Evaluation of extraction and dye methodologies of European Madder (*Rubia tinctorum*)

By
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This thesis is dedicated to
my mother and father; who have
always supported me, my brother Sean,
my best bud Kristina; who does not understand why I do this kind of stuff,
to my good friends Sheila, Megan, Amanda, Tiffany and Clark;
who have encouraged me to pursue my dreams.

ABSTRACT

Attention is being focussed on the use of natural dyes, in part due to environmental concerns. Natural dyes have been dismissed as being unpredictable and highly variable, although these dyes have not been tested to determine if this belief is valid. The purpose of this study was to assess and promote the use of natural colorants within the context of sustainable development. Commercial use of dye from renewable resources is hampered by the lack of knowledge concerning such colorants. Adoption of the use of naturally sources colorants is further hampered by the claims concerning their inconsistency and unpredictability. Eleven methods for extracting and dyeing with European Madder (*Rubia tinctorum*) were selected, converted to metric and standardised. The methods were repeated ten times, with five specimens per replication. The specimens were measured with a Hunterlab Tristimulus Colorimeter in CIELAB. The data from each method was then used to calculate the mean colour difference for each method. The *ATTCC test method (173-1998) CMC: Calculations of small color differences for acceptability* was used to calculate ΔE cmc for each measurement. The tolerance limit where set at $\Delta E_{cmc} \leq 1.2$ at a 95% confidence level. For each method, there was a null hypothesis that there would be no statistical difference between the colour of each of the specimens within that method. It was found that six of the eleven methods produced results that failed to reject the null hypotheses: which means the six methods produced consistent results. This, in turn, means with standardised Practices natural colorants can be successfully utilised for the dyeing of textile and like materials.

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INTRODUCTION

Madder (Rubia tinctorum) root is a natural dye that has been used since 3000 BC (Cannon & Cannon, 1994) to impart a red hue on textiles and other materials. Like other natural dyes, it was displaced from the commercial textile dye market by the advent of synthetic dyes in the latter half of the 19th century. Yet madder root dyes continue to be used today by craft and hobbyist dyers, and are used in high quality artist pigments (Green, 1995).

One of the perceived inadequacies of natural dyes is the reliability of the dyestuffs because the quality of the products varied and therefore the results were not reliable. "No two batches of natural dyes are ever exactly alike in hue and strength" (Hatch, 1993, p.432). The seeming unpredictability of the dyestuffs, combined with higher prices compared to synthetic dyestuffs (Green, 1995; Schaefer, 1941) meant that natural dyestuffs were eliminated from most commercial production. Since the development of synthetic dyes, dyers and those involved with the development of dye equipment and technology have generated methods to better control the variables in synthetic dye baths. These technological advancements have not been applied to natural dyestuffs.

The consistency of any dye bath is dependent on how well the variables are controlled; "many variables must be controlled in order to produce high quality dyeings. Variables in dyeing may be of several types including substrate [the material that is being coloured] variations, variation in chemicals (including water), variations in preparation of the substrate for dyeing and procedural variations" (Perkins, 1996, p.106).

The research completed in this work looked at procedural variations from numerous Madder root dye recipes. The dye recipes are not consistent, having varying processing times, maximum temperatures, extraction lengths, dyeing lengths, fibre/colorant ratios, and additives, which may affect dye-bath pH. Some methods also combine extraction and dyeing while others retain them as separate steps. If the extraction and dyeing methods are tested by using current standardised textile science equipment (and the scientific method of testing); the effect that the extraction and dyeing methods have on the hues produced by madder root could be determined.

Complex problems have more than one solution, therefore it is not just finding a solution but finding a solution that solves the problem without creating more problems. Sustainable development is a system of thinking that looks at problems not from a single perspective but from many standpoints to eliminate problems, find new solutions, and to ultimately solve the problem. Sustainable development is defined as a "process of change in which the exploitation of resources, the direction of investments, the orientation of technological development and institutional change are all in harmony, and enhance both current and future potential to meet human needs and aspirations" (World Commission on Economic Development, 1989, p. 46).

Textiles are a major component of the human world. They are used for practical purposes, for decorative purposes, or for combined practical and decorative purposes. The dyeing of textiles is a type of textile decoration, and currently the commercial fashion and textile sectors use synthetic dyes almost exclusively. Synthetic dyes are created from non-renewable resources such as petrol-chemicals, and are not recoverable from textiles with current technology. Therefore, even if the fibre is recyclable there is still a loss of material from a finite source - the dyestuff. Natural dyes, especially plant dyes, are made from renewable resources. Many of the original synthetic dyes were simply copies of naturally occurring colorants and are still used today (Dean, 1999). An increase in the utilisation of natural dyes in the fashion, textile and apparel sectors would be a change in the exploitation of resources, shifting away from finite resources to renewable resources.

The textile industry is a major polluter (International Environment Consultants ltd., 1982), and although the industry is looking for solutions, most solutions are retrofit or alter an existing process (often called end pipe solutions) because they come at the end of a process. Natural dyes can also cause pollution if used improperly, but recently there have been developments in the field of natural dye technology which have looked at development of methods of dyeing with low to no pollution (Morsy, El-Hamaky & El-Ebissy, 2001). Research, which explores the use of natural dyes, and how to achieve consistent hues from dyestuff serves to support research that is looking for entrance pipe solutions or redesigning the process to eliminate the pollution.

Technology that comes from research into non-polluting dyeing may encourage the textile, apparel and fashion sectors to invest time, money and energy into furthering this research as well as change the way they develop their products. "Although most attention has been paid to modifying synthetic dyeing processes the need to realise the importance and explore the technology of natural dyes is arguably more urgent. Any effort to reassess and promote the use of natural dyes deserves encouragement" (Ali, 1993). The institutions such as chemical companies and research centres that comprise the dye industry were developed based on the belief that one cannot achieve consistent colour from natural dyes. Any changes in technology that dispels this belief should change how these institutions act. Changes in practices may occur within an institution because the institution is resolved to change or changes are made to the regulations which govern these institutions. As non-renewable resources become more expensive, changes in the practices of the dye industry become increasingly important thus ensuring the stability of the dye industry and the environment.

Purpose of Study and Statement of Problem

The aim of this study is to record and explore through scientific testing methods the colour produced by madder root on a natural fibre. A review of literature identified a variety of extraction and dye methods for Rubia tinctorum. This study chose 11 methods of extracting and dyeing with Rubia tinctorum to ascertain the variation within the methods and record the effluent produced by the methods.

Justification

Since there is very little recent scientific data on natural dyes in general and specifically the colour produced by Rubia tinctorum, a record of the colours beyond the inaccurate names (such as garnet, lacquer and deep red) was needed. Natural dyes have not been extensively studied with modern scientific techniques since the synthetic dyes were introduced in the textile sector. Yet there have been many technical innovations in the field of textile and dye production since that time. These technical advances have typically not been applied to natural dyes. It is important to evaluate these dyes with current technology and techniques to determine if they can meet commercial standards of the textile and apparel sectors.

Synthetic colorants are created from non-renewable resources (i.e. petrochemicals) while, in general, natural dyes are generated from renewable resources such as plants and animals. The use of renewable resources for dyes represents a shift in the exploitation of resources towards a more sustainable system, which will ensure that there are resources for future generations. A shift to a renewable resource will have economic benefits as it will provide alternative crops that have a high value and quality (Angelini, Pistelli, Belloni, Bertoli and Panconesi, 1997).

Objectives

The main objective of the research was to ascertain if the fabric coloration resulting from the selected dye extraction and dye application methods are consistent. Eleven methods were studied and the resulting hues recorded. The data collected from the experiments were used to determine if the methods are consistent and if different methods produce similar hues. Since the data were collected with a Hunterlab Tristimulus Colorimeter in CIELAB, the calculation of colour difference from the specimens was made using the ATTCC test method

(173-1998) CMC: Calculations of small color differences for acceptability. The second objective of the study was to record pH and colour of effluent produced.

Research Questions and Hypotheses

The research questions for this study were the following: What type of effluent is produced (in terms of pH and colour) from each method? Does each dye method produce a consistent dyeing? The results from the effluent are exploratory, so they will not be compared to a standard. For consistency of the dyeings, the statistical significance is determined by the tolerance limits of 1.2 ΔE_{cmc}. If a method falls completely in this limit, the method was considered consistent. The hypotheses and null hypotheses for the consistency of the dyeings are as follows:

H_1 Hypotheses 1 - There will be a statistically significant difference between the colour for each specimen within dye method one or $H_1 = \mu_1 > 1.2$.

Ho_1 Null Hypotheses 1 - There will be no statistically significant difference between the colour for each specimen within dye method one or $Ho_1 = \mu_1 \leq 1.2$.

H_2 Hypotheses 2 - There will be a statistically significant difference between the colour for each specimen within dye method two or $H_2 = \mu_2 > 1.2$.

Ho_2 Null Hypotheses 2 - There will be no statistically significant difference between the colour for each specimen within dye method two or $Ho_2 = \mu_2 \leq 1.2$.

H_3 Hypotheses 3 - There will be a statistically significant difference between the colour for each specimen within dye method three or $H_3 = \mu_3 > 1.2$.

Ho_3 Null Hypotheses 3 - There will be no statistically significant difference between the colour for each specimen within dye method three or $Ho_3 = \mu_3 \leq 1.2$.

H_4 Hypotheses 4 - There will be a statistically significant difference between the colour for each specimen within dye method four or $H_4=\mu_4>1.2$.

Ho_4 Null Hypotheses 4 - There will be no statistically significant difference between the colour for each specimen within dye method four or $Ho_4=\mu_4\leq1.2$.

H_5 Hypotheses 5 - there will be a statistically significant difference between the colour for each specimen within dye method five or $H_5=\mu_5>1.2$.

Ho_5 Null Hypotheses 5 - There will be no statistically significant difference between the colour for each specimen within dye method five or $Ho_5=\mu_5\leq1.2$.

H_6 Hypotheses 6 - there will be a statistically significant difference between the colour for each specimen within dye method six or $H_6=\mu_6>1.2$

Ho_6 Null Hypotheses 6 - There will be no statistically significant difference between the colour for each specimen within dye method six or $Ho_6=\mu_6\leq1.2$.

H_7 Hypotheses 7 - There will be a statistically significant difference between the colour for each specimen within dye method seven or $H_7=\mu_7>1.2$

Ho_7 Null Hypotheses 7 - There will be no statistically significant difference between the colour for each specimen within dye method seven or $Ho_7=\mu_7\leq1.2$.

H_8 Hypotheses 8 - There will be a statistically significant difference between the colour for each specimen within dye method eight or $H_8=\mu_8>1.2$

Ho_8 Null Hypotheses 8 - There will be no statistically significant difference between the colour for each specimen within dye method eight or $Ho_8=\mu_8\leq1.2$.

H_9 Hypotheses 9 - There will be a statistically significant difference between the colour for each specimen within dye method nine or $H_9=\mu_9>1.2$.

Ho_9 Null Hypotheses 9 - There will be no statistically significant difference between the colour for each specimen within dye method nine or $Ho_9=\mu_9\leq1.2$.

H_{10} Hypotheses 10 - There will be a statistically significant difference between the colour for each specimen within dye method ten or $H_{10}=\mu_{10}>1.2$.

Ho_{10} Null Hypotheses 10 - There will be no statistically significant difference between the colour for each specimen within dye method ten or $Ho_{10}=\mu_{10}\leq1.2$.

H_{11} Hypotheses 11 - There will be a statistically significant difference between the colour for each specimen within dye method eleven or $H_{11}=\mu_{11}>1.2$.

Ho_{11} Null Hypotheses 11 - There will be no statistically significant difference between the colour for each specimen within dye method eleven or $Ho_{11}=\mu_{11}\leq1.2$.

Operational definitions

Consistent Dyeing	A dyed specimen have statistically low variability, the $\Delta Ecmc \leq 1.2$ units
Colour	The visual sensation produced by light of different wavelengths throughout the visible region of the spectrum. Measured by the hue, value and chroma.
Colorant	Material from which the dyestuffs are extracted for this study ground dried madder (Rubia tinctorum) root
Chroma	The brightness or vividness or purity of a colour.

Complex colours	Colours made up of more than one dyestuff (often the dyestuffs individually produce different hues). Complex colour would therefore have a low chroma because it is not made of a single hue but of many.
Dye application	The process of heat over a given time to water, dyestuff and fabric which attaches the dye molecules to the fabric via bonding or other means.
Dye Liquor	The pigments, dyestuff in water and other ancillary chemicals.
Dye method	Process by which the dyestuff is extracted and applied to the fabric.
Dyestuff	Chemical compound either synthetically produced or extracted from natural material that imparts colour attaches to the fibre and imparts colour.
Extraction	The method that moves the pigments/dyestuffs from the dyestuff to the dye liquor.
Hard Water	A solution of water that has a hardness between 800-1000 ppm with a pH of 7.3 created from distilled water, 480 mg/L of Sodium dicarbonate, 600 mg/L of Calcium Sulfate dihydrate, 600 mg/L of Magnesium Sulfate Anhydrous and 20 mg/L Potassium Chloride.

Hue	The attribution of colour by virtue of which is discernible as red, yellow, green, blue, purple and so forth, the common name of a colour, the A and B measurement in a LAB Reading.
Levelling agent	A surface-active agent that aids in uniform colour on textiles which is a non-ionic organic compound. Glauber's salt or sodium sulphate decahydrate ($Na_2SO_4 \bullet 10\ H_20$) was used in one method for this purpose.
Madder	European madder plant Rubia tinctorum.
Mordant	A chemical compound, which aids the fibre's ability to bond with dyestuffs. In the research done here, the mordant was aluminium potassium sulphate $AlK(SO_4)_2 \bullet 12\ H_20$.
Non heat extraction	The colorant is allowed to soak in water at room temperature.
Non ionic Wetting Agent	Solution of .5 g/litre of triton.
pH	The acidity or alkalinity of a solution, expressed numerically as the logarithm to the base 10 of the reciprocal of the activity of hydrogen ions in moles per litre. Seven is neutral, less than 7 is an acid and greater than 7 is an alkaline.

Room temperature	21 - 23°C.
Simmering point	Water temperature reaches 95°C.
Soaking time	Non heat extraction of dyes from the colorant.
Specimens	Test fabric cut into 8.7cm diameter circles.
Test fabric	Unbleached, plain woven, 100% wool flannel fabric (style 522 from Test Fabrics Ltd.)
Value	Is the whiteness to darkness, the L in a LAB reading.
Wetting agent	A non-ionic agent that aids in the wetting of the fabric by breaking the surface tension of the water allowing the water to penetrate the fabric rapidly

Limitations and Delimitations

The research was limited to methods that were published in English over the past 100 years. Published methods in other languages were not considered. Methods that may have been used historically but not published were unavailable for this study.

This research was delimited to methods which use only European madder (Rubia tinctorum) as the colorant. The methods selected are for wool that has been pre-mordanted with alum ($AlK(SO_4)_2 \bullet 12\ H_20$). Only methods that specified the resulting hue will be red were considered. The methods only used madder either as whole, ground and/or powdered roots as the colorant but may call for chemicals that alter the pH. The methods specified the length of the extraction and dyeing and also specified the maximum temperature. The methods are to take less than 36 hours to complete.

Assumptions

The assumptions for the experiment are that the use of the wetting agent will not adversely effect the dyeing process but will instead result in more even dyeing. The pulverised madder will be mixed to a homogeneous consistency, and will contain the same amount of pigment throughout.

LITERATURE REVIEW

Sustainable Development

Sustainable development is a relatively new field, the term has been used since the Cocoyoc declaration on environment and development in the early 1970's (Redclift, 1987). It was debuted to the world as a concept with the release of the World Commission on Environment and Development (WCED) report on development problems around the globe called Our Common Future in 1987. The most often quoted and most general definition of sustainable development originated from Our Common Future and reads: "Sustainable development is development that meets the needs of the present without comprising the ability of future generations to meet their own needs" (WCED, 1987, p. 43). Within the report there are other less-used definitions of sustainable development including the following: "process of change in which the exploitation of resources, the direction of investments, the orientation of technological development and institutional change are all in harmony and enhance both current and future potential to meet human needs and aspirations" (WCED, 1987, p. 46).

As in the WCED definitions, Moffatt (1996) and Brown, Hanson, Liverman, & Merideth (1987) focus their definitions on humans and their well being. Moffatt (1996) writes that sustainable development "is development that is likely to achieve lasting satisfaction of human needs and improvement of the quality of human life" (p. 27). While Brown et al. (1987) view "sustainable development as a development strategy, which manages all assets - natural and human resources, as well as financial and physical assets - for increasing wealth and well being" (p. 716).

Sustainable development is seen "balancing social, economic and ecological goals" (Farrell & Hart, 1998, p.6). This definition is in line with the sustainable development models presented by Khan (1995) and Serageldin (1992). In the balanced approach models, sustainable development is comprised of three types of sustainability: ecological, economic and social. There is interplay between the components of sustainable development; each component cannot be studied separately from the other components.

Textiles are integral part of every aspect of human life and they are found in all currently human populated regions of the world. They are a part of our economic, social and ecological structures and therefore cannot be studied separately from sustainable development. How we use and create textiles is essential to establishing practices that meet the objectives of sustainable development.

Use of renewable resource for dyestuffs

Renewable resources are living resources (such as animals and plants) which have a process of replenishment according to a biological process. Additionally some non-living resources such as solar energy are considered renewable. Non-renewable resources are resources for which there are no processes of replenishment or the process of replenishment is so low that they are effectively non-renewable. Classic examples of non-renewable resources are fossil fuels and non-energy minerals. (Field & Olewiler, 1995)

Sustainable economic activity requires utilising renewable resources within the capacity of the systems to regenerate (Peet, 1992) or using non-renewable resources at a rate equal to the creation of renewable substitutes (Daly, 1991). There are global non-renewable resources such as the atmosphere that do not have renewable substitutes and therefore must be maintained (Mikesell, 1992). It is not only what resources we use, but how we use them that determines the sustainability of the process.

Generally, economic activities create waste products. For economic activity to be sustainable this waste must be either recycled for reuse in another economic process or absorbed by the natural environment (Mikesell, 1992). Not all wastes can be recycled and therefore some waste must be absorbed (Mikesell, 1992). "Sustainable waste management involves minimising waste production and managing waste disposal within the receiving capacities of environmental sinks, and it includes avoiding the production of hazardous substances" (Peet, 1992 p .210). When the quantity of waste is higher than the capacity of the ecosystem to absorb it, the waste then becomes pollution.

McDonough and Braungart (1998) look at waste as part of a cycle. Organic materials can be broken down in the ecosystem (given appropriate criteria) and returned to the natural organic cycle, while non-organic materials strain the ecosystem, as the ecosystem's ability to absorb and break down these materials is limited at best. Based on these premises of organic and non-organic materials, McDonough and Braungart (1998) want all wastes to become food so that they do not become pollution. Organic wastes or 'biological nutrients' should be designed for use and disposal. Then they are returned to the organic cycle to be consumed by micro-organisms and other forms of life to be cycled again, while non-organic, or what McDonough and Braungart (1998) call technical nutrients, should be designed to go back into the technical/industrial cycle.

This means for a product (either biological or technical) to be recycled, it must be designed from the beginning to be cycled. Current recycling efforts are more expensive than necessary because the way we are recycling is to reuse the material after it has become degraded requiring even more energy and resources to upgrade the material so it can be used again. McDonough and Braungart (1998) feel that materials can be designed which can be recycled without additional inputs or even can be 'upcycled' which is their term for returning material to industrial systems with improved quality.

Glover and Pierce (1993) argued that it is not justified to use natural dyes, especially natural dyes which they see as wasteful or expensive to produce (cochineal was their example), when one can synthetically produce similar dyes. Natural dyes that are sourced from plants, insects or molluscs are renewable resources. If these resources were utilised within the capacity of the ecosystems to regenerate them and the wastes of the production and processing were managed appropriately, natural plant and animal dyes can be a sustainable option for the coloration of textiles and like products. Not only is the use of natural dyes seen as a benefit to the ecological of the planet but also a benefit to the economic sustainability of the globe. "From an ecological viewpoint, the substitution of chemical dyes with natural products in textile dyeing may be feasible and may represent not only a strategy to reduce risk and pollution, but also an opportunity for new markets and new businesses which can develop from inclusion of ecology in trade policy" (Angelini et al. 1997, p. 310).

Ecological effects of synthetic dyes and natural dyes

The dyeing of fibres, yarns and fabric is a wet process of the textile industry and generates a significant quantity of liquid waste (International Environment Consultants ltd., 1982). Synthetic finishing effluent can contain toxic material especially from dyeing processes where metallic ions are used (United Nations Environmental Programme, 1994). Effluent from plants varies in quantity and quality depending not on the product or size of the plant but on the type of process, age of the plant and type of technology used (Chen, 1989). Each type of wet process produces it's own distinctive effluent. Effluents are effected by the fibre used, the natural impurities in the fibres, the chemicals used in the finishing and waste chemicals which are not part of the wet processing but are used in the plant, such as lubricants for machines (United Nations Environmental Programme, 1994). Wastewater from a wet processing plant is coloured, high in biochemical oxygen demand (BOD) materials, high in total suspended solid content (TSS), highly alkaline and hot (Chen, 1989), if untreated.

The BOD is the measurement of the rate of oxygen usage due to biological oxidation. The number represents the amount of oxygen a one-litre sample will consume in five days. Chemical Oxidation Demand (COD) is the amount of oxygen required to chemically oxidise organic materials in a liquid. The ratio between the BOD and the COD represents how difficult it is for the waste to biodegrade; ratios of 1:2 or 1:3 are considered to have good potential to degrade and most effluents are in this range. Wool scouring has a ratio of BOD to COD of 1:5 which means it is difficult to bio-degrade; this is augmented by the high levels of suspended solids, oil and grease in its waste water. While wool finishing is in the acceptable BOD / COD ratio, it has the highest chromium content at 4 mg/L (UNEP, 1994). The removal of large quantities of oxygen from waterways for biodegrading wastewater results in loss of plants and animals whose existence requires the oxygen dissolved in the water. Chromium is a highly carcinogenic substance requiring a level four handling from Material Safety Data Sheets since it may be fatal if absorbed through the skin (Material Safety Data Sheets 2000).

Through a series of treatment stages, textile-processing facilities can significantly reduce the amount and type of pollution produced and released. Facilities which have only primary treatment measures such as screening and neutralisation, release waste water which is still toxic to water life such as fish, yet, with secondary and tertiary treatment measures, many facilities can release waste water which is non-lethal and with no apparent colour. Regardless “not all dyes currently used can be degraded or removed with physical and chemical processes, and sometimes the degradation products are more toxic” (Abadulla, Robra, Gubitz, Silva and Cavaco-Paulo, 2000). The above mentioned treatment measures are endpipe solutions, but Chen (1989) and UNEP (1994) did suggest that different methods of application of dyes and other finishes which use less water and waste less chemicals be further investigated.

The use of natural dyes at the commercial level is increasing but Burdett (1996) stated that natural products are not necessarily environmental friendly. There are many natural materials that are dangerous, such as oxalic acid that is found in the leaves of rhubarb. Oxalic acid ($Na_2C_2O_4$) is poisonous if ingested and it is a natural product. Just because a product is from natural sources, or even a renewable resource, does not mean it will solve all the environmental ills of the dye industry. Burdett (1996) sees the role of the dye industry to maintain and promote the awareness of the underlying chemistry of environmental issues related to dye use. Yet his awareness seems to be based on the use of natural dyes in the same manner as they were used before the industrial revolution or in the same manner as synthetic dyes are used.

Burdett (1996) states that the extraction of the natural dyestuffs (by traditional methods) and the dyeing with natural dyestuffs are time consuming. His examples of time-consuming processes included 'Turkey red dyeing' with madder and the collection of dye from the bodies of female cochineal (insects from the family Dactylopius), from South America. He also cites the waste products from natural dyeing processes as potential pollution problems.

McDonough and Braungart (1998) look at wastes as part of a cycle and, if biodegradable, they are not pollution. Organic materials can be broken down in the ecosystem (given appropriate criteria) and returned to the natural organic cycle, while non-organic materials strain the ecosystem, as the ecosystem's ability to absorb and break down these materials is limited at best. Therefore, natural plant dye wastes, if cycled appropriately, will not become pollution but instead food for another process.

The second type of problem Burdett (1996) examines is how natural dyes bond to the fibres. Most classically applied natural dyes use metal ions or mordants. Generally, these metal ions are from tin, aluminium, iron, copper, or chromium (VI), and provide colour fastness and hue alterations. He estimated that the use of these mordants for natural dyes (in the United Kingdom) on a commercial scale would be 1000 times greater than the allowed metal contamination limits in dye exhausts (Burdett, 1996).

There is research with natural dyes, which is developing new ways to extract and dye and which results in better dyes, quicker extractions and safer dyeing techniques. Austrian researchers have been working on developing a one-bath, standard dye procedure for natural dyes in commercial settings (Schramm, Bechtold, Turcanu, Ganglberger & Geissler, 2001). In Egypt, Morsy, El-Hamaky & El-Ebissy, (2001) have been using enzymes to extract dyes from vegetable materials and their fresh approach is proving to have better results than the traditional dyeing methods. Burdett (1996) mentioned his research into fermentation procedures for natural dyestuff, which results in high purity anthraquinoid dyes for commercial use. The modification of pigments produces useful dyes which are applied by normal dye procedures and give higher fastness properties and brighter colours than synthetically produced analogues (Burdett, 1996).

Natural Dyes: A Brief History, Sources and Uses

Natural dyes and colorants were sources of colour for cosmetics, textiles, pottery and basket materials from prehistoric times (Dean, 1999) until the advent of synthetic dyes. Coloration began as the application of non-organic pigments such as crushed or burnt lime, gypsum, iron rust, and ochre (Robinson, 1969; Gillow and Sentance, 2000). Another ancient method involved crushing fruits, berries, flowers, roots and barks to create a thin paste which is applied to the textiles either by brushing or mixed with water and the fabric soaked in the solution. This type of colour application is staining and is not light or wash fast (Robinson, 1969).

The process of colour application called dyeing occurs when the dye molecule attaches to the fibre. There are three types of dyes: substantive, vat and mordant dyes (Robinson, 1969; Dean, 1999; Bliss, 1981; Gillow and Sentance, 2000). Substantive dyes are dyes that require no additional chemicals to attach them to the fibre and are soluble in water. Some substantive dyes only adhere to animal fibres while others only to plant fibres. There are several sources of natural substantive dyes: lichens, turmeric (Curcuma tinctoria), safflower (carthamus tinctorius), annatto (Bixa orellana), and barberry (Barberis vulgaris) (Robinson, 1969). Vat dyes are soluble in alkaline liquids and bond with the fibre by oxidation (Robinson, 1969). The classic example of a vat dye is indigo which is sourced from the indigo plant (indigofera tinctoria) and woad (Isatis tinctoria). The final class of natural dyes is mordant dyes. Mordant dyes require an auxiliary chemical to attach them to the fibre. Often this is a metal such as iron, copper, and aluminium or natural plant extracts, such as tannins or oxalic acid. Most natural dyes are mordant dyes; some examples are Madder (Rubia tinctorum), Cochineal (Coccus cacti), Weld (Reseda luteola) and Dyer's Broom (Genista tinctoria).

The dyeing of textiles became established in Indus civilisation by 2500 BC (Adrosko, 1968), in China by 3000 BC (Bliss, 1981) and parts of South America between 3000-4000 BC (Dean, 1999). The Egyptians understood the use of mordants for dyeing by the middle kingdom (2040 BC -1640 BC) (Adrosko, 1968). Different regions used their own colorants until the development of trade routes.

The natural material originally used as colorants included dried insects, roots, leaves of plants (Adrosko, 1968), heartwood from trees, flowers seeds, bark, minerals (Gillow & Sentance, 2000), shell fish, and lichens (Dean, 1999). Before the 16th century, the technology for dyeing textiles was kept secret by the practitioners; there existed no detailed literature on dyeing technique but there were trade documents and guild records (Rosetti, 1548/1969). In the 16th Century manuals on the textile dyeing were published, the first of which was The Plictho by Gioanventura Rosetti in 1548, many others would later follow giving us a glimpse into the methods and technology used by dyers (Rosetti, 1548/1969).

In 1856, William Perkin discovered, by chance, the first coal tar dye which he called mauve (Dean, 1999). Scientific interest in dyes shifted from natural materials to synthesising known dyes and creating new dyes.

Current data on natural dyes

The technical data found for natural dyes in current literature is focussed on natural dyes for archaeological and anthropological research not for commercial dye production. In non-technical literature there has been a discussion of the colour range from natural dyes. The natural dye palette lacks the range of synthetic dyes, but many colours can be obtained from the natural palette. There are gaps in natural dye research but with a few more years of research natural dyes it is believed that they can catch up to the 100 years of colour development afforded synthetic dyes (Aviks, 1996).

General faults associated with natural dyes

There are several problems associated with the use of natural colorants. The first problem is colourfastness. Many natural colorants and the resulting dyestuffs are considered to lack good colourfastness either to light, washing or perspiration (Adrosko, 1971). Natural dyes which showed good colour fastness became internationally traded dyestuffs (Tortora, 1987). Yet not all natural dyes that were internationally traded had good fastness. In one early treatise, Rosetti (1969/1548), brazilwood was used for cotton and linen, a colorant that faded on these fibres. Edelstein and Borghetty (the translators and editors of the Rosetti book) in their forward noted that in the mid 16th century, there was no method known to dye either cotton or linen red without the fading. Brazilwood was used because of its new availability and very low price (Rosetti, 1969) even though it faded. It was also noted that "no dye is absolutely fast under all conditions . . .

Furthermore, a dye may be fast on one fibre and not on another; or it may be fast when dyed by one method and not another" (Adrosko, 1971, p.64).

Tortora (1987) claims that consistent colourfastness was not achieved until the development of synthetic dyes. There are ten classes of synthetic dyes (Hatch, 1993); each class has different properties. Some dye classes are used for synthetic fibres, others for natural fibres. Some have good fastness to light while others to washing. Many synthetic dyes are exact copies of natural occurring dyestuff including alizarin, the main dyestuff in madder (Rubia tinctorum) roots, and Indigo, the colouring agent found in Woad (Isatis tinctoria) and Indigo (Indigofera tinctoria L) (Dean, 1999). In colour fastness tests done with many of the most widely traded natural dyestuff of the 18th and 19th centuries by Crews (1987), it was found that these natural dyes show the same type of fading as most synthetic dyes. Therefore, the colour fastness problems are not limited to natural dyes but are present with all dyes whether they are from synthesised sources or natural sources. This is why a dyer would need to know the properties of the type of dye they are using to best utilise the dye (whether it is natural or synthetic).

The second problem with natural colorants is the unpredictability of the colour from each dye-bath. The argument is that since natural colorants are natural, the dyestuffs produced from each plant will vary considerably (Joseph, 1981). Many natural dyes are sourced from plants, and the growth and development of plants is influenced by growing conditions which include the soil quality, climatic conditions, and location in which the plants were grown (Adrosko, 1971).

Beyond the growing conditions, the manner in which plants and colorants are processed affects the quality of the dye extracted (Adrosko, 1971). Dye-baths will have subtle differences created by the impurities that are present in the source material (Adrosko, 1968). These impurities are an inherent component of a natural colorant. It is not just the impurities such as wood fibre (Chenciner, 2000) which affect the colour. The colours from natural dyes are complex (Aviks, 1996); the colour complexity is a result of the number of dyestuffs found in a source material or colorant. Some colorants produce only one dyestuff such as Indigo (Indigofera tinctoria L), while other colorants such as Fustic (Chlorophora tinctoria) produces two different dyestuffs (Crews, 1987).

Since the growth and development of the plant affect the production of the dyestuffs in the colorant, dye-baths which are comprised of plants sourced from separate locations or producers will vary. The use of processing standards and the blending of the colorant (in a similar way that a product like coffee beans or tea is blended) would reduce variation caused by single dye lot sourcing.

A third problem seen with the use of natural dyes is economic. For natural dyes to be able to compete with synthetic dyes, natural dyes need to be "economical, consistent in quality and available in quantity" (Kadolph & Langford, 2002, p.337). The production of natural dyes and colouring agents is limited and more costly in comparison to the production of synthetic dyes (Green, 1995). One of the limitations, currently, with natural dyes is the time requirement needed in processing the colorant. More time is needed for extraction of the dyestuffs (using traditional methods) and creation of the colour spectrum (using existing known colorants) since many colours must be created through several dyeings (Adrosko, 1968). The second limitation would be the production of the colorant, but research into the madder roots (a traditional colorant) by Angelini et al. (1997) showed the good agronomic potential of this colorant as an alternative crop in the Mediterranean region.

The fourth problem associated with natural dyes is the volume of waste produced. Examples of wastes include the Murex Brandaris, for which the shells from enough molluscs to produce 1 kg of dye would reportedly cover 200 square miles of land knee deep in shells (Glover & Pierce, 1993). Burdett (1996) cites a second example of waste material from the use of plant sources: 176 million tonnes of fresh vegetable matter or 30 % of the world's agricultural lands per year would be needed to dye just cotton fabrics and yarn. This analysis assumes traditional extraction and dyeing methods and does not consider the use of the residue as natural fertilisers, or other uses.

Madder: Description of plant

Madder (Rubia tinctoria) is a perennial, herbaceous plant, which sprawls upon the ground or climbs other vegetation (Cannon & Cannon, 1994). The leaves are lanceolate shaped or elliptical (Cannon & Cannon, 1994) with little to no leaf stalk (Krochmal & Krochmal, 1974) and occur in whorls of 4 to 6 on stalks up to 3 metres long (Cannon & Cannon, 1994). The stalks are jointed and covered with fine downward pointing prickles (Cannon & Cannon, 1994) that enable the plant to climb through other vegetation. The flowers of the madder plant appear as clusters at the ends of the stalks. The flowers are tiny, yellow to yellow/green in colour with four petals (Cannon & Cannon, 1994). The flowers then develop into green berries which, when mature, become black (Dean, 1998). It is the root of the madder plant, which contains the majority dyestuffs. The roots are long and red (Krochmal and Krochmal, 1974), with larger roots being the thickness of a pencil and woody. (Buchanan, 1995). The dyestuffs are found beneath the outer skin of the root (Schweppe, 1986).

Historical importance of Madder

Ancient dyers used the three primary colours (red, yellow and blue) to produce the spectrum of colours. Reds were produced from insects, madder and brazilwoods (Rosetti, 1548/1969). Madder was an important dyestuff to dyers as it gave a colour fast red on wool and silk, and, after the discovery of the Turkey red dyeing process, a colour fast red on cotton and linen. The name of the madder plant is linked with the word used for the colour red in many European languages (Robertson, 1973) and Oriental languages as well (Chenciner, 2000).

Madder has appeared in the history of many cultures. There is a story that the Egyptians fed madder to sheep, thus causing the sheep's wool to turn red. The fine red robes made from this wool were known as sandykes (Robinson, 1969). An ancient Greek trade document recorded trade of madder between India and Asia Minor. There are records of madder planted around Rome from the first century AD (Roberston, 1973). However, by the fifth century, madder was no longer of commercial importance in Europe (Krochmal & Krochmal, 1974). The dye trade had moved back to the East and Baghdad had become the centre of the dye trade (Wickens, 1983). Madder was imported into Europe from the Near East during the 7th century, when it began to reappear as a crop in Europe (Krochmal & Krochmal, 1974). Charlemagne ordered it grown in the 8th century at his estates. By the 10th century the Dutch were the major suppliers of madder (Wickens, 1983) and, by the 18th century, the secret of Turkey red dyeing was known to European dyers. This method was used to dye cotton a colour fast red, although it took many months to complete and could take up 20 steps.

During Medieval times, the quality of madder was indicated by specific names: mullen or mull was the lowest quality of madder and was not handled by reputable merchants (Schaefer, 1941). Standard quality madder was called gort gemeen, gemeen or gemeens or mirobée, while the highest quality was called crop, krap, garance robée, garance grappée, and or madder (Schaefer, 1941). Blends of the three qualities of madder were sold in addition to different fineness.

The Plictho (from the 16th century) used the word Robia as the usual name for madder. There were also terms which indicated the quantity of madder to be used. Ciocchi mezzani and granzuoli were used to indicate various sizes, lumps or quantities of madder (Rosetti, 1548/1969).

During the 19th century the use of madder declined as it was replaced by synthetic dyes. In 1826 the two main dyestuffs of madder, alizarin and purpurin, were discovered (Davidson 1974 and Cannon & Cannon 1994). Alizarin was synthesised in 1869 by Graebe and Liebermann (Chenciner, 2000). After this discovery, the cultivation and use of madder greatly declined. There was a small resurgence of the use of natural dyes during World War I as the United States of

America was unable to secure dyes from German chemical supply companies. For the last century, the use of natural dyes (including madder) has been limited to craft dyers (Thresh & Thresh, 1974).

Chemistry of Madder Dyes

According to Crews (1987), Madder root contains at least 19 dyestuffs; Chenciner (2000) listed 25 naturally occurring dyestuffs found in Madder by Helmut Schweppe (See Appendix A for complete list of dyestuffs). Five of the dyestuffs found in Madder roots play a major role in colouring according to Cannon & Cannon (1994). The most important group of dyestuffs found in madder roots is the anthroquinones: Pseudo-purpurin, mungisin, rubiadin, alizarin and purpurin (Cannon & Cannon, 1994). Others regard Alizarin (1,2 - dihydroxyanthraquinone) and purpurin (1,2,4 - trihydroxyanthraquinone) as the major dyestuffs (Chenciner, 2000 & Green, 1995), These dyestuff differ chemically by one oxygen molecule (Onal, 1995). Several of the dyestuffs produce red hues while others produce yellow hues (Onal, 1995); this makes the resulting colour complex. Alizarin is the main red dyestuff, while rubiadin and purpurin are the main yellow components (Onal, 1995).

The Production of Madder

Historically, Madder was produced in large quantities and traded internationally (Schaefer, 1941). The most current data (Green, 1995) shows that world production and trade of Madder root is undocumented with no volumes or quantities calculated, as the quantity of madder traded is small. Madder is only produced on a small-scale in the Kashmir region of India (Green 1995). The madder that is produced is consumed for either hobby/craft dyeing and for artist's paints in Western Europe and North America. Green (1995) does not see significant resurgence in Madder, as synthetic alizarin is "superior and cheaper" (p.91).

In Angelini, Pistelli, Belloni, Bertoli and Panconesi (1997), the researchers conducted an industrial assay and looked at the agronomic potential of madder root. They found after 30 months of growth, one hectare of madder produces 5 tons of roots and that 1 ton of root could dye 16.7 tons of yarn. From this data, the researchers concluded that madder could be grown in the Mediterranean region as a dye crop and has good agronomic potential. The Angelini et al. (1997) research views this not only as an opportunity for new markets but as a means of reducing pollution.

Current research Madder dyestuffs

Madder as a colorant has had limited research. Only two articles were found during the literature search which focussed on madder as a dyestuff. The first article (Onal, 1996) probed the use of different mordants in combination with madder dyestuff to investigate the colour range. The second article (Angelini, et al., 1997) is a quantitative analysis of the alizarin content of madder grown in Europe.

Onal (1996) focussed on the colour and colourfastness from different mordants and mordant processes. This research contained many variables: the author looked at different mordants and mordant combinations, different mordant sequencing (pre-mordanting, combination mordant and dye, and post mordanting), three materials (wool, cotton and feathered leather), and varying the pH. The only two constants were the dyestuff used (madder) and the dyeing technique (which was specific to each textile material).

Results produced 168 colours. A wide range of colours was obtained with the exception of dark blue. The darkest colours were obtained with the pH at either 8 or 6 and palest colours were obtained when the pH was either 4 or 2 (these results were for wool only). Onal's (1996) results suggested that pre-mordanting was the best dyeing method of all the dyeing processes examined. This research examined many different traditional mordant sources (aluminium, iron, copper, tin, and chrome) but Onal also explored a new mordanting mixture. This mixture was comprised of NH_3 (Ammonia), urea and $Na_2C_2O_4$ (oxalic acid) and it was found to be an acceptable mordant mixture to get fast colours. The colour fastness results led Onal (1996) to suggest that the colour duration could be up to 400 years for some items such as carpets and kilms.

Angelini, et al. (1997) studied Madder (Rubia tinctorum) grown in four plots in different locations in Europe for their agronomic characteristic, industrial value, domestication potential in the Mediterranean region and value as a new industrial crop. The plots of madder were grown in Italy, Germany (two locations) and France. The roots were harvested every year between flowering and fruit ripening which correlated to 5 months, 15 months and 30 months. The dyestuffs were extracted and quantified.

Three fabrics (cotton, wool and silk) were mordanted with aluminium potassium sulphate ($AlK(SO_4)_2 \bullet 12\ H_20$), then dyed for 1 hour with the extracted madder, rinsed in water and acetic acid and then washed with Marseille soap. Colourfastness to light (xenon arc discharge) was tested and reflectance data and colour differences were measured. Madder was found to have good agronomic potential. The estimated root yield from 30-month-old plants was found to be 5 tons per hectare and that would dye 83.5 tons of yarn. They also determined that the fading resistance was fair to good for madder on wool.

Extraction and Dyeing Methods: Pre 1856 Dye Manuals

Two reprints of dye manuals from before the advent of synthetic dyes were located and reviewed. The only similarities between the two sources were that the authors asserted that the maximum temperature for the dyeing procedure with Madder must be under the boiling point. The mordants, dyeing procedure and after-treatments or additives differ between authors and between the authors' recipes.

In Rosetti (1548/1969) the combination of mordants were alum with cream of tartar (tartaric acid) or alum, cream of tartar and bran. Bemis (1815/1973) also used alum with red argal (which is tartaric acid) for one method, but nutgalls for the second method. There were dyeing procedure differences between Rosetti (1548/1969) and Bemis (1815/1973). Rosetti used a combined extraction and dyeing technique while Bemis extracted the dyestuffs first then dyed the cloth.

Rosetti (1548/1969) and Bemis (1815/1973) do not use the same after treatment or finishes. Rosetti (1548/1969) uses Istria galls (Istria is a peninsula in northwestern Yugoslavia; these are probably gall from that region), fenugreek

(Greek fennel), flour starch, vinegar (acetic acid), and cinnabar (mercuric sulphide) in one method. A second after-treatment required live silver sublimate (possibly mercury or mercuric chloride) or alum of lees (lees is the sediment or grounds) and washed with soap to lighten the cloth. Bemis (1815/1973) also had two finishing methods for his madder dyeings. The first method used Brazilwood (Caesalpinia species) as an over-dye or within the madder bath by adding two gallons of lant or sig. Lant and sig are defined by the Complete Oxford Dictionary as urine especially stale urine or chamber-lye (M. Charlton, personal communication, Feb 7, 2002). For the second method, Bemis suggests adding potash or pearlash. Urine, potash and pearlash are all alkaline substances (Canadian Oxford Dictionary 2000).

Extraction and Dyeing Methods: Post 1856 Methods

Onal (1996) states that different mordants change the colour resulting from Madder. Mordants like chrome are carcinogenic (Material Safety Data Sheet, 2000), while alum is one of the safest mordants and does not alter the hue (Dean, 1999).

There are many different extraction and dyeing techniques found in the dye recipes. The first way to compare the methods is whether the extraction of the dye and dyeing of the textiles are performed in separate steps or together. The combined method occurs when both the fibre and the roots are immersed in water at the same time and heated together. Most of the recipes that had a combined or one step method, used loose colorant (Bliss 1981; Cannon & Cannon,1994; Davenport 1974; Furry and Viemont, 1935; Krochmal & Krochmal, 1974; Thurstan 1936; Wickens, 1983), while Robertson (1973) put the madder roots in a mesh bag. Wickens (1983) suggests that madder placed in a muslin will ‘bring out’ the brown shades, or probably more correctly, inhibit the red dyestuffs. This ‘browning’ of the dye may be due to cotton’s ability to bond via both hydrogen and coordinative bonds with dyestuff molecules. This means cotton can bond to dyes without a mordant (Onal, 1996). The cotton that surrounds the madder roots will be more likely to bond with the madder dyestuff since it is closer to the colorant. After the cotton has bonded with all the dyestuffs possible, the remaining dyestuffs can bond to the wool. If the red dyestuffs were released first, followed by the any brown dyestuffs, the result would be a red that tends towards brown appearing from the use of muslin around the dyestuff.

The second general method is performed in separate steps. First the dyestuffs are extracted from the colorant using water as the solvent; with the application of heat, the dyestuffs migrate from the colorant into the water creating a dye-bath. The colorant material is removed and the fibre is then entered into the dye-bath and heated (Buchanan, 1995; Dean, 1998; Dean, 1999; Las Aranas, 1995; Lesch, 1970; Milner, 1992; Schweppe, 1986; Thresh & Thresh, 1974; Weigle, 1974; and Van Stralen, 1993). Some methods leave the madder roots or colorant in the dye-bath. Davidson (1974) and Dean (1998) stated, if the roots are left in the dye-bath, that a better colour would result. Most of the two step methods utilise the loose colorant with the exception of Schweppe (1986) who uses a cotton cloth to contain the madder colorant in the dye-bath.

Of the methods found, the majority required that the madder (whether it is in root form or powdered) be soaked in room temperature water for 12 to 24 hours. There are a few exceptions: Davenport (1974), Thresh & Thresh (1974), Wickens (1983) and Cannon & Cannon (1994) require no soaking time prior to the application of heat. Dean (1999) suggests that one to two days of soaking will give the best results, while Buchanan's (1995) method directs the chopped roots to be soaked for a month or more at room temperature before the application of heat.

Most methods specify the ratio between the mass of fibre and the mass of madder colorant. A colorant ratio of 2:1 fibre to colorant ratio was common (Bliss, 1981; Davenport, 1974; Davidson, 1974; Furry and Viemont, 1935; Las Aranas, 1995; McRae,1993; Milner, 1992; Thurstan, 1936; Wickens, 1983). Lesch (1970) and Schweppe (1986) used a fibre to colorant ratio of 1:1. Four other methods do not give specific amounts of dyestuff to use (Buchanan, 1995; Dean, 1998; Dean, 1999; Van Stralen, 1993). Several authors suggested very distinct ratios: Weigle, (1974) uses a 4:1 fibre to colorant ratio; while Robertson (1973) has an 8:3 fibre to colorant ratio and Cannon and Cannon (1994) was at 10:3 or 10:4. The lowest ratio found was 8:1 (Krochmal & Krochmal 1974). The Thresh and Thresh (1974) recipe did not give a weight for the madder but instead a volume 3/4-cup of madder for one pound of wool.

The fourth area of divergence in the methods relates to the duration of the dyeing or the length of time the fibre is immersed in the dye-bath over heat. There were four groups of lengths of times. One group specified a thirty-minute time period for the fibre to be heated in the dye-bath (Krochmal & Krochmal, 1974; Schweppe 1986; Weigle, 1974). The second group specified 40 to 45 minutes (Furry and Viemont 1935; Lesch 1970; Robertson 1973). The third group specified one hour (Bliss, 1981; Buchanan, 1995; Dean 1998; Las Aranas 1995; Milner, 1992; Thresh & Thresh, 1974; Thurstan 1936; Van Stralen, 1993). The fourth group specified two hours of dyeing time (Cannon & Cannon, 1994; Davenport, 1974; Wickens, 1983). The longest dyeing time was for five to six hours to get the best results (McRae, 1993). Dean (1999) suggested dyeing until the fibre reaches the colour you want and Davidson (1974) gave no indication of how long the dyeing process should take.

The fifth difference between the methods concerned the temperature the dyestuffs and fibre were allowed to obtain. The first temperature group is located at 60°C (Dean, 1998; Furry and Viemont, 1935; Thresh and Thresh, 1974). The second group centres at 85°C (Buchanan, 1995; Cannon & Cannon, 1994; Milner, 1992; Schweppe, 1986). The third group is at 90°C (Davenport, 1974 & Wickens, 1983) and the fourth group (and largest cluster) is at the simmer point or just under the boiling point (Bliss, 1981; Davidson, 1974; Dean, 1999; Las Aranas, 1995; Lesch, 1970; McRae, 1993; Robertson,1973; Thurstan 1936; Van Stralen, 1993; Weigle, 1974). Only one text suggests a temperature at the boiling point (Krochmal & Krochmal, 1974). Several authors indicated that boiling will adversely affect the dyeing either by releasing yellow or brown dyestuffs (Davidson, 1974, Lesch, 1974; Schweppe, 1986), or destroying the orange and red dyestuffs (Milner, 1983) and, therefore, advised against it.

It is generally assumed that the water used in the dyeing process should be neutral (pH of 7) with some authors advocating soft or rainwater (Adrosko, 1969). It appears, however, that for madder, a water supply that is alkaline or hard is better for achieving reds. In five of the methods there is specific mention of hard water and in four others they use auxiliary chemicals to alter the pH of the dye-bath. Hard water is noted for impairing the actions of soaps and is slightly alkaline. Hard water is defined by the Canadian Water Quality Guidelines (1996) as "the concentration of all metallic cations, except those of alkali metals, present in water. In general, hardness, is a measure of concentration of calcium and magnesium ions in water and is frequently expressed as milligrams per litre calcium carbonate equivalent (p. I-3 to I-4)."

When hard water is used in processes with high pH, the calcium carbonate and magnesium hydroxide precipitates out into the cloth. Additionally, the calcium and magnesium can form a less soluble leuco compound with many dyestuffs. This leuco compound has little affinity for cellulose, rendering the dyestuff less effective (Canadian Water Quality Guidelines, 1996).

In addition to the use of lime or chalk to make the water more alkaline (Cannon & Cannon,1994; Buchanan, 1995), several after treatments or additives were suggested in the methods reviewed. Several of the methods instructed that the fibre be washed with soap after dyeing (Davenport,1974; and Krochmal & Krochmal, 1974; Las Aranas, 1995). Thurstan (1936) explained that washing with soap improves and brightens the colour. Lesch's recipe specified tartaric acid with Glauber's salt. The only other recipe that called for an acid was Davidson

(1974). The Davidson method recommended acetic acid but also suggests adding lime or using hard water that seems to contradict the use of acids. Davidson (1974) suggests a hand full of bran to brighten the colour. Bran also is suggested by Schweppe (1986) to give a more brilliant dyeing and was used in both Bemis (1815/1973) and Rosetti (1548/1969). The use of bran maybe to alter the pH of the dye-bath as an article by Guarino, Casoria and Menale (2000) used bran and hay as a source of acid to aid in the fermentation of a woad dye-bath.

METHODOLOGY

Research Design

The predictability or consistency of a dye(s) is critical to commercial viability of any natural colorant or source of dyestuff(s). Therefore, this research proposed to measure the consistency of Rubia tinctorum as the colorant and source of dyestuffs. From the literature reviewed, eleven methods of extracting and dyeing with Rubia tinctorum were chosen. These methods were selected based on the length of time and the materials utilised (any method which contained materials that are toxic were excluded). The published methods were taken from the source documents, converted into metric and a protocol was written for each method. Each method was repeated ten times with five specimens per replication (a total of fifty specimens per method). For each replication, the pH of the effluent was measured (unfiltered and filtered) and was recorded. The colorant to water ratio for all methods was the same at 1:200 so that comparisons could be made between effluents. For each specimen, twelve measurements of the hue and value were measured with a Hunterlab Tristimulus Colorimeter (using the CIELAB system).

Population and Sample

The population for this research was all methods of extraction and dyeing with Rubia tinctorum root for sheep's wool using potassium aluminium sulphate as the mordant. The sample was chosen from the methods found in the literature review. All the recipes were designed 100% sheep's wool, that has been pre-mordanted with potassium aluminium sulphate ($AlK(SO_4)_2 \bullet 12\ H_2O$) and stipulated the resulting hue would be red. The methods only used Rubia tinctorum roots (ground) as the colorant and may require other non-toxic additives that may alter the performance of the dyestuffs. The methods specified the duration of the extraction (with and without heating), the duration of the dyeing, the maximum temperature for the extraction and dyeing processes, and the fibre to colorant ratio. The final delimitation for the methods was the length of the process, a maximum of 36 hours was established; the time limit included the extraction (heated and non-heated) and dyeing time. (See Appendix B for original methods and see Appendix C for the interpretation of the original methods and Appendix D for the protocols developed from the interpretations).

Materials

Bran	100% natural wheat bran (food quality) purchased at a local grocery store.
Distilled water	Produced at the University of Manitoba, obtained from the Textile Testing Service.
Chemical Filters	Filter from Textile Lab used to filter the effluent after pH measurement taken and before L* A* B* reading taken.
Colorant	Commercially purchased Rubia tinctorum root from Earthguild and Louet, (see Appendix E for address and contact information). The colorant was pulverised and thoroughly mixed, conditioned to standard conditions of Relative Humidity 65%, Temperature 20°C and stored in the conditioning room.

Hard water	Created from the recipe from Gagnon, Vaillancourt and Pazdermilk (1998). Hardness between 800-1000 ppm with a pH of 7.3 created from distilled water, 480 mg/L of Sodium dicarbonate, 600 mg/L of Calcium Sulphate dihydrate, 600 mg/L of Magnesium Sulphate Anhydrous and 20 mg/L Potassium Chloride. To modify and control the pH of the water buffers, the following purchased buffers were used: Potassium Carbonate-Potassium Borate-Potassium Hydroxide with a pH of 10 and Potassium Biphthalate with a pH of 4.
Milk filters	Filters used to filter the dye-bath in methods 3, 6 and 9 were purchased from a farm equipment supplier.
Mordant	Potassium Aluminium Sulphate ($AlK(SO_4)_2 \bullet 12 H_2O$) applied in accordance with method in Angelini et al. (1997). In this mordanting method, the samples are mordanted at 20% weight of alum at 100°C for 60 minutes at atmospheric pressure.
Test fabric	Style 522 from Test Fabric Ltd. (see Appendix E for contact information), 100% wool unbleached in a twill weave, and cut into 8.7-cm diameter circles. Unbleached fabric was used for two reasons; firstly, bleaches are harmful to the environment; secondly, even after washing, bleached fabric retains a base residue that causes fluctuations in the pH value of the dye bath (Huang, 2000).
Wetting Agent	Non-ionic wetting agent at solution of .5 g/litre of triton.

Variables

The measured variables were the CIE L*A*B* of undyed fabric, the CIE L*A*B* of dyed specimens fabric, pH of unfiltered and the pH of the filter effluent. The independent variables were determined by the methods, and included the fibre to colorant ratio, inclusion or absence of bran, duration of extraction, duration of fibre dye-bath, maximum temperature of the heated extraction and dyeing, and type of water. The dependent variable is the variability of the colour from the specimens within each method.

Preparation of Colorant

The Madder root was purchased from two suppliers of natural dyes, Earthguild and Louet (see Appendix E for addresses and contact information), in chopped root form. The colorant was then ground/pulverised in a blender until it was fine enough to be sifted through a sieve. The colorant was thoroughly mixed and placed in the conditioning room at standard conditions of 65% relative humidity and 20°C temperature. To condition the colorant, it was left in the conditioning room for 12 hours then a volume was measured and weighed. Twenty-four hours later the same volume of colorant was measured again. If the weight was the same, a conditioned state was reached, if the weight had increased then conditioning had not been reached. After reaching equilibrium with the conditioning room, the colorant was stored in the conditioning room thereafter.

Protocol for Specimen - Cutting

The first step in the experiment was to prepare the test fabric for the experiment. A cutting plan was drawn up to cut out the 550 samples. This cutting plan took into account that, for a given replication and method, the specimens should have different weft and warp yarns. The test fabric was cut using an 8.7-cm circular diameter die; the specimens were then labelled with the specimen and replication number as well as the letter that identified the method. The specimens were then placed in the conditioning room at standard conditions Relative Humidity 65% Temperature 20°C for at least 8 hours according to test method CAN/CGSB 4.2 No.2-M88.

Ten randomly chosen specimens were used to determine the test fabric colour in CIELAB measures. To eliminate the possibility of directional variation, the specimens were measured with the warp and weft at 90° for both face up and face down (AATCC Committee RA36, 2001b). The average colour of the undyed fabric was determined to be L* = 88.47, A* = -2.08, B* = 15.15 with standard deviations of 0.16, 0.11 and 0.54 respectively; the E_{cmc} for the test fabric was .31 cmc units with a standard deviation of .23. (See Appendix F for the CIELAB data of the undyed fabric) The protocol for measuring the specimens was as follows:

1. The specimens were placed in plastic airtight bag for transport to the Hunterlab Tristimulus Colorimeter.
2. The Hunterlab Tristimulus Colorimeter was calibrated according to the manual.
3. The specimens were removed from the bag just prior to measurement.

4. The specimens were measured with a white, un-calibrated plate behind them. (The un-calibrated, white tile was used behind the specimens because the fabric was not completely opaque and the material underneath would have affected the readings).
5. Using a 2 inch orifice, the 10 specimens were measured face up and face down, with both warp and weft at 90° and the data recorded on Record Sheet A (see sample of the form in Appendix G).

Preparing Hard Water Solution

A standard hard water solution was created to meet the requirements of some of the methods. To adjust the pH to the required 7.3, the following purchased buffers were used: Potassium Carbonate-Potassium Borate-Potassium Hydroxide that has a pH of 10, and Potassium Biphthalate that has a pH of 4. Distilled water from the University of Manitoba was found to have a slightly acidic reading. The pH of the water for the hard water solution was checked prior to each dye-bath preparation to ensure the correct pH was present. The protocol for preparing the hard water solution follows:

1. Determine the quantity of solution to be made;
2. Calculate the weight of chemicals needed;
3. Measure the quantity of chemicals and water needed;
4. Add chemicals to water and place in an airtight container;
5. Prior to use in the dye-bath, the pH of the water was measured and adjusted to 7.3 using buffers.

Mordanting the Specimens

The same mordanting method was applied to all the specimens, based on the method described in Angelini et al. (1997) using Potassium Aluminium Sulphate ($AlK(SO_4)_2 \bullet 12\ H_2O$) at 20% of the weight of the test fabric. The test fabric was maintained at 100°C for 60 minutes under atmospheric pressure. The protocol for mordanting was as follows:

1. Weigh the specimens for each replication and record on Record Sheet B (sample found in Appendix G).
2. Calculate the amount of mordant required to mordant all the specimens for each method.
3. Make wetting solution from non-ionic wetting agent at .5g/L.
4. Wet specimens to be mordanted in wetting solution for five minutes.
5. Weigh mordant for half the method, add mordant to a 1-litre beaker filled with .75 litres of distilled water.
6. Stir until mordant is dissolved.
7. Add half the specimens to the beaker, and raise the temperature until boiling. Repeat for the other half of the specimens.
8. Boil for 60 minutes stirring every 5 minutes.
9. Remove specimens and cool until room temperature is attained.
10. Rinse in distilled water.
11. Hang to dry via clothes pins in lab.

Note: Specimens were not returned to the conditioning room since the weight of the specimens had been previously determined and recorded so that the amount of colorant could be calculated.

Protocol for Dye-bath Preparation

Each of the eleven methods tested has its own protocol and are listed in Appendix D. the following is the general protocol for dyeing the specimens.

1. Measure (as per method) the specified amount of colorant and record on data sheet B (sample of the form found in Appendix G) using the weight of the specimens for the replication to calculate the colorant needed.
2. Calculate volume of water required to make a .5% dye solution and record on data sheet B.
3. Depending on the method being tested, place the colorant loose or in a cotton bag in a clean beaker.
4. Measure volume of distilled water or hard water solution (as per method), check pH of hard water solution and alter, if necessary, using buffers.
5. Add water to beaker and let stand for non-heated extraction time as required then place on heat source and begin heated extraction process.

Preparation of Specimens for Dyeing

1. Remove specimens from clothespins and sort by replication.
2. Make wetting solution from non-ionic wetting agent at .5g/L.
3. Wet specimens in solution for five minutes, keeping replications separate.
4. Place wetted specimens into dye bath according to the method being tested.

Protocol for Extraction and Dyeing

Each original method was converted to metric measures, and defined times and temperatures were set. Several recipes called for the dye bath to simmer; this was standardised to 95°C. Temperature ranges were narrowed to a single number, and time ranges also narrowed to a single time. See Appendix D for step by step protocol for each method.

Protocol for Effluent

Following the dyeing of the specimens, the effluent was measured for the following variables: pH and colour (CIELAB). The pH was measured with a flat bed recorder and the colour was measured with a Hunterlab Tristimulus Colorimeter with an L sensor, which is more appropriate for measuring liquids.

1. Cool effluent to room temperature.
2. Measure pH of unfiltered effluent and record.
3. Filter effluent with chemical paper filter.
4. Store in closed earlmeyer flasks.
5. Transport to Hunterlab Tristimulus Colorimeter with L sensor.
6. Calibrate Hunterlab Tristimulus Colorimeter.
7. Measure 60 mm of effluent in petri dish used with Hunterlab Tristimulus Colorimeter with an un-calibrated white tile behind.
8. Measure effluent with Hunterlab Tristimulus Colorimeter on CIELAB scale and record on data sheet C (sample of form found in Appendix G).
9. Dispose of effluent down the sink followed by large amounts of water as per instructions from Hazardous Waste Management.

Protocol for measuring specimens

The protocol for measuring the dyed specimens is similar to the protocol for measuring the test fabric but differs in the size of orifice and the number of measurements. Several of the methods resulted in blotchy specimens and, since the Hunterlab Tristimulus Colorimeter takes an average reading for the orifice used, it was decided that several measurements with a smaller 1-inch orifice would give a better indication of the variability of the specimens. The measurements of the test fabric were done with the 2-inch orifice prior to the dyeing and the test fabric appeared uniform to the eye. As with the test fabric measurements, to eliminate the possibility of directional variation, the specimens were measured with the warp and weft at 90° for both face up and face down (AATCC Committee RA36, 2001b). Three randomly chosen locations for each face and warp combination were taken make twelve measurements per specimen. The protocol for the measuring specimens follows:

1. Press the specimens according to CAN/CGSB 4.2 No. 33.2-M86.
2. Recondition specimens in conditioning room according to CAN/CGSB 4.2 No.2-M88 for at least 8 hours.
3. Place specimens in plastic airtight bag for transport to Hunterlab Tristimulus Colorimeter with M sensor and 1 inch orifice.
4. Calibrate Hunterlab Tristimulus Colorimeter.
5. Measure specimens with white un-calibrated plate behind them, taking three measurements of the direction and face combination for a total of twelve measurements as CIELAB data, and record on Data Sheet D (sample of form

found in Appendix G).

Measurement System for Specimens

The specimens were measured with a Hunterlab Tristimulus Colorimeter Model D25M-9 with an M sensor. The measurements utilised the CIELAB system and recorded in a Microsoft Excel™ data file. A 1-inch orifice was used to measure the specimens. Each specimen was measured for each direction and face combination (face up warp at 90°, face up weft at 90°, face down warp at 90° and face down weft at 90°) at three different locations. These gave 12 measurements for each specimen.

The specimens were compared using a modification of AATCC test method 173-1998 CMC: Calculation of small color differences for acceptability (AATCC Committee RA36 2001a). AATCC test method 173-1998 was created to measure the colour difference between a standard and a trial. This test method was modified to calculate the differences between each of the 12 measurements per specimen to a standard. The measurements and the variability of the measurements were used to determine whether the eleven methods resulted in consistent dyeings.

The standard chosen for comparison was the average L* A* B* of each method. The other options explored were: one arbitrary standard for all methods; the extreme measures from the methods; and the mode or the median from the methods. It was felt that the use of an arbitrary standard such as the average for the undyed fabric or a standard red would give unusable results because of the non-uniformity of CIELAB colour space and calculation results in an absolute value of measure in the AATCC test method 173 -1998. One standard for all methods would have been outside of the colour space of all data points for all methods. A standard outside the data points would result in the consistency of the measurement from the standard but not the consistency amongst of the data points of a method. Additionally, using of AATCC test method 173-1998, when there were large colour differences, is outside the capacity for which the equation was created.

The use of a standard from the colour space of each method occupied was chosen by the following logic. An extreme reading such as the lightest specimen (highest L* reading) was eliminated as a choice since an extreme reading was more likely to an outlier. It was felt that this would cause the same type of problem as one standard for all, albeit to a lesser degree. Using the mode or median from the data points could only be accomplished if one could determine the ranking or most common reading of three linked measures, L*, A* or B*. This resulted in the choice for the standard to be the mean of L* A* B* for each method.

The unit of measure for the AATCC test method 173-1998 is ΔE_{cmc} . It is more highly correlated to visual assessments of colour than other measures because measures such as ΔE^* do not account for the non-uniformity of CIELAB colour space (AATCC Committee RA36 2001a). The definition of ΔE_{cmc} is "a single number defining the total color difference in CMC [Colour Measurement Committee] units of a trial from a standard" (AATCC Committee RA36 2001a). The ellipsoid unit, which equals one colour (which has a value of one ΔE_{cmc}) in

CIELAB colour space is circular at the axis of the A and B. As the colour increases in A and/or B, the ellipsoidal unit becomes an oval of larger and larger size (see figure 1).

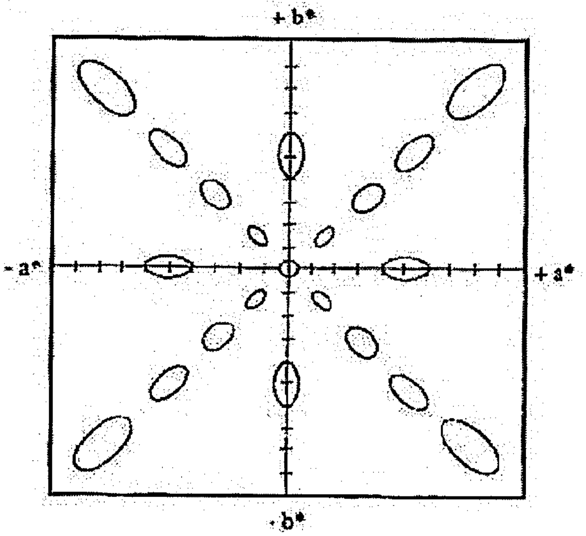

Figure 1. AATCC 173 -1998 if the CIELAB Colour space were uniform, these sections would be of equal sized circles

The test method 173-1998 contained the computer code for a software program that calculates the ΔE_{cmc} from tristimulus values. The computer code was programmed into a Microsoft Excel™ data file. This allowed data to be entered only once and provided for proof-reading and correction of transposing errors. The computer code from the test method was implemented in Excel with macros and formulas to calculate the ΔE_{cmc}. A copy of the formulas and macros used in the data file is contained in Appendix H, Table H1. The AATCC test method 173-1998 provided data to establish that the program was working properly. The results of running this data are found in Appendix H Table H2.

Tolerance for Acceptability

The difference in colour for each measurement was calculated using the CMC (2:1) equation found in AATCC test method 173-1998. To determine if the methods were acceptable, a volume of acceptance had to be established.

Volume of acceptance is defined by Δ Ecmc ≤ *cf,* which is the commercial factor (AATCC Committee RA36 2001a, par. 4.3.2.2). In Section 5, Interpretation of Results, it is established the criteria used for accepting or rejecting a trial based on the volume of acceptance. Research found no reported commercial factors, even though a 20% variation coefficient for CMC (2:1) equation is statistically acceptable with a 95% confidence limit (Jordan, 2001). Therefore, the tolerance or *cf* for this study was set to 1.2 as the upper limit at 95% confidence level.

Statistical Analysis

The results from the eleven methods were examined in two manners to determine which methods had the most uniform results. First, the volume of acceptance based on AATCC test method 173-1998 was analysed. The second method looked at the variance components from random effects modelling.

The data produced by the AATCC test method was an absolute value, thus the resulting data has a positive skew (right skew), which prevented analysis of the data without modifications. For the volume of acceptance the log of the data was taken to produce a normal distribution then the 95% confidence intervals were generated for the mean of the ΔE_{cmc} responses using z-table. These results were then converted with the exponential so they could be compared. For the random effects modelling the ΔE_{cmc} data was cubed to give a more normal distribution.

Since this study was set up to follow the methods found in the literature, the experimenter did not arrange the factors. This meant that a random effect model could be used to look at the variability of the results. Random effects modelling is used when the factors in an ANOVA design “were not deliberately arranged by the experimenter but which were sampled from a population of possible samples instead” (Statsoft Inc., 2001).

Random effects models produce variance components, which denote the estimate of the amount of variance, and can be attributed to those factors found in the experiment (Statsoft Inc., 2001). In this study there are three variance components: measurement, specimens and replication. Measurement looks at the variability of the measurement for each given specimen. The specimen component shows the variance for the specimen within a replication; and replication shows the variance within a method by replication. When the components are totalled, they give the variance for the method as a whole.

As stated before, the data produced by the AATCC test has a positive skew. The variability tests are very sensitive to the skew so, to attain a data set which has a more normal distribution, the ΔE_{cmc} was cube rooted. The converted data was used to analyse the variance of the in ΔE_{cmc} using a Nested Random Effects Model run in SAS by Dr. Dennis Murphy (University of Manitoba, Statistical Advisory Service).

PRESENTATION AND INTERPRETATION OF RESULTS

Tristimulus Values

The data collected from the measurements of the specimens was the L* A* B* values. The ΔE_{cmc} of each measurement (within a method) was calculated from the average of the tristimulus values (see table 1 for results). L* which is the lightness to darkness measurement, where 100 is pure white and 0 is pure black. The methods with the highest L* values were the methods that used the least amount of colorant. Method 5, 6 and 7 used ratios of 8:1, 9.3:1 and 4:1 fibre/colorant ratio. Method 8 additionally has a high L* value, but this method used a 1:1 fibre/colorant ratio. Method 8 had two factors that mostly likely caused the lightness of the specimens. Method 8 used bran as an additive, and restricted the colorant and bran mixture in a bag. The restriction of the colorant probably reduce the amount of dyestuff that were extracted, and the bran possibly altered the pH of the dye-bath which may have played some role in the L* value of the method. A* is the red or green measurement, where a positive number is red and negative number is green. The four methods which had the high L* values correspondingly had lower A* values. The measurement of yellow or blue is the B* value. Yellow is a positive number, while blue is a negative number. Method 1 which had the lowest L* (making it the darkest) had the lowest B* value at 28.73. Method 8, which was light and lower in red, had the highest B* value at 39.00, the remainder of the methods had a value around 30-34.

Table 1 Tristimulus Values and ΔE_{cmc} lists the mean tristimulus values and ΔE_{cmc}, as well as the standard deviations for the means.

Method	Mean L*	St. dev.	Mean A*	St. dev.	Mean B*	st. dev.	Mean ΔE_{cmc}	st. dev.
1	32.42	1.13	45.40	0.41	28.73	1.17	0.85	0.55
2	35.66	1.85	43.61	0.52	30.71	1.39	1.19	0.65
3	33.89	1.49	42.26	0.95	33.20	1.81	1.19	0.80
4	44.01	2.74	45.39	1.37	34.35	1.39	1.59	0.96
5	49.12	3.87	40.93	2.41	33.74	1.10	2.03	1.24
6	64.86	2.88	31.44	3.24	31.41	2.24	2.27	1.20
7	52.52	3.23	38.00	2.32	33.36	1.48	1.74	1.12
8	49.64	2.26	39.69	1.83	39.00	1.42	1.42	0.80
9	35.61	2.13	43.03	1.00	30.53	1.49	1.33	0.74
10	39.92	1.65	44.32	0.82	31.74	1.09	1.08	0.64
11	36.35	1.50	44.81	0.65	31.72	1.14	1.04	0.59

Volume of Acceptance

The volume of acceptance from each data set was calculated using the CMC (2:1) equation found in AATCC test method 173-1998. The tolerance limit for the volume of acceptance was cf≤1.2 ΔE_{cmc} units, for 95% confidence level. Any method, which fell partially or completely outside this limit, was rejected.

To compare the results from the ΔE_{cmc} calculation, the data was converted so it had a more normal distribution. The log of the data was taken then the 95% confidence intervals were generated for the means of the ΔE_{cmc} responses using z-table. These results were then converted with the exponential so they could be compared.

Table 2 z- intervals at 95% confidence levels for Means of methods. A- acceptable: fell within limits; R- rejected: fell partially or complete outside limits.

Method	Log of the mean lower limit	Log of the mean upper limit	Exponential of the Log of the mean lower limit	exponential of the Log of the mean upper limit	0 to 1.2 Acceptance Limit
1	-0.51	-0.39	0.60	0.68	A
2	-0.06	0.04	0.94	1.04	A
3	-0.12	0.00	0.89	1.00	A
4	0.19	0.30	1.21	1.35	R
5	0.44	0.55	1.55	1.74	R
6	0.61	0.71	1.85	2.04	R
7	0.30	0.40	1.35	1.50	R
8	0.15	0.24	1.16	1.27	R
9	0.07	0.17	1.08	1.19	A
10	-0.17	-0.06	0.84	0.94	A
11	-0.17	-0.08	0.84	0.93	A

Table 2 lists the results of the 95% confidence interval. Six of the eleven methods fall within the limits of 0 to 1.2. Methods 1, 2, 3, 9, 10, and 11 are acceptable because upper and lower limits were below $\Delta E_{cmc} \leq 1.2$. Method 1 has the lowest mean ΔE_{cmc} value at .85 cmc units.

Methods 5, 6 and 7 have the high ΔE_{cmc} values and were rejected. These methods had the lowest fibre/colorant ratio and therefore the lowest quantities of water because the volume of water used for each method was determined by the quantity of colorant. The ratio was set at of 200ml water to 1 gram of colorant (in some cases this meant a reduction of the water ratio, and differed from the original method instructions). For example method 6, 161 ml of water was used to dye the ~ 7.5 grams of fibre per replication (see Appendix C for further details). It was actually this method 6, which changed the ratio from 100 ml of water to 200 ml since, at a ratio 100:1, the 80-ml of water barely covered the 5 specimens (even when moved into the smallest glass beaker). The standardisation of the colorant water ratio allowed for comparisons of pH and colour between the method's effluent. It is unclear whether the volume of water or the amount of dyestuff contributed to the greater variation observed in methods 5, 6 and 7. The role of both water volume (compared to fibre volume) and quantity of colorant requires further investigation.

The three methods, in which the colorant was contained in cotton bags (4,7 and 8), were rejected. The cotton-bags may have limited the amount of dye extracted from the madder. Three other methods utilised some means of preventing the pulverised madder from having contact with the test fabric. Methods 3, 6 and 9 all filtered the madder root particulate out before entering the test fabrics. It is not clear that the separation of the pulverised madder from the test fabric through filtering the dye-bath resulted in a more uniform dyeing, since one method that used it this technique was rejected. The use of cotton bags to contain the pulverised madder appears to have affected the results but requires further investigation.

In commercial textile dyeing, salts are used in the dyeing process as a levelling agent. In this study, salts were only used if specified in the original directions. Method 3 was the only method to use a levelling agent, but no conclusion can be drawn as to the effect of the levelling agent.

<u>Hypotheses Testing</u>

The general Hypotheses was there would be a statistically significant difference between the colour for each specimen within dye method one or $H_m = \underset{.}{0}\ \square_m < 1.4$ (where m represents the method number). The general Null Hypotheses was there would be no statistically significant difference between the colour for each specimen within dye method one or $Ho_m = \mu_m > 1.2$. The results of the hypotheses testing follow.

Ho_1 Null Hypotheses 1 - There will be no statistically significant difference between the colour for each specimen within dye method one or $Ho_1 = \mu_1 \leq 1.2$.

Fail to reject: $.68 \leq 1.2$

Ho_2 Null Hypotheses 2 - There will be no statistically significant difference between the colour for each specimen within dye method two or $Ho_2 = \mu_2 \leq 1.2$.

Fail to reject: $1.04 \leq 1.2$

Ho_3 Null Hypotheses 3 - There will be no statistically significant difference between the colour for each specimen within dye method three or $Ho_3 = \mu_3 \leq 1.2$.

Fail to reject: $1.00 \leq 1.2$

Ho_4 Null Hypotheses 4 - There will be no statistically significant difference between the colour for each specimen within dye method four or $Ho_4 = \mu_4 \leq 1.2$.

Reject: $1.35 > 1.2$

Ho_5 Null Hypotheses 5 - There will be no statistically significant difference between the colour for each specimen within dye method five or $Ho_5 = \mu_5 \leq 1.2$.

Reject: $1.74 > 1.2$

Ho_6 Null Hypotheses 6 - There will be no statistically significant difference between the colour for each specimen within dye method six or $Ho_6=\mu_6\leq 1.2$.

Reject: $2.04>1.2$

Ho_7 Null Hypotheses 7 - There will be no statistically significant difference between the colour for each specimen within dye method seven or $Ho_7=\mu_7\leq 1.2$.

Reject: $1.50>1.2$

Ho_8 Null Hypotheses 8 - There will be no statistically significant difference between the colour for each specimen within dye method eight or $Ho_8=\mu_8\leq 1.2$.

Reject: $1.27>1.2$

Ho_9 Null Hypotheses 9 - There will be no statistically significant difference between the colour for each specimen within dye method nine or $Ho_9=\mu_9\leq 1.2$.

Fail to reject: $1.19\leq 1.2$

Ho_{10} Null Hypotheses 10 - There will be no statistically significant difference between the colour for each specimen within dye method ten or $Ho_{10}=\mu_{10}\leq 1.2$.

Fail to reject: $.94\leq 1.2$

Ho_{11} Null Hypotheses 11 - There will be no statistically significant difference between the colour for each specimen within dye method eleven or $Ho_{11}=\mu_{11}\leq 1.2$.

Fail to reject: $.93\leq 1.2$

Variability in Random Effects Modelling

The random effects model produced variance components for measurement, specimen, replication and total of the variance for each method. This model shows where the variance was located and for all methods. For the majority of the methods (8 of 11) the highest variance component was the measurements (See figure 2 for a stack bar-plot as a percentage for more details).

Table 3 shows the numerical values for the variance components. The data shows that methods 4,5, 6 and 7 have higher total variance, yet method 8 (which is rejected) has a lower total variance than method 3 or 1 which were both accepted. Method 11 had the lowest total variance in random effects modelling. Method 9 had the lowest variance between replications, while method 10 had the lowest variance between specimens and method 8 had the lowest variance between measurements.

Figure 2. Stacked bar graph of variance components

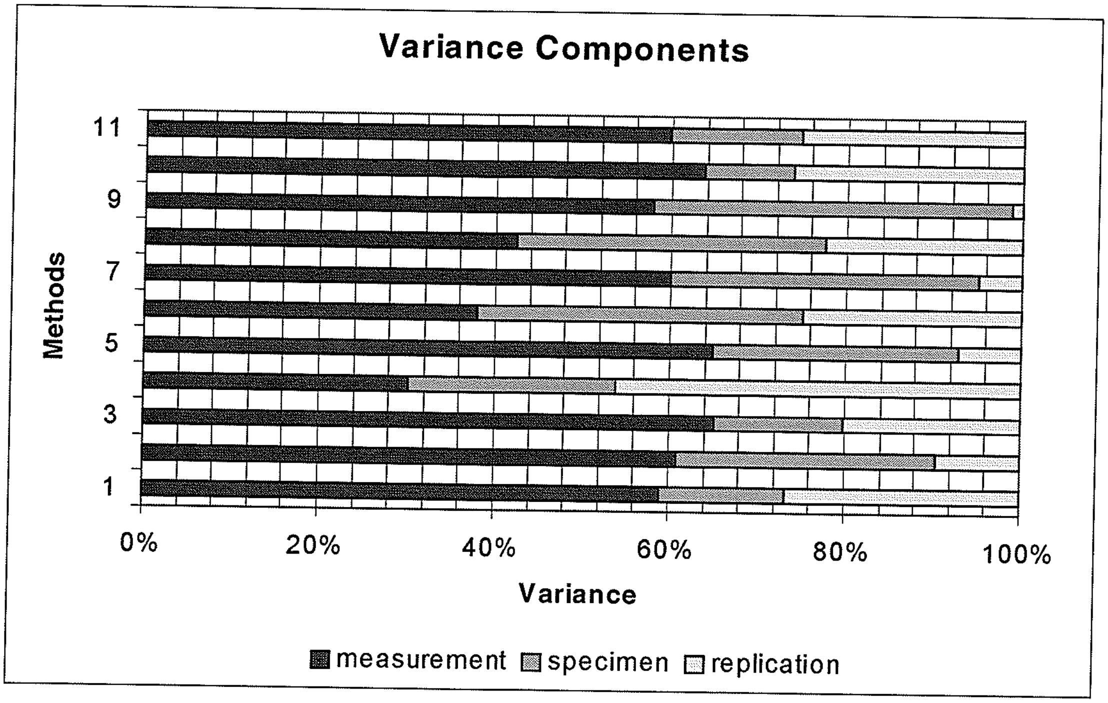

Table 3. Variance components of methods taken from Cube root of ΔE_{cmc}

Method	Variance Cube root of ΔE_{cmc}			
	Measurements	Specimens	Replications	Total
1	0.0277	0.0067	0.0126	0.0469
2	0.0262	0.0128	0.0041	0.0431
3	0.0366	0.0083	0.0114	0.0563
4	0.0200	0.0155	0.0305	0.0660
5	0.0458	0.0198	0.0051	0.0707
6	0.0227	0.0222	0.0149	0.0597
7	0.0364	0.0212	0.0030	0.0606
8	0.0187	0.0154	0.0098	0.0439
9	0.0245	0.0172	0.0005	0.0423
10	0.0284	0.0046	0.0116	0.0447
11	0.0211	0.0055	0.0093	0.0369

Effluent Results

The effluent measurements were taken for informational purposes, not to meet a standard. The effluents of the replications were measured and summaries of the results are listed in Table 4. There are several interesting results that will need further investigation. The first is with regard to pH: methods 1 and 8 have the highest pH at ~4.53. In method 1 effluent was still visually coloured red which would tend to indicate the effluent was not exhausted. In method 8, the effluent was not red in colour but yellow like much of the other effluents, but method 8 used bran in the extraction process: the use of the bran may have effected the pH of the dye-bath. An investigation of the correlation between pH and exhaustion should be explored. The other interesting result is from method 10 L*A*B* result: specifically the B* measurement of 60.87 was much higher than the other B* results. It is unclear why this method produced effluent that was yellower than the other methods.

Table 4. Effluent pH and CIELAB results

Method	pH filtered	Mean L*	mean A*	mean B*
1	4.53	63.51	18.86	47.73
2	3.89	78.07	-7.07	48.26
3	3.30	76.58	-3.73	48.47
4	4.14	74.77	0.56	38.63
5	3.50	78.59	-1.42	25.64
6	3.84	76.42	4.52	25.73
7	3.43	76.80	-3.35	39.87
8	4.54	75.09	-1.17	38.33
9	3.84	75.03	0.87	37.13
10	3.84	77.39	-8.26	60.87
11	3.77	71.74	7.54	31.75

CONCLUSIONS

This thesis explored the technology used for Madder, a natural colorant and endeavoured to examine the belief that natural colorants produce inconsistent results. The goal to reassess and promote the use of natural colorants within the context of sustainable development was explored.

The main objective of this study was to determine if any of the eleven methods tested would produce consistent results. The extraction and dye methods were standardised and repeated ten times. It was found that six of the eleven hypotheses resulted in a fail to reject the null hypotheses that there would be no statistical difference between the colour of each of the specimens within the method. This means that six methods produced consistent results. This in turn means with standardised practices natural colorants can be successfully be utilised for the dyeing of textile and like materials.

The five methods that did not meet consistency standards either used a low volume of water to complete the extractions and dyeings and/or used a cotton-bag to restrict the colorant. A re-testing of all the methods with a standard water volume (as opposed to standard ratio) needs to be completed to determine if the volume of water was the factor that effected the consistency of these methods. Additionally other methods of containing the colorant need to be explored, as it is highly likely that cotton bags/satchels are not supplying enough water flow to extract as much dyestuff as with out the containment. It is logical to keep the particles of madder roots away from the fabric as these particles can cause small spots or a pebbly complexion. The logical progression to take to incorporate natural dyes into commercial situations would be to extraction and filtering (the particles of madder) out of the dye liquor.

The most consistent dyeing came from method 1, which was the oldest of the methods done in this testing. This method, along with methods 3 and 8, used the most colorant at a 1:1 fibre/colorant ratio. However, unlike methods 3 or 8, it produced a darker colour and more consistent results.

The methods used in this study had procedural variations such as non-heat extraction length, maximum temperature, extraction or dye application length, fibre/colorant ratio and additives. These procedural variations between methods did result in differences between the methods. The methods themselves proved to have consistent results. The effluent produced by the methods also varied. The effluent from all the methods was coloured (varying in depth and shade) and was acidic and therefore would need treatment before entering waterways.

Natural colorants as a source of dyestuffs have been thought to result in inconsistent dye-baths. The inconsistency was often attributing to the nature of the colorants themselves, which are plants (or animals) that have innate differences between specimens from within a region and from region or growing locations. This notion of inconsistency may result from lack of control of the many variables in extraction and dyeing processes, particularly sourcing of the colorant. Traditionally, madder (Rubia tinctorum) was graded by quality, in a similar way that many textile fibres such as, cotton or wool are graded. With the use of processing and quality standards and the blending of colorant from different sources, the variation caused single dye lot sourcing would be reduced. The inconsistency resulting from unstable practices typical of hobby or craft dyers (who have been the only dyers to continue to use natural colorant in North America) to extract and dye, would be eliminated with extraction protocols and standards, and standardised dye methods.

Natural colorants can be sourced from renewable resources, which are a more sustainable option for the exploitation of resources. The use of natural colorants in the textile industry on a commercial scale would change the orientation of technological developments and change how the institutions function.

Sustainable development's purpose is to enhance the needs and aspiration of humans both for current and future generations. Through balancing economic, social and ecological structures, a sustainable society can be formed. Textiles are an essential component of human society, therefore it is fundamental to establishing practices in the textile industry that move towards a sustainable solution to the production and use of textiles. The movement to natural colorant as a source of dyestuffs, if managed appropriately, can be a sustainable option to the use of chemical dyes as well as an opportunity for new markets.

However, it would be naive to think that the use of natural colorants alone would solve all the pollution and waste problems within the textiles dye industry. Natural colorants are merely one component within the system. To change the system, many components, whether they are physical, human, political, economic or social will need to be changed to attain the sustainable future we need.

Recommendation for further research

There are numerous questions that arise from this study. Firstly, what would the variability of these methods be with a true commercial or industrial dyeing set-up? This study was not conducted using commercial dye equipment, nor even through modifications to equipment such as launderometer, but rather glass beakers, electric heat plates and manual agitation were the means of performing the dyeings. The use of small dye machines specifically designed for testing would be the next logical step to take. The agitation and water flow in this specialised equipment would far exceed the quality one can accomplish with a glass beaker and manual stirring.

After determining the results from commercial equipment, the samples should be tested for properties such as crocking and colourfastness to water and light to determine the if they meet the standards for commercial dyers and manufacturers.

Other questions which need to be addressed are which method extracts the highest quantity dyestuffs and what colour results from this extraction method? Following that which method of dyeing has the best dye take up? It is important to quantify the amount of dye that can be extracted with these methods to determine the quantity of plant material that is needed to meet any demand for the dyestuffs. Additionally quantifying which method extracts the highest quality and quantity of dyestuffs, would determine the direction further research should take to improve the extraction process.

It will also be important to determine what colours or hues are obtained with different dye ratios? What is the deepest or darkest colour attainable with madder dyestuffs? If lower fibre to colorant ratios is used, do they require different methods to ensure a consistent dyeings. The low fibre to colorant ratio brings up the issue of what is the volume of water needed per gram of material (fibre, yarn or fabric) to obtain the most uniform colour?

The effect of pH on the dye system also needs investigation if the methods require a substance that will alter the pH of the dye-bath. What is the effect of the dye-bath pH on the resulting colour? Is there a relationship between dye-bath pH and the rate of exhaustion? Furthermore what are the non-polluting and sustainable materials can be used to safely alter the dye-bath pH? Extrapolating further, is there a relationship between plant growth conditions such as pH and mineral content to resulting colour? Likewise can we use sustainable non-polluting fertilisers to attain desired colour from madder?

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APPENDIX A

Dyestuffs found in Madder Family

Alizarin
Purpurin
Pseudopurpirin
Rubiadin
Munjistin
Morindone
Xanthopurpurin
Rubiadin-1-methyl ester
Hystazarin-3-methyl ester
Anthrogallol
Anthrogallol-2- methyl ester
Anthrogallol-1,3 dimethyl ester
Anthrogallol-1,2 dimethyl ester
Soranidiol
6-methylxanthopurpurin
Lucidin
Alizarin-1-methyl ester
2-Benzylxanthopurpurin
6-Methylquinizarin
Damnacanthol
Damnacanthal
Nordamnacanthal
Physcion
Rubiadin-3-beta-primeveroside
Galosin

Chenciner 2000 p.302

APPENDIX B

Table B1. Methods as recorded in Source material

Number	Source	Method as in literature
1	Furry , M. S. and Viemont, B. M. (1935). Home dyeing with natural dyes. United States Department of Agriculture Miscellaneous publications No. 230 Washington D.C. (p. 25)	For each pound wool mordanted with alum allow: 8 ounces madder. . . . A dark Lacquer red is obtain by using twice as much madder. Mordant the wool in alum and soak the madder overnight as before. In the morning add enough water for the dyebath, immerse the material, thoroughly rinsed and squeezed out the water, and heat gradually. Do not boil, but keep at 140°F to 160°F, stirring constantly for 2 hours. Let cool in the bath, rinse and dry.
2	Thurstan, V (1936). The use of vegetable dyes for beginners. Leicester UK: The Dryad Press. (p13-14)	1lb. Wool previously mordanted with alum and cream of tartar 8oz. madder. A little powdered chalk if the water is soft Method . The madder may have been put to soak the night before; this makes it easier to use, but is not necessary. It should be put into the dye-bath, and stirred very well as it is brought slowly to the boil, and keep just under boiling point for about twenty minutes. Then a little more water is added and the wool entered and simmered for an hour. Allow the wool to remain in the dye liquor till cold. Then wash in several waters and pass through a boiling soap-bath, this brightens and improves the colour.

Number	Source	Method as in literature
3	Lesch, A (1970). Vegetable dyeing:151 color recipes for dyeing yarns and fabrics with natural materials . New York: Guptill Publications (p. 34)	Ingredients 1 pound wool yarn, previously mordanted with alum 1 pound madder roots 4 tablespoons tartartic acid ½ cup Glauber's salts To make dye bath: Cut the madder roots into 1/4" to 1/2" lengths and place in a five gallon enamel container. Cover with three and half gallons of water and soak for twelve hours. The roots will expand and absorb some of the water. At the end of twelve hours, add one gallon of water to the soaking mixture and simmer for about forty-five minutes. Cool. Remove the roots. The liquid becomes the dye bath. To dye wool yarn: Add the wet, alum mordanted wool yarn to the dye bath and simmer for fifteen to twenty minutes, depending on the shade desired. Dissolve four tablespoons of tartaric acid and half a cup of Glauber's salts in one pint of Hot water and add to the dye bath. Simmer another fifteen to twenty minutes. Cool. Rinse in warm water until the rinse is clear. Shake the water from the yarn and hang to dry
4	Robertson, S. M. (1973). Dye plants. New York: Van Nostrand Reinhold Company (p. 78)	2 oz (60 g) or 3-4 tbsp commercially produced madder powder or at least 3 times this amount of chopped roots 1 gallon hard water Mordant: alum gives Chinese lacquer red . . . Method: Some dyers steep the madder overnight in the water to be used for dyeing. If you are using powder, ad it to the water and stir; if you use roots, put them in a mesh bag and enter together with the clean, wetted wool. It is very important to heat the bath very slowly - it should take 1 to 2 hours to reach the simmer. Do not allow the bath to get above simmering point, as the yellow color is exacted at higher temperatures. For garnet red, keep an even lower temperature - below 140°F (60° C). Simmer the wool for 30 to 40 minutes after it reaches the simmer. Leave the wool in the bath to cool. Rinse the wool once thoroughly, then wash in soapy water, rinse twice and dry.

Number	Source	Method as in literature
5	Krochmal A, and Krochmal C. (1974). The complete illustrated book of dyes from natural sources. Garden City, NY: Doubleday & Company Inc. (p. 166)	Dye bath Madder 2 ounces water soak the madder overnight in 1 quart of water. The next day add cold water to make 2 gallons, and bring to a boil. Add the dampened, mordanted wool. Boil gently for 30 minutes. Rinse and dry. The next day wash in warm soapy water. Then rinse and dry.
6	Thresh, R and Thresh, C. (1974). An introduction to natural dyeing. Santa Rosa CA: Thresh Publications (p.25)	For red use: 3/4 cup Madder roots (coarse ground) 1 ½ tablespoons alum mordant ½ teaspoons cream of tartar water Cover madder with water and soak overnight. Heat to 140°F. Do not exceed this temperature. Remove from heat after 15 minutes. Cool and strain dye liquor, reserving plant material in cheesecloth. Tie securely with string to form bag. Place bag containing plant material in dye liquor. . . . Add water to dye liquor to make 1 ½ gallons of solution. Place cheesecloth bag in pot. Heat to 140°F. Do not exceed this temperature. Enter mordanted wool. Hold temperature at 140°F for 1 hour, stir regularly. Remove from heat, cool wool in pot.

Number	Source	Method as in literature
7	Weigle, P (1974) Madder Root In Natural Plant Dyeing:29 No. 2 Brooklyn Botanic Garden Record Plants & Gardnes A handbook. (p 16)	To dye 2 oz. of wool. . . Place ½ ounce of pulverized madder root (Rubia tinctorum) in 2 separate muslin bags and soak in 2 quarts of water overnight. The following day heat the madder and water gradually to the boiling point. Let it boil vigorously for only 10 minutes. Remove the madder from the dyebath and divide the dye evenly in 2 dyepots . . . place the 2 alum - premordanted skeins in 1 dyebpot . . .. Simmer the yarn in the pots for 30 minutes. Remove all the skeins from the dyebaths. . . . Rinse all the skeins thoroughly.
8	Schweppe, H. (1986). Practical hints on dyeing with natural dyes. Washington D.C. : Smithsonian Institution. (p. 27)	Wrap 100 grams of disintegrated or pulverized madder root loosely in a cotton cloth, and soak the bundle for 12 hours in 6 liters of water. Bring the water very slowly (within in hour) to the simmer; let it simmer for 10 minutes, and then remove the vessel from the heating plate. Take out the bundle with the madder, and make up the dyebath with water to six liters. Wet thoroughly with water from the water tap 100 grams of wool (20 skeins of 5 grams each, previously tied together with cord, see page 2), mordanted with 25% of alum and 6% of cream of tartar (see page 6), and then squeeze the water out. Enter the wool into the prepared dyeing liquor at 40°C, and dye for 30 minutes at 70-80°C. Remove the wool from the dyebath after cooling, rinse it thoroughly and let it dry in the air. A more brilliant dyeing is obtained when the same amount of wheat bran as of madder is added to the dye liquor

Number	Source	Method as in literature
9	Las Aranas Spinners and Weavers Guild, (1995). Dyeing with natural materials. Albuquerque, NM: Self published (p. 26)	Madder may be purchased in root or sawdust form and should be soaked for 24 hours or more in gallon of water. Use 8 ounces madder per 1 pound of wool. If using root, chop into 1 inch pieces before soaking. Add water to make 4 gallons and simmer 1 hour. Remember that boiling will brown the dye. Cool the dyebath and strain. Add clean, wet wool and simmer 1 hour. Cool in dyebath and rinse well. To brighten the color, add 2 tbsp. mild soap flakes, such as Ivory Snow to the first rinse.
10	Cannon, J. and Cannon, M. (1994). Dye plants and dyeing. London UK: The Herbert Press. (p.76)	Dyeing with madder must take place slowly. Premordanted wool is placed in the dye bath with 30 to 40 per cent of it weight of powdered madder. Chalk or slaked lime is added, particularly in areas with soft water. The temperature is then slowly raised to 85°C (185°F), which must not be exceeded nor continued for more than two hours. . . . Washing in hot soapy water helps to eliminate any yellow tints present.
11	Milner, A. (1992). The Ashford book of dyeing. Wellington New Zealand: Bridget Williams Books Limited. (p. 41)	For 100 gm of fibre use: 50 gm of madder Soak madder overnight in the dyebath. Bring it slowly to simmer point, stirring well during heating. Simmer for 30 minutes. Cool then enter wet fibre and simmer for 1 hour. Allow the fibre to cool in the bath before removing to rinse. The temperature of the dyebath for madder is kept below 82°C (180°F) because heat extracts the stronger brown pigments and the orange and brick red shades disappear.

APPENDIX C

Table C1. Factors in Dye methodology for Method 1

	Original Method	Adopted Method
Weight of wool used 1	1 lb	7.5 g
Weight of Colorant used 2	1 lb	7.5 g
Pre-Mordanted3	alum	Potassium aluminium sulphate
Time of non-heated extraction/soaking time	overnight	16 hours
Volume of distilled water	enough water to immerse the material	1500 ml
Volume of hard water 4	n/a	n/a
Separate colorant from fibre	n/a	n/a
Separate Extraction from dyeing	n/a	n/a
Extraction time 5	n/a	n/a
Wetting agent	not specified	triton at .5% solution
Dye-bath temperature	Do not boil 140°F -160°F	71°C
Additives	n/a	n/a
Fabric Heated in Dye-bath 5 (minutes)	2 hours	120 minutes
Cool in dye-bath	let cool in bath	let cool in bath to room temperature
Post treatments	Rinse and dry	rinse with 40°C distilled water until water runs clear; hang via clothes pins in lab until dry

Table C2. Factors in Dye methodology for Method 2

	Original Method	Adopted Method
Weight of wool used 1	1 lb.	7.5 g
Weight of Colorant used 2	8 oz.	3.75 g
Pre-Mordanted3	alum and cream of tartar	potassium aluminium sulphate
Time of non-heated extraction/soaking time	the madder may have been left out to soak the night before. .. but is not necessary	None
Volume of distilled water	n/a	n/a
Volume of hard water 4	a little powered chalk if the water is soft	750 ml
Separate colorant from fibre	n/a	n/a
Separate Extraction from dyeing	keep just under a boil for twenty minutes: the wool entered and simmer for one hour	extract dye at 95 C then add fibre and continue extracting and dyeing
Extraction time 5	20 minutes	20 minutes
Wetting agent	n/a	triton at .5% solution
Dye-bath temperature	under a boil	95°C
Additives	n/a	n/a
Fabric Heated in Dye-bath 5 (minutes)	60 minutes	60 minutes
Cool in dye-bath	allow the wool to remain in the dye liquor till cool	Cool dye-bath to room temperature
Post treatments	wash in several waters and pass through a boiling soap bath	Rinse with distilled water until water runs clear, wash with (CGSB 19.1 Test method 1), rinse with distilled water until water runs clear, hang via clothes pins in lab

Table C3. Factors in Dye methodology for Method 3

	Original Method	Adopted Method
Weight of wool used [1]	1 pound	7.5 g
Weight of Colorant used [2]	1 pound madder roots	7.5 g
Pre-Mordanted[3]	alum	Potassium aluminium sulphate
Time of non-heated extraction/soaking time	12 hours	12 hours
Volume of distilled water	3 ½ gallons + 1 gallon	1500 ml
Volume of hard water [4]	n/a	n/a
Separate colorant from fibre	remove roots after extraction	Filter the colorant particles
Separate Extraction form dyeing	extract at a simmer, cool bath remove roots	Extract dyes at 95□C, cool bath, filter, then immerse specimens in dye-bath
Extraction time [5]	45 minutes	45 minutes
Wetting agent	n/a	Triton at .5% solution
Dye-bath temperature	simmer	95°C
Additives	Glauber's salts ½ cup tartaric acid 4 tablespoons	Tartaric acid .45 g Glauber's Salt .68 g
Fabric Heated in Dye-bath [5] (minutes)	15-20 minutes then add Glauber's salts and tartaric acid, simmer 15-20 minutes more	40 minutes (after 20 minutes add salt and acid)
Cool in dye-bath	cool	Cool dye-bath to room temperature
Post treatments	rinse in warm water until the rinse is clear, shake water from yarn and hang to dry	Rinse with distilled water until water runs clear, hang via clothes pins in lab

Table C4. Factors in Dye methodology for Method 4

	Original Method	Adopted Method
Weight of wool used 1	1 lb.	7.5 g
Weight of Colorant used 2	2oz (60g) or 3/4 tbsp. commercially produced madder powder or al least three times amount chopped roots	3.75 g
Pre-Mordanted3	alum	Potassium aluminium sulphate
Time of non-heated extraction/soaking time	some dyers steep the madder overnight	n/a
Volume of distilled water	n/a	n/a
Volume of hard water 4	1 gallon	750 ml
Separate colorant from fibre	if using roots, put them in mesh bag and enter them together with the clean wetted wool	Colorant in cotton bag
Separate Extraction form dyeing	n/a	n/a
Extraction time 5	n/a	n/a
Wetting agent	n/a	Triton at .5% solution
Dye-bath temperature	below 140°F, taking 1-2 hour to reach this temperature	60°C
Additives	n/a	n/a
Fabric Heated in Dye-bath 5 (minutes)	30-40 minutes	40 minutes
Cool in dye-bath	leave the wool in the bath to cool	Cool in dye-bath until room temperature

Post treatments	Rinse the wool once thoroughly then wash in soapy water, rinse twice and dry	Wash specimens in soapy water (CGSB 19.1 test method 1 soap solution) rinse with distilled water until water runs clear, hang via clothes pins in lab

Table C5. Factors in Dye methodology for Method 5

	Original Method	Adopted Method
Weight of wool used 1	1 pound	7.5 g
Weight of Colorant used 2	2 oz.	.94 g
Pre-Mordanted3	alum	Potassium aluminium sulphate
Time of non-heated extraction/soaking time	overnight	16 hours
Volume of distilled water	1 quart plus 2 gallons	188 ml
Volume of hard water 4	n/a	n/a
Separate colorant from fibre	n/a	n/a
Separate Extraction from dyeing	n/a	n/a
Extraction time 5	n/a	n/a
Wetting agent	n/a	Triton at .5% solution
Dye-bath temperature	boil gently	100°C
Additives	n/a	n/a
Fabric Heated in Dye-bath 5 (minutes)	30 minutes	30 minutes
Cool in dye-bath	n/a	n/a
Post treatments	Rinse and dry next day; wash in warm soapy water then rinse and dry	wash with soapy water (CGSB 19.1 test method 1 soap solution) rinse with distilled water until water runs clear, hang via clothes pins in lab

Table C6. Factors in Dye methodology for Method 6

	Original Method	Adopted Method
Weight of wool used 1	1 pound	7.5 g
Weight of Colorant used 2	3/4 cup of madder roots (coarse ground)	.81 g
Pre-Mordanted3	alum and cream of tartar	Potassium aluminium sulphate
Time of non-heated extraction/soaking time	overnight	16 hours
Volume of distilled water	1 ½ gallon solution	162 ml
Volume of hard water 4	n/a	n/a
Separate colorant from fibre	strain dye liquor, reserving plant material in cheesecloth. Tie securely with string to form bag. Place bag containing plant material in dye liquor.	Extract dyestuff, then filter dye-bath; place remaining material in cotton bag and immerse specimens and cotton bag in dye-bath
Separate Extraction form dyeing		Extract at 60°C then filter and place colorant in bag and enter with fabric in dye-bath
Extraction time 5	15 minutes	15 minutes
Wetting agent	n/a	Triton at .5% solution
Dye-bath temperature	140°F	60°C
Additives	n/a	n/a
Fabric Heated in Dye-bath 5 (minutes)	1 hour	60 minutes
Cool in dye-bath	cool wool in pot	cool in dye bath until room temperature
Post treatments		rinse with distilled water until water runs clear, hang via clothes pins in lab

Table C7. Factors in Dye methodology for Method 7

	Original Method	Adopted Method
Weight of wool used [1]	2 oz	7.5 g
Weight of Colorant used [2]	½ oz of pulverised madder root	1.88 g
Pre-Mordanted[3]	alum and cream of tartar	Potassium aluminium sulphate
Time of non-heated extraction/soaking time	overnight	16 hours
Volume of distilled water	2 quarts	376 ml
Volume of hard water [4]	n/a	n/a
Separate colorant from fibre	muslin bags	Colorant contained in cotton bags
Separate Extraction from dyeing	let boil vigorously for only 10 minutes, remove the madder from the dye-bath	Extract at a boil then remove cotton bags containing colorant
Extraction time [5]		10 minutes
Wetting agent	n/a	Triton at .5% solution
Dye-bath temperature	simmer	95°C
Additives	n/a	None
Fabric Heated in Dye-bath [5] (minutes)	30 minutes	30 minutes
Cool in dye-bath	n/a	Remove from dye-bath and let fabric cool to room temperature
Post treatments	rinse all skeins thoroughly	rinse with distilled water until water runs clear, hang via clothes pins in lab

Table C8. Factors in Dye methodology for Method 8

	Original Method	Adopted Method
Weight of wool used [1]	100 grams of wool	7.5 g
Weight of Colorant used [2]	100 grams of madder	7.5 g
Pre-Mordanted[3]	alum and cream of tartar	potassium aluminium sulphate
Time of non-heated extraction/soaking time	12 hours	12 hours
Volume of distilled water	6 litres	1500 ml
Volume of hard water [4]	n/a	n/a
Separate colorant from fibre	madder root loosely in cotton cloth	colorant and bran contained in cotton bag
Separate Extraction from dyeing	extract for ten minutes	extraction at 95□C
Extraction time[5]	60 minute to reach simmer, then maintain for 10 minutes	60 minutes to reach 95□C then maintain 10 minutes
Wetting agent	n/a	triton at .5% solution
Dye-bath temperature	70-80°C	70-80°C
Additives	bran- same amount of wheat bran as madder	Bran 7.5 g
Fabric Heated in Dye-bath [5] (minutes)[5]	30 minutes	30 minutes
Cool in dye-bath	remove the wool from dye-bath after cooling	cool in dye bath until room temperature
Post treatments	rinse it thoroughly and let it air dry	rinse with distilled water until water runs clear, hang via clothes pins in lab

Table C9. Factors in Dye methodology for Method 9

	Original Method	Adopted Method
Weight of wool used 1	1 pound	7.5 g
Weight of Colorant used 2	8 oz.	3.75 g
Pre-Mordanted3	alum	Potassium aluminium sulphate
Time of non-heated extraction/soaking time	24 hours	24 hours
Volume of distilled water	1 gallon plus 4 gallons	750 ml
Volume of hard water 4	n/a	n/a
Separate colorant from fibre	n/a	filter the dye-bath after extraction
Separate Extraction from dyeing	extract , strain	Extraction at 95°C
Extraction time 5	60 minutes	60 minutes
Wetting agent	n/a	triton at .5% solution
Dye-bath temperature	simmer	95°C
Additives	n/a	n/a
Fabric Heated in Dye-bath 5 (minutes)	60 minutes	60 minutes
Cool in dye-bath	cool in dye-bath	cool in dye bath until room temperature
Post treatments	to brighten the colour, add 2 tbsp. mild soap flakes to first rinse	rinse with distilled water until water runs clear, wash with 5% Zero solution. Rinse again with distilled water until it runs clear, hang via clothes pins in lab

Table C10. Factors in Dye methodology for Method 10

	Original Method	Adopted Method
Weight of wool used 1	n/a	7.5 g
Weight of Colorant used 2	30-40 percent weight of powdered madder	3 g
Pre-Mordanted3	Alum	Potassium aluminium sulphate
Time of non-heated extraction/soaking time	n/a	n/a
Volume of distilled water	n/a	n/a
Volume of hard water 4	n/a	600 ml
Separate colorant from fibre	n/a	n/a
Separate Extraction from dyeing	n/a	n/a
Extraction time 5	n/a	n/a
Wetting agent	n/a	triton at .5% solution
Dye-bath temperature	85°C or 185°F	85°C
Additives	n/a	n/a
Fabric Heated in Dye-bath 5 (minutes)	no more than 120 minutes	120 minutes
Cool in dye-bath	n/a	cool in dye bath until room temperature
Post treatments	washing in hot soapy water helps to eliminate any yellow tints present.	wash with soapy water (CGSB 19.1 test method 1) then rinse with distilled water until water runs clear, hang via clothes pins in lab

Table C11. Factors in Dye methodology for Method 11

	Original Method	Adopted Method
Weight of wool used 1	100 grams	7.5 g
Weight of Colorant used 2	50 grams	3.75 g
Pre-Mordanted3	alum	Potassium aluminium sulphate
Time of non-heated extraction/soaking time	overnight	16 hours
Volume of distilled water	n/a	750 ml
Volume of hard water 4	n/a	n/a
Separate colorant from fibre	n/a	n/a
Separate Extraction form dyeing	simmer [82°C] 30 minutes. Cool then enter wet fibre and simmer ..	Extraction at 82°C before entering fibre but colorant material not removed from bath
Extraction time 5	30 minutes	30 minutes
Wetting agent	n/a	Triton at .5% solution
Dye-bath temperature	simmer [82°C]	82°C
Additives	n/a	n/a
Fabric Heated in Dye-bath 5 (minutes)	60 minutes	60 minutes
Cool in dye-bath	allow fibre to cool in bath	Cool in dye bath until room temperature
Post treatments	rinse	Rinse with distilled water until water runs clear, hang via clothes pins in lab

1. Adopted method weight based was measured for each replication for the purposes of this table the weight will be 7.5 g.
2. All madder roots were pulverised, sifted and thoroughly mixed, conditioned and store at relative humidity 65% and temperature 20 °C see preparation of colorant.
3. All test fabric was pre-mordanted using procedure listed in Mordanting Specimens.
4. Hard water prepared using procedure outlined in Preparing Hard Water.
5. Plus time to heat up dye-bath.

APPENDIX D
METHOD BY METHOD PROTOCOL
(with weights and measures)

Table D1. Method 1

Replication	Weight of specimens (g)	Weight of colourant (g)	Volume of water (mL)	Weight of additives (g)
1	7.54	7.54	1508	n/a
2	7.47	7.47	1494	n/a
3	7.57	7.57	1514	n/a
4	7.56	7.56	1512	n/a
5	7.56	7.56	1512	n/a
6	7.53	7.53	1506	n/a
7	7.53	7.53	1506	n/a
8	7.56	7.56	1512	n/a
9	7.53	7.53	1506	n/a
10	7.56	7.56	1512	n/a

1. Prepare dyebath with distilled water and colourant and let stand at room temperature for 16 hours.
2. Immerse the test fabric in prepared dyebath
3. Place beaker in oil bath, raise temperature over one hour to 71° C
4. Stir every five minutes
5. Maintain in oil bath for 120 minutes
6. Remove beaker from the oil bath and let cool to room temperature
7. Remove specimens and squeeze out excess dyebath
8. Rinse with 40 C distilled water until the water runs clear
9. Hang to dry via clothes pins in lab

Table D2. Method 2

Replication	Weight of specimens (g)	Weight of colourant (g)	Volume of water (mL)	Weight of additives (g)
1	7.51	3.76	752	n/a
2	7.50	3.76	752	n/a
3	7.51	3.76	752	n/a
4	7.52	3.76	752	n/a
5	7.55	3.77	754	n/a
6	7.47	3.74	754	n/a
7	7.52	3.76	752	n/a
8	7.51	3.76	752	n/a
9	7.55	3.77	754	n/a
10	7.54	3.76	752	n/a

1. Prepare dyebath with hard water solution and colourant.
2. Place beaker on heating element
3. Raise temperature to almost to a boil (95 °C)
4. Maintain at 95 °C for 20 minutes.
5. Immerse test fabric in dyebath
6. Maintain at 95 C for 60 minutes.
7. Stir every five minutes
8. Remove beaker for element
9. cool dyebath until bath is room temperature (22 °C).
10. Remove specimens squeeze out excess dyebath
11. Rinse with distilled water until the water runs clear
12. Wash with boiling soap-bath
13. Rinse with distilled water until the water runs clear
14. Hang to dry via clothes pins in lab

Table D3. Method 3

Replication	Weight of specimens (g)	Weight of colourant (g)	Volume of water (mL)	Weight of additives (g)	
				tartaric acid	Glauber's Salt
1	7.58	7.58	1516	0.45	0.68
2	7.55	7.55	1510	0.45	0.68
3	7.57	7.57	1514	0.45	0.68
4	7.58	7.58	1516	0.45	0.68
5	7.57	7.57	1514	0.45	0.68
6	7.51	7.51	1502	0.45	0.68
7	7.57	7.57	1514	0.45	0.68
8	7.58	7.58	1516	0.45	0.68
9	7.61	7.61	1522	0.46	0.68
10	7.58	7.58	1516	0.45	0.68

1.Prepare dyebath with distilled water and colourant and let stand at room temperature for 12 hours.
2.Place beaker on element
3.Raise temperature to under a boil 95°C
4.Maintain for 45 minutes.
5.Stir every five minutes
6.Remove dyebath from heat and cool to room temperature
7.Filter to remove colourant
8.Immerse test fabric to the dye bath
9.Return to element and raise temperature to 95°C for 20 minutes,
10.Dissolve tartaric acid and Glauber's salts into dyebath and stir well.
11.Maintain 20 minutes more
12.Remove from heat and cool dyebath to room temperature.
13.Remove specimens and squeeze out excess dyebath
14.Rinse with warm distilled water until the water runs clear
15.Hang to dry via clothes pins in lab

Table D4. Method 4

Replication	Weight of specimens (g)	Weight of colourant (g)	Volume of water (mL)	Weight of additives (g)
1	7.53	3.77	754	n/a
2	7.55	3.77	754	n/a
3	7.54	3.77	754	n/a
4	7.52	3.76	752	n/a
5	7.52	3.76	752	n/a
6	7.39	3.7	740	n/a
7	7.47	3.74	748	n/a
8	7.49	3.75	750	n/a
9	7.46	3.73	746	n/a
10	7.41	3.71	742	n/a

1. Place colourant in a cotton bag and enter together with the wetted test fabric in to the hard water solution.
2. Place beaker in oil bath, heat the dyebath very slowly 120 minutes to reach the maximum temperature.
3. Maximum temperature is 60 °C
4. Stir every five minutes.
5. Maintain at that temperature for 40 minutes.
6. Remove from heat, let the test fabric cool to room temperature 22 °C in dyebath
7. Remove specimens and squeeze out excess dyebath
8. Rinse with distilled water until the water runs clear
9. Wash the wool in soapy water (CGSB 19.1 test method 1 soap solution)
10. Rinse with distilled water until the water runs clear
11. Hang to dry via clothes pins in lab

Table D5. Method 5

Replication	Weight of specimens (g)	Weight of colourant (g)	Volume of water (mL)	Weight of additives (g)
1	7.60	0.95	190	n/a
2	7.51	0.94	188	n/a
3	7.60	0.95	190	n/a
4	7.50	0.94	188	n/a
5	7.53	0.94	188	n/a
6	7.54	0.95	190	n/a
7	7.59	0.95	190	n/a
8	7.54	0.94	188	n/a
9	7.58	0.94	188	n/a
10	7.53	0.94	188	n/a

1. Prepare dyebath with distilled water and colourant and let stand at room temperature for 16 hours.
2. Place on heating element
3. Bring dyebath to a boil
4. Add the wetted test fabric
5. Boil gently for 30 minutes.
6. Stir every five minutes
7. Remove specimens and squeeze out excess dyebath
8. Rinse with distilled water until the water runs clear
9. Hang to dry via clothes pins in lab
10. Next day, wash in warm soapy water. (CGSB 19.1 test method 1 soap solution)
11. Rinse with distilled water until the water runs clear
12. Hang to dry via clothes pins in lab

Table D6. Method 6

Replication	Weight of specimens (g)	Weight of colourant (g)	Volume of water (mL)	Weight of additives (g)
1	7.50	0.81	162	n/a
2	7.50	0.81	162	n/a
3	7.56	0.81	162	n/a
4	7.53	0.81	162	n/a
5	7.52	0.81	162	n/a
6	7.59	0.81	162	n/a
7	7.52	0.81	162	n/a
8	7.54	0.81	162	n/a
9	7.55	0.81	162	n/a
10	7.54	0.81	162	n/a

1. Prepare dyebath with distilled water and colourant and let stand at room temperature for 16 hours.
2. Place beaker in oil bath
3. Heat to 60 °C . Do not exceed this temperature.
4. Remove from heat after 15 minutes.
5. Cool
6. Filter through milk filter, reserve dyestuff in a cotton bag.
7. Place bag containing dyestuff dye liquor.
8. Return beaker to oil bath
9. Heat to 60 °C . Do not exceed tis temperature.
10. Enter test fabric.
11. Hold temperature at 60 °C for 60 minutes
12. Stir every five minutes.
13. Remove from oil bath
14. Cool test fabric in dye liquor until room temperature 24 °C
15. Remove specimens and squeeze out excess dyebath
16. Rinse with distilled water until the water runs clear
17. Hang to dry via clothes pins in lab

Table D7. Method 7

Replication	Weight of specimens (g)	Weight of colourant (g)	Volume of water (mL)	Weight of additives (g)
1	7.51	1.88	376	n/a
2	7.47	1.87	374	n/a
3	7.5	1.87	374	n/a
4	7.52	1.89	378	n/a
5	7.54	1.88	376	n/a
6	7.45	1.86	372	n/a
7	7.48	1.87	374	n/a
8	7.49	1.87	374	n/a
9	7.48	1.87	374	n/a
10	7.45	1.86	372	n/a

1. Prepare dyebath with distilled water and colourant. Contain colourant in cotton bag and enter into wate, let stand at room temperature for 16 hours.
2. Place beaker on heating element
3. Raise temperature over 60 minutes to boil
4. Stir every five minutes
5. Let it boil vigorously for only 10 minutes
6. Remove the dyestuff bags from dyebath
7. Immerse specimens into the dye liquor
8. Maintain below a boil for 30 minutes.
9. Stir every five minutes
10. Remove from heat
11. Remove specimens and squeeze out excess dyebath
12. Cool specimens to room temperature
13. Rinse with distilled water until the water runs clear
14. Hang to dry via clothes pins in lab

Table D8. Method 8

Replication	Weight of specimens (g)	Weight of colourant (g)	Volume of water (mL)	Weight of additives (g) Bran
1	7.49	7.49	1498	7.49
2	7.47	7.47	1494	7.47
3	7.55	7.55	1510	7.55
4	7.56	7.56	1512	7.56
5	7.57	7.57	1514	7.57
6	7.54	7.54	1508	7.54
7	7.55	7.55	1510	7.55
8	7.55	7.55	1510	7.55
9	7.54	7.54	1508	7.54
10	7.54	7.54	1508	7.54

1. Prepare dyebath with distilled water and colourant and bran. Contain colourant, and bran in a cotton bag, let stand at room temperature for 12 hours.
2. Place beakers on heating elements
3. Raise temperature over 60 minutes to 95 °C
4. Stir every five minutes
5. Maintain at that temperature for 10 minutes
6. Remove from heat and remove the dyestuff
7. Wet test fabric then squeeze the excess water out.
8. Enter the test fabric into the prepared dyeing liquor at 40 °C
9. Raise temperature to 70-80 °C .
10. Maintain at that temperature for 30 minutes.
11. Stir every five minutes
12. Cool to room temperature
13. Remove specimens and squeeze out excess dyebath
14. Rinse with distilled water until the water runs clear
15. Hang to dry via clothes pins in lab

Table D9. Method 9

Replication	Weight of specimens (g)	Weight of colourant (g)	Volume of water (mL)	Weight of additives (g)
1	7.55	3.77	755	n/a
2	7.51	3.75	751	n/a
3	7.52	3.76	752	n/a
4	7.55	3.77	755	n/a
5	7.55	3.77	755	n/a
6	7.54	3.77	754	n/a
7	7.54	3.77	754	n/a
8	7.53	3.76	753	n/a
9	7.60	3.80	760	n/a
10	7.50	3.75	750	n/a

1. Prepare dyebath with distilled water and colourant and let stand at room temperature for 24 hours.
2. Place beaker on heating element
3. Raise temperature to 95 °C
4. Maintain for 60 minutes.
5. Stir every five minutes
6. Cool the dyebath and filter
7. Immerse specimens
8. Maintain at 95 °C for 60 minutes.
9. Stir every five minutes
10. Remove from heat
11. Cool in dyebath unitl room temperature
12. Remove specimens and squeeze out excess dyebath
13. Rinse with distilled water until the water runs clear
14. Wash with 5% zero solution
15. Rinse with distilled water until the water runs clear
16. Hang to dry via clothes pins in lab

Table D10. Method 10

Replication	Weight of specimens (g)	Weight of colourant (g)	Volume of water (mL)	Weight of additives (g)
1	7.53	3.01	602	n/a
2	7.51	3.00	600	n/a
3	7.48	2.99	598	n/a
4	7.54	3.02	604	n/a
5	7.51	3.00	600	n/a
6	7.50	3.00	600	n/a
7	7.49	3.00	600	n/a
8	7.53	3.01	602	n/a
9	7.54	3.02	604	n/a
10	7.44	2.98	596	n/a

1. Prepare dyebath with hard water solution and colourant.
2. Place beaker on heating element
3. Raise the temperature to 85 °C
4. Maintain at 85 °C for 120 minutes
5. Stir every five minutes
6. Remove from heat
7. Remove specimens and squeeze out excess dyebath
8. Wash in hot soapy water (CGSB 19.1, test method 1 soap solution)
9. Rinse with distilled water until the water runs clear
10. Hang to dry via clothes pins in lab

Table D11. Method 11

Replication	Weight of specimens (g)	Weight of colourant (g)	Volume of water (mL)	Weight of additives (g)
1	7.53	3.77	754	n/a
2	7.51	3.76	753	n/a
3	7.54	3.77	754	n/a
4	7.53	3.77	754	n/a
5	7.5	3.75	750	n/a
6	7.47	3.74	748	n/a
7	7.5	3.75	750	n/a
8	7.53	3.77	754	n/a
9	7.48	3.74	748	n/a
10	7.53	3.77	754	n/a

1. Prepare dyebath with distilled water and colourant and let stand at room temperature for 16 hours.
2. Place beaker on heating element.
3. Raise temperature over 30 minutes to 82 °C
4. Stir every five minutes
5. Maintain at 82 °C for 30 minutes.
6. Cool the dye bath to 50 °C then enter wet fibre
7. Raise temperature to 82 °C
8. Maintain for 60 minutes.
9. Allow the test fabric to cool in the bath to 22 °C
10. Remove specimens and squeeze out excess dyebath
11. Rinse with distilled water until the water runs clear
12. Hang to dry via clothes pins in lab

APPENDIX E

Suppliers

EarthGuild
Address: 33 Haywood Street, Asheville North Carolina, 28801 USA
Phone number: 1-800-327-8448 or (828) 255-7818
Fax Number: (828) 255-8593
Web address: http://www.earthguild.com
Email: inform@earthguild

Louet Sales
Address: R.R. 4, Prescott Ontario, K0E 1T0 Canada
Phone number: (613) 925-4502
Fax Number: (613) 925-1405
Web address: http://www.louet.com
Email:info@louet.com

Test Fabric Ltd.
Address: PO Box 26, West Pittston, PA 18643 USA
Phone number: (570) 603_0432
FAX number: (570) 603_0433
Web address: http://www.testfabrics.com
Email: testfabric@aol.com

APPENDIX F CIELAB RESULTS FOR TEST FABRIC

Method	Specimen	Replication	Direction	Face	Measure	L2	A2	B2	DE / cmc
0	1	0	2	1	1	88.39	-1.91	14.22	0.6545
0	1	0	1	2	1	88.38	-1.91	14.25	0.6346
0	1	0	1	2	1	88.61	-1.92	14.17	0.6878
0	1	0	2	2	1	88.60	-1.91	14.12	0.7227
0	2	0	1	1	1	88.57	-2.17	15.31	0.1422
0	2	0	2	1	1	88.54	-2.14	15.33	0.1352
0	2	0	1	2	1	88.65	-2.14	15.23	0.1016
0	2	0	2	2	1	88.69	-2.14	15.24	0.1140
0	3	0	1	1	1	88.32	-2.08	15.20	0.0632
0	3	0	2	1	1	88.33	-2.07	15.17	0.0529
0	3	0	1	2	1	88.54	-2.07	15.01	0.1015
0	3	0	2	2	1	88.55	-2.05	14.96	0.1368
0	4	0	1	1	1	88.42	-2.11	15.43	0.1936
0	4	0	2	1	1	88.37	-2.13	15.37	0.1593
0	4	0	1	2	1	88.57	-2.09	15.29	0.1015
0	4	0	2	2	1	88.56	-2.09	15.28	0.0938
0	5	0	1	1	1	88.26	-2.03	15.87	0.5153
0	5	0	2	1	1	88.24	-2.06	15.87	0.5104
0	5	0	1	2	1	88.43	-2.04	15.76	0.4314
0	5	0	2	2	1	88.38	-2.05	15.78	0.4441
0	6	0	1	1	1	88.56	-2.17	15.35	0.1620
0	6	0	2	1	1	88.55	-2.17	15.32	0.1456
0	6	0	1	2	1	88.67	-2.13	15.26	0.1120
0	6	0	2	2	1	88.65	-2.17	15.29	0.1429
0	7	0	1	1	1	88.14	-1.84	14.24	0.6675
0	7	0	2	1	1	88.14	-1.85	14.24	0.6646
0	7	0	1	2	1	88.23	-1.83	14.24	0.6657
0	7	0	2	2	1	88.16	-1.99	14.25	0.6352
0	8	0	1	1	1	88.58	-2.21	15.31	0.1718
0	8	0	2	1	1	88.60	-2.22	15.29	0.1749
0	8	0	1	2	1	88.70	-2.21	15.22	0.1640
0	8	0	2	2	1	88.74	-2.20	15.20	0.1610
0	9	0	1	1	1	88.40	-2.14	15.93	0.5396
0	9	0	2	1	1	88.39	-2.12	15.92	0.5332
0	9	0	1	2	1	88.52	-2.10	15.83	0.4712
0	9	0	2	2	1	88.48	-2.12	15.85	0.4838
0	10	0	1	1	1	88.41	-2.14	15.21	0.0760
0	10	0	2	1	1	88.41	-2.16	15.19	0.0906
0	10	0	1	2	1	88.57	-2.13	15.04	0.1071
0	10	0	2	2	1	88.59	-2.14	15.05	0.1111
					AVE	88.47	-2.08	15.15	0.3069
					MAX	88.74	-1.83	15.93	0.7227
					MIN	88.14	-2.22	14.12	0.0529
					STDEV	0.16	0.11	0.54	0.2345
					l	2.00			
					c	1.00			
					L	2.00			
					C	1.00			

APPENDIX G
Forms

Form A - Specimen Record Form
Form B - L*A*B* Measurement - Test Fabric
Form C - L*A*B* Measurement - Dyed Specimen
Form D - Effluent Results

Form A - Specimen Record

Method _____ Date ________________ 2001 Colourant to water ratio 1:200

Room temperature _________ °C Relative Humidity _____________%

Fibre to colourant ratio ___:___ Weight of mordant _________

Replication	weight of specimens (grams)	calculated weight of colourant (grams)	actual weight of colourant (grams)	volume of water (ml)
1				
2				
3				
4				
5				
total weight				

Method _____ Date ________________ 2001 Colourant to water ratio 1:200

Room temperature _________ °C Relative Humidity _____________%

Fibre to colourant ratio ___:___ Weight of mordant _________

Replication	weight of specimens (grams)	calculated weight of colourant (grams)	actual weight of colourant (grams)	volume of water (ml)
6				
7				
8				
9				
10				
total weight				

Form C - L*A*B* Measurement - Dyed Specimen

Method ______ Specimen ______ Replication______

Date________________________

	L*	A*	B*
spwafu1			
spwafu2			
spwafu3			
spwefu1			
spwefu2			
spwefu3			
spwafd1			
spwafd2			
spwafd3			
spwefd1			
spwefd2			
spwefd3			

Form C - L*A*B* Measurement - Dyed Specimen

Method _____ Specimen ______ Replication_______

Date______________________

	L*	A*	B*
spwafu1			
spwafu2			
spwafu3			
spwefu1			
spwefu2			
spwefu3			
spwafd1			
spwafd2			
spwafd3			
spwefd1			
spwefd2			
spwefd3			

Form B - L*A*B* Measurements - Test Fabric

Date ________________________

Specimen	face up warp			face up weft			face down warp			face down weft		
	L*	A*	B*	L*	A*	B*	L*	A*	B*	L*	A*	B*

Form D - Effluent Results

Date________________________________

Method	Rep.	pH of unfiltered effluent	pH of filtered effluent	L*	A*	B*
	1					
	2					
	3					
	4					
	5					
	6					
	7					
	8					
	9					
	10					

APPENDIX H
Macros and formulas for Excel file

Table H1. - Macros and formula for excel to run ΔEcmc calculation

Cell	Cell Name	Formula in cell or data	Visual Basic Macro
A	Method		
B	Specimen		
C	Replication		
D	Direction		
E	Face		
F	Measure		
G	L2	L* measurement	
H	A2	A*measurement	
I	B2	B* measurement	
J	L1	copy of location of standard for L	
K	A1	copy of location of standard for A	
L	B1	copy of location of standard for B	
M	DD2	G#-J#	
N	C1	=SQRT((L#^2)+(K#^2))	
O	C2	=SQRT((H#^2)+(I#^2))	
P	DDC	=O#-N#	
Q	SSL	=(M#^2)+((H#-K#)^2)+((I#-L#)^2)	
R	AA	=Q#-(M#^2)-(P#^2)	

S	AA1	=AAA(K#,L#)

```
Attribute VB_Name = "AA1"
Function AAA(A1, B1)
If (A1 * B1) = 0 Then
   AAA = Sgn(A1 + B1)
End If
End Function
```

T	BB1	=BBB(L#,K#)

```
Attribute VB_Name = "BB1"
Function BBB(B1, A1)
If (A1 * B1) = 0 Then
   BBB = Sgn(Abs(B1))
End If
End Function
```

U	H1	=HHH(K#,L#,S#,T#)

```
Attribute VB_Name = "H1"
Function HHH(A1, B1, AA1, BB1)
If (A1 * B1) = 0 Then
   HHH = 90 * (BB1 - AA1 + 1)
Else:
   HHH = 180 - Sgn(B1) * 90 - Atn(A1 / B1) * 57.3
End If
End Function
```

V	T	=TTT(U#)

```
Attribute VB_Name = "T"
Function TTT(H1)

If H1 <= 164 Or H1 >= 345 Then

   TTT = 0.36 + Abs(0.4 * Cos((H1 + 35) / 57.3))
Else:
   TTT = 0.56 + Abs(0.2 * Cos((H1 + 168) / 57.3))
End If
End Function
```

W	AA2	=A2A(H#,I#)

```
Attribute VB_Name = "AA2"
Function A2A(A2, B2)

If (A2 * B2) = 0 Then

   A2A = Sgn(A2 + B2)

End If
End Function
```

X	BB2	=B2B(I#,H#)

```
Attribute VB_Name = "BB2"
Function B2B(B2, A2)
If (A2 * B2) = 0 Then
   B2B = Sgn(Abs(B2))
End If

End Function
```

Y	H2	=H2H(H#,I#,W#,X#)

```
Attribute VB_Name = "H2"
Function H2H(A2, B2, AA2, BB2)
If (A2 * B2) = 0 Then

   H2H = 90 * (BB2 - AA2 + 1)
Else:
   H2H = 180 - Sgn(B2) * 90 - Atn(A2 / B2) * 57.3
End If
End Function
```

Z	SL	=SSL(J#)

```
Attribute VB_Name = "SL"
Function SSL(L1)

If L1 <= 16 Then
   SSL = 0.511
Else:
   SSL = 0.040975 * L1 / (1 + 0.01765 * L1)
End If
End Function
```

AA	SC	=((0.0638*N#)/(1+0.0131*N#))+0.638)	
AB	F	=SQRT(N#^4/N#^4+1900)	

AC	SH	=AA#*(V#*AB#+1-AB#)	
AD	DDH	=DDH(R#)	

```
Attribute VB_Name = "DH"
Function DDH(AA)
If AA > 0 Then
   DDH = Sqr(AA)
Else:
   DDH = 0
End If

End Function
```

AE	DL/ISL	=M#/(location of l value*Z#)	
AF	DC/cSC	=P#/(location of c value*AA#)	
AG	DHH	=AD#/AC#	
AH	DA	=Y#-U#	
AI	Y1	=Y1Y(AH#)	

```
Attribute VB_Name = "Y1"
Function Y1Y(DA)
If Abs(DA) > 180 Then
   Y1Y = -1
Else:
   Y1Y = 1
End If
End Function
```

AJ	Y2	A1#*AH#	
AK	DH/SH	D1H(AJ#,AG#)	

```
Attribute VB_Name = "D"
Function D1H(Y2, DHH)
If Y2 <= 0 Then
   D1H = -1 * DHH
Else:
   D1H = DHH
End If
End Function
```

AL	DE/cmc	=SQRT(AE#^2+AF#^2 +AK#^2)	

Table H2. Test data for CMC equation

Test Pair	L2	A2	B2	L1	A1	B1	Excel DE/cmc	AATCC DE/cmc
1	86.85	5.59	7.29	87.39	5.32	7.19	0.4157	0.42
2	81.16	-3.35	-3.52	80.44	-3.35	-3.84	0.4517	0.45
3	85.18	-2.26	55.52	85.84	-2.45	55.67	0.2681	0.27
4	59.03	-16.64	14.86	60.11	-15.42	14.97	0.9655	0.97
5	42.36	0.64	-3.68	43.64	0.35	-3.39	0.8113	0.81
6	39.90	26.57	-0.57	39.75	27.95	2.35	2.3382	2.33
			l	2.00				
			c	1				

Note: The results from AATCC test method differ for test pair 6 from the excel file. When the excel data is round up it reads 2.34, .01 higher than the AATCC test method 173-1998 results. I then ran the data through the Basic program and found that it gave the same result, I believe there is an error in the test methods' data. Below are the results from the Basic computer program for test pair 6.

Figure H1 Print out of Basic program results for trial pair # 6

```
METHOD No.1

Input CMC(l:c) weighting factors 'l','c'? 2,1
Input L*,a*,b* of standard? 39.75,27.95,2.35
L,a,b Hue angle of standard 39.75  27.95  2.35

Input Specimen #? 1
Input L*,a*,b* of specimen? 39.90,26.57,_0.57

L,a,b and hue angle of specimen #1: 39.9 , 26.57 ,_.57 ,
358.7776

DL/lSl        DC/cSc      DH/SH        Decmc (2 : 1)
____________________________________________________________

7.835449E_02    _.756429     2.211044     2.33817
```