations for % Exhaustion for Bi-Functional 60°C, Osage Orange

HFCL_OO_433

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	1.0816	14.468	0.2704	0	15.82
Cold Rinse 1	0.0468	14.6799	0.0117	1.0816	15.82
Cold Rinse 2	0.6672	13.8576	0.1668	1.1284	15.82
Hot Soap	1.7344	11.8564	0.4336	1.7956	15.82
Cold Rinse 3	0.6016	11.538	0.1504	3.53	15.82
Cold Rinse 4	0.2412	11.4204	0.0268	4.1316	15.82

Dye on fabric (g)	11.4472	72.36	% of total dye
Dye discharged (g)	4.3728	27.64	% of total dye

Appendix 35. Raw Data from HueMetrix for Bi-Functional 60°C, Madder Root

RAW DATA (g/L) HFCL.MR.434

	Drimarene Yellow CL-2R		Drimarene Rubine CL-3BL		Drimarene Blue HF-RL				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	0.0050		0.0160		0.0020				
water	0.0050	0.0053	0.0160	0.0160	0.0020	0.0020		0.0233	
	0.0060		0.0160		0.0020				
	0.0130		0.0200		0.0040				
final cold rinse	0.0110	0.0123	0.0190	0.0193	0.0040	0.0040	0.0357		0.0123
	0.0130		0.0190		0.0040				
	0.0060		0.0150		0.0010				
water	0.0090	0.0073	0.0160	0.0157	0.0040	0.0023		0.0253	
	0.0070		0.0160		0.0020				
	0.0240		0.0250		0.0050				
third cold rinse	0.0230	0.0237	0.0260	0.0257	0.0050	0.0053	0.0547		0.0293
	0.0240		0.0260		0.0060				
	0.0070		0.0160		0.0020				
water	0.0050	0.0060	0.0160	0.0157	0.0020	0.0013		0.0230	
	0.0060		0.0150		0.0000				
	0.0490		0.0410		0.0100				
hot soap	0.0500	0.0497	0.0410	0.0413	0.0100	0.0097	0.1007		0.0777
	0.0500		0.0420		0.0090				
	0.0060		0.0160		0.0020				
water	0.0080	0.0063	0.0150	0.0160	0.0020	0.0017		0.0240	
	0.0050		0.0170		0.0010				
	0.0210		0.0300		0.0030				
second cold rinse	0.0230	0.0217	0.0280	0.0293	0.0030	0.0033	0.0543		0.0303
	0.0210		0.0300		0.0040				
	0.0090		0.0150		0.0030				
water	0.0100	0.0087	0.0150	0.0153	0.0030	0.0027		0.0267	
	0.0070		0.0160		0.0020				
	0.0230		0.0320		0.0040				
first cold rinse	0.0250	0.0240	0.0320	0.0320	0.0040	0.0040	0.0600		0.0333
	0.0240		0.0320		0.0040				
	0.0070		0.0160		0.0020				
water	0.0040	0.0057	0.0150	0.0153	0.0010	0.0017		0.0227	
	0.0060		0.0150		0.0020				
	0.0410		0.0510		0.0040				
dyebath drain	0.0430	0.0417	0.0520	0.0517	0.0060	0.0050	0.0983		0.0757
	0.0410		0.0520		0.0050				
	0.0090		0.0170		0.0050				
water	0.0090	0.0083	0.0150	0.0160	0.0020	0.0030		0.0273	
	0.0070		0.0160		0.0020				

Appendix 36. Calculations for % Exhaustion for Bi-Functional 60°C, Madder Root

HFCL_MR_434

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	1.2096	14.008	0.3024	0	15.52
Cold Rinse 1	0.0403	14.2601	0.0101	1.2096	15.52
Cold Rinse 2	0.4848	13.6641	0.1212	1.2499	15.52
Hot Soap	1.2432	12.2313	0.3108	1.7347	15.52
Cold Rinse 3	0.4704	11.9541	0.1176	2.9779	15.52
Cold Rinse 4	0.2232	11.8237	0.0248	3.4483	15.52

Dye on fabric (g)	11.8485	76.34	% of total dye
Dye discharged (g)	3.6715	23.66	% of total dye

Appendix 37. Raw Data from HueMetrix for Bi-Functional 60°C, Black Walnut

RAW DATA (g/L) HFCL.BW.429

	Drimarene Yellow CL-2R		Drimarene Rubine CL-3BL		Drimarene Blue HF-RL				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	0.0080		0.0160		0.0020				
water	0.0080	0.0073	0.0150	0.0157	0.0020	0.0020		0.0250	
	0.0060		0.0160		0.0020				
	0.0110		0.0160		0.0040				
final cold rinse	0.0090	0.0097	0.0160	0.0160	0.0030	0.0033	0.0290		0.0040
	0.0090		0.0160		0.0030				
	0.0060		0.0160		0.0020				
water	0.0070	0.0067	0.0150	0.0157	0.0020	0.0023		0.0247	
	0.0070		0.0160		0.0030				
	0.0140		0.0170		0.0060				
third cold rinse	0.0140	0.0143	0.0170	0.0173	0.0060	0.0063	0.0380		0.0133
	0.0150		0.0180		0.0070				
	0.0070		0.0160		0.0030				
water	0.0060	0.0067	0.0160	0.0160	0.0020	0.0023		0.0250	
	0.0070		0.0160		0.0020				
	0.0270		0.0190		0.0140				
hot soap	0.0230	0.0260	0.0190	0.0190	0.0140	0.0140	0.0590		0.0340
	0.0280		0.0190		0.0140				
	0.0070		0.0150		0.0020				
water	0.0080	0.0073	0.0160	0.0157	0.0030	0.0027		0.0257	
	0.0070		0.0160		0.0030				
	0.0140		0.0180		0.0070				
second cold rinse	0.0160	0.0163	0.0170	0.0173	0.0080	0.0077	0.0413		0.0157
	0.0190		0.0170		0.0080				
	0.0040		0.0160		0.0020				
water	0.0080	0.0057	0.0160	0.0160	0.0030	0.0023		0.0240	
	0.0050		0.0160		0.0020				
	0.0210		0.0180		0.0080				
first cold rinse	0.0200	0.0190	0.0180	0.0177	0.0090	0.0080	0.0447		0.0207
	0.0160		0.0170		0.0070				
	0.0080		0.0160		0.0030				
water	0.0070	0.0083	0.0150	0.0153	0.0020	0.0027		0.0263	
	0.0100		0.0150		0.0030				
	0.0340		0.0210		0.0120				
dyebath drain	0.0340	0.0337	0.0210	0.0210	0.0130	0.0127	0.0673		0.0410
	0.0330		0.0210		0.0130				
	0.0080		0.0150		0.0020				
water	0.0080	0.0077	0.0150	0.0153	0.0020	0.0023		0.0253	
	0.0070		0.0160		0.0030				

Appendix 38. Calculations for % Exhaustion for Bi-Functional 60°C, Black Walnut

HFCL_BW_429

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	0.656	3.93	0.164	0	4.75
Cold Rinse 1	0.0136	4.077	0.0034	0.656	4.75
Cold Rinse 2	0.2496	3.7684	0.0624	0.6696	4.75
Hot Soap	0.544	3.1508	0.136	0.9192	4.75
Cold Rinse 3	0.2128	3.0208	0.0532	1.4632	4.75
Cold Rinse 4	0.072	2.994	0.008	1.676	4.75

Dye on fabric (g)	3.002	63.20	% of total dye
Dye discharged (g)	1.748	36.80	% of total dye

Appendix 39. Raw Data from HueMetrix for Poly-Functional 60°C, Osage Orange

RAW DATA (g/L) SE.OO.438

	Avitera Yellow SE RAW	average	Avitera Red SE RAW	average	Avitera Light Blue SE RAW	average	total dye	total water	adjusted dye
	0.0030		0.0000		0.0010				
water	0.0030	0.0023	0.0010	0.0007	0.0020	0.0020		0.0050	
	0.0010		0.0010		0.0030				
	0.0060		0.0010		0.0010				
final cold rinse	0.0060	0.0063	0.0010	0.0010	0.0020	0.0017	0.0090		0.0040
	0.0070		0.0010		0.0020				
	0.0020		0.0010		0.0020				
water	0.0010	0.0010	0.0020	0.0017	0.0010	0.0010		0.0037	
	0.0000		0.0020		0.0000				
	0.0170		0.0020		0.0040				
third cold rinse	0.0140	0.0157	0.0020	0.0020	0.0030	0.0037	0.0213		0.0177
	0.0160		0.0020		0.0040				
	0.0010		0.0020		0.0010				
water	0.0010	0.0003	0.0020	0.0017	0.0010	0.0010		0.0030	
	-0.0010		0.0010		0.0010				
	0.0340		0.0020		0.0060				
hot soap	0.0360	0.0347	0.0020	0.0020	0.0070	0.0063	0.0430		0.0400
	0.0340		0.0020		0.0060				
	-0.0010		0.0020		0.0000				
water	0.0000	-0.0003	0.0020	0.0020	0.0000	0.0003		0.0020	
	0.0000		0.0020		0.0010				
	0.0190		0.0020		0.0040				
second cold rinse	0.0190	0.0190	0.0020	0.0020	0.0050	0.0047	0.0257		0.0237
	0.0190		0.0020		0.0050				
	0.0000		0.0020		0.0000				
water	0.0010	0.0003	0.0020	0.0020	0.0000	0.0000		0.0023	
	0.0000		0.0020		0.0000				
	0.0300		0.0030		0.0050				
first cold rinse	0.0300	0.0300	0.0030	0.0030	0.0050	0.0050	0.0380		0.0357
	0.0300		0.0030		0.0050				
	0.0030		0.0010		0.0010				
water	0.0010	0.0013	0.0010	0.0013	0.0010	0.0007		0.0033	
	0.0000		0.0020		0.0000				
	0.0710		0.0060		0.0100				
dyebath drain	0.0720	0.0707	0.0060	0.0057	0.0110	0.0097	0.0860		0.0827
	0.0690		0.0050		0.0080				
	0.0010		0.0020		0.0010				
water	0.0010	0.0017	0.0020	0.0017	0.0020	0.0013		0.0047	
	0.0030		0.0010		0.0010				

Appendix 40. Calculations for % Exhaustion for Poly-Functional 60°C, Osage Orange

SE_OO_438

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	1.3232	9.256	0.3308	0	10.91
Cold Rinse 1	0.0472	9.5278	0.0118	1.3232	10.91
Cold Rinse 2	0.3792	9.0656	0.0948	1.3704	10.91
Hot Soap	0.64	8.3604	0.16	1.7496	10.91
Cold Rinse 3	0.2816	8.1684	0.0704	2.3896	10.91
Cold Rinse 4	0.072	8.1588	0.008	2.6712	10.91

Dye on fabric (g)	8.1668	74.86	% of total dye
Dye discharged (g)	2.7432	25.14	% of total dye

Appendix 41. Raw Data from HueMetrix for Poly-Functional 60°C, Madder Root

RAW DATA (g/L) SE.MR.439

	Avitera Yellow SE RAW	average	Avitera Red SE RAW	average	Avitera Light Blue SE RAW	average	total dye	total water	adjusted dye
	0.0000		0.0020		0.0000				
water	0.0000	0.0003	0.0020	0.0020	0.0000	0.0003		0.0027	
	0.0010		0.0020		0.0010				
	0.0040		0.0020		0.0020				
final cold rinse	0.0030	0.0040	0.0030	0.0023	0.0020	0.0020	0.0083		0.0057
	0.0050		0.0020		0.0020				
	0.0010		0.0020		0.0010				
water	0.0010	0.0013	0.0010	0.0017	0.0000	0.0007		0.0037	
	0.0020		0.0020		0.0010				
	0.0070		0.0040		0.0030				
third cold rinse	0.0090	0.0080	0.0030	0.0033	0.0040	0.0033	0.0147		0.0110
	0.0080		0.0030		0.0030				
	0.0000		0.0020		0.0010				
water	0.0000	0.0000	0.0020	0.0020	0.0000	0.0003		0.0023	
	0.0000		0.0020		0.0000				
	0.0140		0.0060		0.0050				
hot soap	0.0140	0.0140	0.0050	0.0057	0.0050	0.0050	0.0247		0.0223
	0.0140		0.0060		0.0050				
	0.0000		0.0020		0.0010				
water	-0.0010	-0.0003	0.0020	0.0020	0.0000	0.0007		0.0023	
	0.0000		0.0020		0.0010				
	0.0100		0.0060		0.0050				
second cold rinse	0.0100	0.0100	0.0060	0.0060	0.0040	0.0043	0.0203		0.0180
	0.0100		0.0060		0.0040				
	0.0000		0.0020		0.0010				
water	0.0000	0.0007	0.0020	0.0017	0.0000	0.0007		0.0030	
	0.0020		0.0010		0.0010				
	0.0130		0.0080		0.0050				
first cold rinse	0.0130	0.0137	0.0080	0.0080	0.0050	0.0050	0.0267		0.0237
	0.0150		0.0080		0.0050				
	0.0010		0.0010		0.0020				
water	0.0010	0.0003	0.0020	0.0017	0.0020	0.0013		0.0033	
	-0.0010		0.0020		0.0000				
	0.0330		0.0170		0.0090				
dyebath drain	0.0350	0.0343	0.0170	0.0170	0.0100	0.0093	0.0607		0.0573
	0.0350		0.0170		0.0090				
	0.0010		0.0010		0.0010				
water	0.0010	0.0010	0.0010	0.0010	0.0010	0.0010		0.0030	
	0.0010		0.0010		0.0010				

Appendix 42. Calculations for % Exhaustion for Poly-Functional 60°C, Madder Root

SE_MR_439

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	0.9184	12.002	0.2296	0	13.15
Cold Rinse 1	0.0218	12.2044	0.0054	0.9184	13.15
Cold Rinse 2	0.288	11.8498	0.072	0.9402	13.15
Hot Soap	0.3584	11.4738	0.0896	1.2282	13.15
Cold Rinse 3	0.176	11.3434	0.044	1.5866	13.15
Cold Rinse 4	0.1008	11.2754	0.0112	1.7626	13.15

Dye on fabric (g)	11.2866	85.83	% of total dye
Dye discharged (g)	1.8634	14.17	% of total dye

Appendix 43. Raw Data from HueMetrix for Poly-Functional 60°C, Black Walnut

RAW DATA (g/L) SE.BW.437

	Avitera Yellow SE		Avitera Red SE		Avitera Light Blue SE				
	RAW	average	RAW	average	RAW	average	total dye	total water	adjusted dye
	0.0010		0.0020		0.0020				
water	0.0000	0.0000	0.0020	0.0020	0.0000	0.0007		0.0027	
	-0.0010		0.0020		0.0000				
	0.0030		0.0020		0.0010				
final cold rinse	0.0020	0.0023	0.0020	0.0020	0.0020	0.0013	0.0057		0.0030
	0.0020		0.0020		0.0010				
	0.0000		0.0020		-0.0010				
water	0.0010	0.0003	0.0010	0.0017	0.0000	0.0003		0.0023	
	0.0000		0.0020		0.0020				
	0.0070		0.0030		0.0040				
third cold rinse	0.0060	0.0067	0.0030	0.0027	0.0030	0.0037	0.0130		0.0107
	0.0070		0.0020		0.0040				
	0.0030		0.0020		0.0010				
water	0.0000	0.0010	0.0020	0.0020	0.0010	0.0007		0.0037	
	0.0000		0.0020		0.0000				
	0.0130		0.0030		0.0080				
hot soap	0.0130	0.0137	0.0030	0.0033	0.0070	0.0077	0.0247		0.0210
	0.0150		0.0040		0.0080				
	0.0010		0.0020		0.0000				
water	0.0000	0.0007	0.0020	0.0017	0.0010	0.0007		0.0030	
	0.0010		0.0010		0.0010				
	0.0070		0.0030		0.0050				
second cold rinse	0.0080	0.0077	0.0020	0.0027	0.0060	0.0053	0.0157		0.0127
	0.0080		0.0030		0.0050				
	0.0000		0.0020		0.0000				
water	0.0010	-0.0003	0.0020	0.0020	0.0000	0.0000		0.0017	
	-0.0020		0.0020		0.0000				
	0.0080		0.0020		0.0050				
first cold rinse	0.0090	0.0083	0.0030	0.0027	0.0050	0.0047	0.0157		0.0140
	0.0080		0.0030		0.0040				
	0.0000		0.0020		0.0000				
water	0.0010	0.0007	0.0020	0.0020	0.0010	0.0003		0.0030	
	0.0010		0.0020		0.0000				
	0.0170		0.0040		0.0090				
dyebath drain	0.0170	0.0167	0.0050	0.0047	0.0090	0.0087	0.0300		0.0270
	0.0160		0.0050		0.0080				
	0.0000		0.0020		0.0010				
water	0.0020	0.0010	0.0010	0.0017	0.0000	0.0003		0.0030	
	0.0010		0.0020		0.0000				

Appendix 44. Calculations for % Exhaustion for Poly-Functional 60°C, Black Walnut

SE_BW_437

g of dye at the end of:	Discharged	In machine On Fabric	In machine Retained	Discharged in Previous Drains	Total
Dyebath	0.432	3.76	0.108	0	4.3
Cold Rinse 1	0.006	3.8604	0.0015	0.432	4.2999
Cold Rinse 2	0.2032	3.608	0.0508	0.438	4.3
Hot Soap	0.336	3.2388	0.084	0.6412	4.3
Cold Rinse 3	0.1712	3.1088	0.0428	0.9772	4.3
Cold Rinse 4	0.054	3.0916	0.006	1.1484	4.3

Dye on fabric (g)	3.0976	72.04	% of total dye
Dye discharged (g)	1.2024	27.96	% of total dye

Appendix 45. Fastness Data

	NAT.OO	NAT.MR	NAT.BW	DFMCP.BW.428	MCT.BW.430	Bi.BW.429	VS.BW.441	Poly.BW.427	Direct.BW.444
AATCC 61-2013	90.5	98	104	107	106.5	105.5	106	106	106.5
2A wash									
Change	2	3	3	4.5	4.5	4	4.5	4.5	4.5
Stain									
Acetate	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Cotton	4	4	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Nylon	3.5	4	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Polyester	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Acrylic	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Wool	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
AATCC 8-2013									
Crock									
Wet	4	4	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Dry	2.5	2.5	3	4.5	4.5	4.5	4.5	4.5	4.5
AATCC 15-2013									
Perspiration									
Change	4.5	4.5	4.5	4.5	4.5	4	4.5	4.5	4.5
Stain									
Acetate	4	4	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Cotton	4	4	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Nylon	3	3.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Polyester	4	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Acrylic	4	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Wool	3.5	4	4.5	4.5	4.5	4.5	4.5	4.5	4.5
AATCC 107-2013									
Water									
Change	4.5	4.5	4.5	4.5	4.5	4	4.5	4	4.5
Stain									
Acetate	4	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Cotton	3.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Nylon	2.5	4	4	4.5	4.5	4.5	4.5	4.5	4
Polyester	4	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Acrylic	4	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Wool	3.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
AATCC 16.3-2014									
20 Hr Light	3.5	2.5	4	3.5	3	3.5	2.5	3	3.5

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