Alternative Production for Pollution Reduction
Executive Summary

This report details the work that was conducted on alternative production by the project team. It includes factory observations, water quality analysis from factory processes, laboratory dyeing trials and factory bulk trials.

The results show that many of the factories are operating below optimal efficiency. What this means is that not all the dye added to the dye bath that could be fixed to the fabric is being fixed, so a proportion of it is being lost in the waste water. There are many reasons for this but some fundamental reasons are that some dye managers do not fully understand the chemistry of reactive dyes and therefore mix incompatible dyes and use them under the wrong conditions of temperature and pH. Another issue is that factories do not always achieve the right shade when the fabric is first dyed and as a result have to re-dye or re-shade the fabric, wasting time and resources, and increasing costs and pollution.

The project team offered the factories a number of solutions for addressing these problems and physically demonstrated them by conducting bulk dyeing trials with improved recipes in participating factories. The results in terms of changes in the factories have sadly been limited but factory managers and staff now have increased awareness of the issues and some are gradually making changes. Some of the factories have purchased and installed improved laboratory and factory dyeing equipment which will significantly improve efficiency and reduce costs. They have also changed their recipes to use compatible dyes and some have changed dye supplier as they tested the quality of the dyes that they were receiving and found that they were of poor quality and could not therefore offer high fixation or good reproducibility.

Although change is slow it is taking place, and with the knowledge created and disseminated in this process to participating factories and other factories in the area and across Bangladesh, through workshops and the Bangladesh Garment Manufacturers and Exporters Association, it is hoped that the changes will spread and ultimately make a significant difference to pollution reduction.
Contents

1 Background.......................................................................................................................... 1
1.1 Observations of Existing Dyeing Processes.................................................................... 2
  1.1.1 Dyes and Chemicals ................................................................................................. 2
  1.1.2 Machinery ................................................................................................................ 3
  1.1.3 Dye Selection ........................................................................................................... 3
  1.1.4 Recipes .................................................................................................................... 4
  1.1.5 Liquor Ratio ............................................................................................................ 4
  1.1.6 Profile ....................................................................................................................... 4
  1.1.7 pH Recording ........................................................................................................... 6
  1.1.8 Lab to Bulk ............................................................................................................... 6
  1.1.9 Re-dyeing and Re-shading ...................................................................................... 7
2 Sampling Dye Process Stages ............................................................................................ 8
  2.1 Determination of Exhaustion and Fixation ................................................................... 8
  2.2 Pollution monitoring .................................................................................................... 9
  2.3 Determination of dye compatibility ............................................................................ 9
  2.4 Report to Factories ..................................................................................................... 10

3 Trials .................................................................................................................................. 11
  3.1 Laboratory Trials ....................................................................................................... 11
    3.1.1 Changing dye recipe ............................................................................................. 11
    3.1.2 Changing dye suppliers ....................................................................................... 14
  3.2 Findings from laboratory trials .................................................................................. 14
    3.2.1 Report to factories ............................................................................................... 15
  3.3 Bulk trials .................................................................................................................... 15
    3.3.1 Changing dyeing profile .................................................................................... 16
    3.3.2 Changing dye type ............................................................................................... 16
  3.4 Findings from Bulk Trials .......................................................................................... 16

4 Recommendations ............................................................................................................ 18
  4.1 Controlling lab to bulk ............................................................................................... 18
  4.2 Selecting Compatible Dyes .......................................................................................... 18
  4.3 Optimizing the process ............................................................................................... 18
  4.4 Optimizing Dye Recipe ............................................................................................... 19
  4.5 Good House Keeping ................................................................................................. 19
    4.5.1 Storage of chemicals and dyes ............................................................................ 19
    4.5.2 Handling ............................................................................................................... 19
    4.5.3 Date logging ........................................................................................................... 20
4.5.4 Equipment.............................................................................................................. 20
4.5.5 Preparing inputs..................................................................................................... 20
4.5.6 Supervision of the process..................................................................................... 20

5 Changing the Mind Set.............................................................................................. 21

Annex A: Observations and Recommendations for Factory 25 ...................... 22
Annex B: Sample Report Laboratory trial with Bifunctional Dyes .............. 34
1 Background

An evaluation of industrial pollution in South and Southeast Asia by the World Bank found many small and medium enterprises (SMEs) generating pollution loads in excess of international standards. In relation to Bangladesh the report found that: “*national regulation of industrial effluents has been weak, with severe shortages of supporting funds and trained personnel. Formal monitoring and enforcement procedures have had little impact on plants’ environmental performance*” (Hettige et al., 1996 p.1892). The report highlighted the importance of engaging with industry and of community action, or informal regulation, in successful pollution mitigation strategies (Hettige et al., 1996). These features are at the core of the project approach, the project works to engage stakeholders and to *provide incentives for change*. The project attempts to reduce the pollution generated from textile dyeing operations by assessing existing dyeing practices and conducting factory trials to determine what adjustments to production and effluent treatment processes could be beneficial in terms of improving efficiency and reducing pollution.
2 Assessment of Existing Dye practices

The assessment of dye practices was undertaken through:

- Observation of existing dyeing processes in the laboratory and on the factory floor;
- Sampling of liquor and effluent from dye process stages; and
- Reporting to the factory on assessment, including suggestions for changes.

2.1 Observations of Existing Dyeing Processes

Observations of the processes followed in the laboratory, to develop dye recipes, and on the factory floor were conducted. These included assessing the dyeing profile usually followed by the factory in terms of time, temperature, pH and when chemicals are added. The monitoring and control of time, temperature and pH were observed in lab and factory floor, including whether or not the correct equipment was used and if it appeared to be working satisfactorily.

It was observed that some of the factories have technical staff with some degree of knowledge in textile chemistry and dye application, which has enabled them to develop adequate application procedures similar to those outlined by European dyestuff manufacturers. In other factories less qualified staff rely on the ‘Dyers Manual’ supplied by the dyestuff companies, which give recommendations for the application of their specific dyes. This can be a problem as these do not always provide adequate information and at least one manual provides application procedures that are not correct and, if followed, can lead to un-level dyeing and/or poor fixation of the dyes being applied.

Some staff have little knowledge of chemical processes but try to give the impression that they do. For example, the term ‘azo free’ has been used by almost all of the factories visited though not one has given a satisfactory explanation of what this term means.

2.1.1 Dyes and Chemicals

It was found that the fabrics being dyed in the project area range from 100% cotton to blends of cotton with polyester or viscose, and wool dyeing is being conducted by two dye houses in the project area. The dye operations utilize both reactive and disperse dyes with some sulphur dyes (mainly black shades). The predominant dye type used is reactive dyes, with sulphato-ethylsulphone (SES), the mono-chloro-triazine (MCT) reactive groups. The factories also use chloro pyrimidine reactive dyes for dyeing from both European suppliers and the domestic market (India, Pakistan & Taiwan). The factories generally use Remazol dyes, DyStar, Germany Cibacron F dyes, Ciba, Switzerland Eberzol dyes,) Everlight Chemical Industries Inc, Taiwan.
A number of other chemicals are also used as auxiliaries in the dyeing process, for pretreatment, washing and finishing. These include wetting agents (KK), anti-crease agent (ESK, ECS), caustic soda (CaOH), soda ash (NaCO₃), hydrogen per oxide (H₂O₂), stabiliser (TiCl₂ CBB), hydrogen peroxide killer/neutraliser, acetic acid, DBC (Cibasil), levelling agent (Optavonsr) and anti-foam (RG airtex).

2.1.2 Machinery

The textile factories are involved in a variety of different production processes including printing and dyeing. The dyeing machinery ranges from older winch types to modern pressurized jet machines. These machines vary in their efficiency. The winch types usually have limited temperature control and require a significant amount of manual operation which can lead to errors during dyeing; such as filling to the incorrect liquor volume, heating to the wrong temperature and dosing chemicals or dyes at an unsuitable rate. They also require higher liquor to fabric ratios to ensure level dyeing. The newer jet machines tend to operate from a computerized controller for temperature and chemical or dye dosing leading to greater reproducibility between dye batches so that fewer dye batches are rejected by the customer due to incorrect shade or unlevelness. These types of machines also contribute to a reduction in water consumption, energy and chemicals since the computer controller can accurately control liquor volumes and temperature. However the control mechanism can be overridden and the machine controlled manually, this then leads to the introduction of human error and what was a sophisticated piece of machinery is reduced to the basic winch. Such practices have been observed in some of the factories.

In general factory owners have opted to install medium cost, semi-automatic winch machines (for example Fong). For many of these the economic depreciation period is over and they no longer perform adequately. They also have some flaws such as leakage from the steam line which means that they do not achieve the required temperature. Some factories have now started to upgrade their machinery and are installing more automated machines that perform well, with low liquor ratios and shorter dyeing times (like Sclavos).

2.1.3 Dye Selection

While selecting dyes the factories usually consider only cost but rarely consider factors that relate to the quality of the dye, including the quality of the dye produced by the manufacturer and the subsequent changes in quality due to the age of the dye, poor storage and handling. Crucially dye managers need to consider the compatibility of dyes in a mixture, including the reactive group and the size of the molecule. They often only opt for higher quality dyes for dyeing light shades as these are more difficult to achieve.
Factory managers are often not concerned with the full economic cost associated with selecting dyes. This includes not only the cost of the dye per kilogram, but the quantity of dye required, which should reduce if good quality dyes of high colour strength are used, the time taken for dyeing, and the need for re-dyeing and re-shading which should also reduce if good quality dyes are used as results should have better reproducibility and levelness.

2.1.4 Recipes

Dye managers are usually sent sample of fabric by textile buyers and asked to match the colour. In many cases they do this by developing recipes based on their past experience and matching the colour by eye. However increasingly dyers are generating recipes and checking results using colour matching software. The use of modern software reduces the potential for error and for shade adjustments in bulk production.

2.1.5 Liquor Ratio

The liquor to fabric ratio is an important factor in the dyeing recipe and it was sometimes observed that some of the water level monitors were difficult to read and the machine operators do not always fill the machines to the water quantity specified in the recipe. The water meters are not working properly and sometimes the factory people do not fill the bath accurately. The consequence of this is that the concentration of dye and auxiliaries is inaccurate and the fabric will not be on-shade.

2.1.6 Profile

The factories practise different dyeing processes for different shades, principally the high temperature method (Figure 1) and the constant temperature method (Figure 2), the latter of which is usually used for light shades. The factors that make up a dyeing profile are: the time for dying and the time at which chemicals are added or temperature is altered; the temperature; when soda ash is added in relation to the addition of dye; and the pH attained after the addition of soda ash.
The factories usually use open rinsing for washing and this consumes a great deal of water. It has been found that around 20,000 litre of water are consumed in the dyeing off approximately 200 kg of fabric.
**Time**

The total time required including pre-treatment and dyeing is approximately 8 hours for any shade. If however the shade does not match with the sample then they have to run the machine at a particular temperature for an additional time period and thus the total time for the batch can vary.

**Temperature**

As the factories usually follow a constant temperature method for light shades they ramp the temperature of dyeing machine to 60°C and allow the dyeing machine to run at this temperature for around 3 to 4 hours. Within this time period they add dyes, soda ash and salt one after another.

For dark shades the common practice is to add salt and dye altogether at room temperature and after a certain period of time soda ash is added to start dye fixation on to the fabric. The temperature is then ramped to 70°C, 80°C or 85°C until the shade is matched. As soon as the machine temperature reaches at 70°C a fabric sample from the dye bath is taken and compared with the existing buyer’s sample. If it is not matched the incremental temperature increase is continued until the correct shade is reached. Thus it was observed that a standard method for any particular recipe is not followed.

**2.1.7 pH Recording**

pH control is inadequate in many factories and some do not measure pH at all. During the process sampling no pH monitoring was observed. It is important for the pH meter to be temperature compensating because manually temperature adjusted pH meters can lead to complications and errors, thereby reducing the benefit of pH measurement. Good quality pH strips cost approximately Tk 7 each to buy but they are not as accurate and may have problems with deep dark colours as they rely on colour change as the indicator.

In floor production the factory staff only take pH readings before dyeing when the liquor is almost neutral and after the addition of soda ash. It was observed that their pH meter was not working properly most of the time and they depended on universal indicator paper which is not recommended internationally. Some factories have pH meters but they do not calibrate them regularly so the pH they measure is not accurate or reliable. For example, the pH after addition of soda ash should be pH 11.5 for VS dyes but it was observed that it was often below pH 11.

**2.1.8 Lab to Bulk**

There are differences between factors in the laboratory and on the factory floor. For example agitation of fabric and machine efficiency. There are also differences in procedures such as the
number and type of auxiliaries added, for example soda ash is added in the laboratory for alkali
treatment but in bulk production both caustic and soda ash are added to get the correct shade.
There are also differences in the number of wash-offs and the vigour of washing.

The factory floor staff usually slightly alter the recipe and dye process provided by the
laboratory. They usually increase or decrease the shade percentage of the dyes based on their
past experience as the equipment on the floor and other factors that are different from the
laboratory mean that if they follow the recipe exactly as provided by the laboratory they will not
achieve the correct shade. They also use a different profile on the factory floor and in the
laboratory. Although this is necessary, the lack of record keeping of changes and difference
between the factory floor and the laboratory means that errors and re-shading are common.

2.1.9 Re-dyeing and Re-shading

Continuous observation and discussion with dye managers revealed that errors due to incorrect
recipes or not following the recipes closely are common. Some of the dye managers mentioned
that they around 10-15 percent of fabric needs to be re-shaded and 5-10 percent re-dyed.
3 Sampling Dye Process Stages

To assess the efficiency of the production process it was necessary to carry out water quality analysis of certain parameters to calculate how much dye and other chemicals are present in the wastewater. Sampling was therefore undertaken in different factories and the samples were analysed for the following parameters: pH, chemical oxygen demand (COD), biological oxygen demand (BOD), sodium, sulphate, total dissolved solids (TDS), total suspended solids (TSS) and colour (absorbance).

The absorbance measurements were used to calculate the percentage of dye that had been fixed on to the fabric and therefore the percentage that was lost in the dye bath. The optimal fixation varies according to the dye type being used (MCT, VS or bifunctional) but should be around 70 percent or more. The results of this were reported on to the factories involved (Appendix 1).

3.1 Determination of Exhaustion and Fixation

The absorbance values of dyeing process samples were used to calculate the fixation rate and efficiency of the processes, in conjunction with observations this aided the identification of potential modifications to the dyeing process. To calculate exhaustion and fixation the following equations are used:

\[
\text{Exhaustion (E \%) = \left[\frac{(OD_0 - OD_1)}{OD_0}\right] \times 100}
\]

\[
\text{Fixation (F \%) = \left[\frac{OD_0 - (OD_1 + OD_2 + \cdots + OD_x)}{OD_0}\right] \times 100}
\]

\[
\text{Total Efficiency (TE \%) = \left(\frac{E \times F}{100}\right)}
\]

Where:
- Optical Density (OD) = absorbance (or Chemical oxygen demand, COD)
- \(OD_0\) = Start absorbance with all dye in dye bath
- \(OD_1\) = Absorbance at the end of the dyeing (dye exhausted onto fabric)
- \(OD_1 + OD_2 + \cdots + OD_x\) are rinses after washing

It is also possible to calculate the fixation through a combination of absorbance measurement and calculation of the extinction coefficient of the individual dyes in the dyeing recipe. This method was tested in one of the factories.

The drawback of both these methodologies is that they require an absorbance spectrophotometer, which the factories do not have as part of their usual dyeing equipment. The project team are therefore continuing to work with one of the factories to introduce a
method to measure fixation using reflectance spectroscopy as most of the factories now have “data color” machines that use spectroscopy to match shades.

3.2 Pollution monitoring

The samples analysed from the production process where primarily to provide an understanding of the process and the chemicals used, to calculate efficiency and to provide a baseline against which to measure improvements after the introduction of cleaner production options. They were not specifically intended to be used as a measure of the effluent leaving the factory, however, it is possible to use them to an extent to calculate this (although end of pipe samples are better for this purpose).

It was found that all parameters measured except pH exceeded the national environmental quality standards for textile factory effluent for all samples. On the basis of the calculations of overall concentrations of the parameters analysed for, it can be said that the effluent exceeded the standards for all but pH. However the average calculation is extremely rough as the quantity of rinse water used has been estimated and if this is considerably more than the value used in the calculation then the average values could be much lower. For pH it was found that some process effluents were above standards but the average was within limits. To accurately determine the concentrations in the final effluent leaving the factory it is necessary to continuously sample the outflow pipe for a 24 hour period.

No standard has been set for sulphate but the standard for sulphide, which sulphate is easily converted to in the environment, is 2mg/l. Data obtained showed that it is desirable to reduce the level of sulphate entering the factory waste stream.

3.3 Determination of dye compatibility

One of the dyer’s major objectives is to produce goods with the exact shade desired by the client. This usually requires the use of a mixture of dyes, often a mixture of red, blue and yellow. These should all be dyes with about the same substantivity and requiring similar conditions to facilitate reaction with the fibre. This means that dyes should be chosen with the same reactive groups, either MCT, VS or a combination of MCT and VS (mixed bifunctional dyes). They should also be from the same dye supplier as these dyes will have been created to effectively work with each other and will have very similar properties. If this is done then the dyes will require similar dyeing conditions, in terms of time and temperature profile, and pH for optimal dyeing results and fixation.

Unfortunately it was found that not all factory staff were sufficiently knowledgeable about dye chemistry and the consequences of using incompatible or less compatible dyes.
3.4 Report to Factories

As soon as field visit regarding continuous observation and sampling carried out report was sent to each factory which includes the observation, fixation and exhaustion and total efficiency, pollution monitoring, action point to be taken to optimize processes, result and discussion, options for good housekeeping and an overall summary. One of the sample report is attached. (see appendix)
4 Trials

These observations and findings resulting in the project team working to develop better recipes using compatible dyes and dyeing profiles that were more appropriate for the dyes being used. These were tested many times in laboratory trials at the Bangladesh Textile Engineering College. Laboratory scale trials were also conducted at factories and these were followed by bulk scale trials.

The results of the trials showed that optimizing the dyeing profile does improve the exhaustion and fixation. However the trials initially used the dye combinations favoured by the factories, and these were not always compatible dyes. As a result the dyeing time was increased and the temperature raised to ensure that the dyes reacted with the fibre. This resulted in less dye being wasted, which saved money and was good for the environment, but meant that the dyeing took longer and was therefore more costly in terms of time wasted and energy for heating the dye bath.

The project team then worked to develop optimal recipes with compatible dyes to demonstrate that it was possible to improve fixation (reduce dye wasted), have a dyeing time of similar length to existing dyeing times, and improve reproducibility and right first time dyeing.

4.1 Laboratory Trials

Laboratory trials are carried out using small amounts of fabric (5g of fabric) dyed in a sample dyeing machine. This is done to determine the recipe for bulk production that matches the sample sent by the textile buyer.

A number of different laboratory trials were conducted in which various parameters were changed to try to determine the method that would provide the correct shade as well as high fixation, low dye use and ultimately pollution reduction without incurring the factory excessive costs. Trials were carried out for both light shade and darker shade. The project team mainly considered the following two issues while conducting laboratory trials. These were changing the dye recipe and changing dye suppliers.

4.1.1 Changing dye recipe

Different trials were carried out considering dye recipe which mainly include

- Dyeing profile
- Dye type
- Liquor ratio
- Auxiliaries
**Dyeing Profile**
At the beginning of the project trials were carried out for light shades using the factory laboratory method.

**Factory Laboratory Method 1**

![Diagram of Factory Laboratory Method 1](image)

**Figure 3: Factory laboratory method 1**

**Project Laboratory Method 1**

The profile in this method is different to usual laboratory practice in that:
1. The temperature is ramped and held and 60°C and 80°C
2. Soda ash is added at 60°C

![Diagram of Project Laboratory Method 1](image)

**Figure 4: project laboratory method 1(HBF Profile)**
Some trials were carried out using the Factory method for dark shade (Figure 2) and the Project laboratory method 1 (HBF profile) though the quantity of dyes used was changed.

**Factory Laboratory Method 2**

![Diagram of Factory Laboratory Method 2](image)

**Figure 5: Factory laboratory method 2**

**Project Laboratory Method 2**

The profile of project laboratory method (Figure 6) is different to usual laboratory practice (Figure 5) in that the soda ash is added separately at 80°C.

![Diagram of Project Laboratory Method 2](image)

**Figure 6: Project laboratory method 2**

**Project laboratory method 3**

Project laboratory method was used for light shades for which vinyl sulphone dyes have been used.
Figure 7: Project laboratory method 3

It is evident from the profile that the proposed project method always suggests adding soda ash at higher temperature as soda ash initiates dye fixation and it was found that higher fixation was achieved when soda ash was added later.

Liquor Ratio
A trial was conducted for the dark shade with a lower liquor ratio. The highest exhaustion and fixation was achieved using the project method 2 and using a lower liquor ratio of 1:8.

Auxiliaries
A few trials were carried out to test the use of sodium chloride (common salt) rather than sodium sulphate (glauber salt). In the trial a lesser amount of refined sodium chloride salt was used in both solid and liquid form, instead of glauber salt in the laboratory dyeing process to see if would give the same or better exhaustion and fixation as glauber salt. Results were not conclusive and further experiments are needed to be carried out to see if less amount of sodium chloride can be used. It would be desirable to change to common salt as glauber salt is responsible for the sulphate pollution of the water bodies, which leads to the production of hydrogen sulphide gas, which is extremely poisonous.

4.1.2 Changing dye suppliers
In this case the team used all hetero bifunctional (HBF) dyes but from different dye suppliers. First of all the team started test dyeing with dyes from the dye supplier 1 (Dysin), and compared with dyes of dye supplier 2 (Atlas).

4.2 Findings from laboratory trials
The results do not show too much difference between the two methods. Some findings of the laboratory showed that:
The best fixation in laboratory trials when using the Factor recipe was achieved using the HBF dyeing profile with a 10% reduction in orange dye. A 10% reduction in all dyes also gave a high fixation (> 73%), which would be beneficial in terms of reduced pollution and costs.

High fixations of up to 81% were achieved using all HBF dyes from Supplier 1, using the HBF profile. High fixations of up to 79% were also achieved using HBF dyes and the Factory profile. Suggesting that if the factories were to change dyes, even if they will not change profiles this could prove to be beneficial.

However, HBF dyes are more expensive and will add to costs unless it can be shown that less dye can be used to achieve the correct shade or that the percentage of “right first time” dyeings is improved. This was however not shown in these tests as the highest fixations were achieved for the full recipe.

The same results were shown using dyes from different dye supplier although fixation was slightly higher.

The fixations achieved for glauber salt and common salt were almost identical at 82%. It was found that the liquid form generally offered better results in terms of fixation but that the time taken to dissolve the salt was a limitation as around 70-90 kg needs to be dissolved for each dyeing.

A comparative study of the costs shows that though using similar dye types will increase the cost if all HBF dyes by around Tk 800 for 100 kg of fabric dyed, it will result in a higher percentage of right first time dyeings and less dye and is therefore likely to offer an overall cost saving if the full economic cost of dyeing is considered and not just the dye cost.

4.2.1 Report to factories

Reports were sent to factories after conducting laboratory trials. This report mainly deals with the data on fixation and exhaustion of dyes and also on recommendations based on the method which achieved highest fixation. See Annex A for an example of one of the factory feed back reports.

4.3 Bulk trials

Bulk trials were the next logical step to determine whether or not the findings in the laboratory could be replicated under factory conditions and if the barriers from “lab to bulk” could be overcome.
4.3.1 Changing dyeing profile

For bulk dyeing a dark shade was dyed using the factory’s choice of dyes but a project dyeing profile. The proposed project method was compared with the factory method (Figure 2). The change made was to dye at both 60°C and 80°C as the factory recipe used both MCT and VS dyes, which require the following parameters:

- VS – 60°C and pH 11.5
- MCT – 80°C and pH 10.5

Consequently the proposed project dyeing profile was developed (figure 7). A critical difference between the two profiles is the temperature at which the soda ash is added. In the proposed project profile it is added later when the bath has reached 60°C. There are also differences in the time taken to dye the fabric and this may have implications for the profitability of the factory.

![Diagram of proposed project method for bifunctional dyes]

Figure 8: Proposed project method for bifunctional dyes

4.3.2 Changing dye type

Two bulk trials were conducted with all HBF dyes and using the proposed project method which is designed for HBF dyes.

4.4 Findings from Bulk Trials

- There is no significant difference between the factory method and project method using the dye recipe proposed by the factory.
- There is a difference if all HBF dyes are used rather than a mixture of incompatible dyes.
• It was found while conducting a bulk trial that the factory do not take a reading after the addition of alkali and although they use a strong alkali (caustic soda) there is some concern that they are not achieving the required pH.
• The project method also used a closed rinsing. This took more time but saved a considerable quantity of water.
• Common salt was used in bulk trial and it was found that for dark shades using common salt can be a good practice as better fixation was achieved and it is less polluting than sodium sulphate. However factory staff complain that it is hard to dissolve and often contains impurities which affect the quality and levelness of the dyeing.
5 Recommendations

The trails resulted in a number of recommendations being made to factory managers and dye managers. The project team held discussions and negotiations with them to see which they would consider implementing and to work with them to try to introduce changes in the factory.

5.1 Controlling lab to bulk

The project team advised the factory staff to record all changes to recipes and dyeing conditions when going from lab to bulk. In this way they will avoid the “trial and error” approach that many currently adopt. It is regularly observed that a 10% shade addition is required when going from lab to bulk, then this can be added to the recipe from the start. This should improve the frequency of “right first time” dyeing. These variations between the lab and the factory floor mean that there needs to be strong communication between laboratory staff and staff on the factory floor. Lab Managers and Dye House Floor Managers need to establish a good relationship and work together towards following the optimal recipes created in the laboratory and reproducing them on the factory floor. Careful observation and monitoring need to take place to ensure that the correct shade is produced, and any variables are considered and compensated for during the transfer from laboratory to bulk.

5.2 Selecting Compatible Dyes

Factories tend to use a mixture of MCT, VS and HBF reactive dyes. The project team recommended that the dye managers start to develop recipes with just one of these dye types to ensure that they are compatible. Some factories have already changed their processes and now do this.

Many dye suppliers now provide exhaustion curves for each dye and some provide software that compare exhaustion curves for a selection of dyes. If two dyes have similar curves they can be considered to be compatible. More dye managers and factory managers need to take account of the exhaustion curves of the dyes that they use.

5.3 Optimizing the process

The dyeing time-temperature profile is very important and should be based on the dyes used. It should be clearly documented for each recipe developed, and the recipes and procedures carried out in the floor production.

Since there is a often great deal of uncertainty about the particular type of reactive group in a given reactive dye, dye selection must often be from one particular manufacturer’s dye range and the dyeing profile should be based on the manufacturers recommendations.
5.4 Optimizing Dye Recipe

Optimizing dye recipe includes optimizing the liquor ratio, accurately matching the shade using colour matching software and considering the fixation of dyes. The correct liquor ratio for the recipe must be maintained otherwise incorrect concentrations of dyes and other chemicals will be present in the dye bath and the right shade will not be achieved first time. The liquor ratio will be altered when extra water is added to mix the dyes, the salt and the alkali. This should be factored into the liquor ratio in the recipe.

5.5 Good House Keeping

There is evidence in some factories of poor ‘housekeeping’, resulting in cross-contamination of dyes and in production of incorrect shades. For example, if the same utensil is used to meter out first a black dye for one recipe and then a yellow for another, without washing between dyes, the yellow dye will become contaminated with the black dye remaining on the utensil. This will result in a duller yellow shade than required, leading to the need for reprocessing and, depending on depth of shade of the contaminated dyeing, possible ‘over-dyeing’ to another shade. Open containers and humid conditions can also lead to hydrolysis of the dye and result in the problems associated with hydrolysis.

5.5.1 Storage of chemicals and dyes

The correct storage and handling of dyes and chemicals is also necessary in order to gain reproducible dyeing to the right shade in the shortest time i.e. ‘right first time’. .

- Chemicals should not be stored in the laboratory for more than 1 month.
- If dyes are received in boxes, the inner plastic bags should transferred to containers or plastic drums that can be re-sealed to reduce contact with air and moisture.
- When a new barrel of dye is opened a sample must be sent to the laboratory for test dyeing. The label on the barrel should be changed to record the date that a sample was sent to the laboratory.

5.5.2 Handling

When measuring out chemicals or dyes Containers should be open for the minimum time possible, to minimise contact with moisture. 
Masks should be worn when handling fine powders such as dyes to prevent inhalation.
Gloves should be worn when handling chemicals and dyes to prevent contact with skin and dermatitis.
5.5.3 **Date logging**

- Chemicals received by the laboratory should be recorded into a logbook. The information should include: the chemical type; the date it was received by the factory; and the date it entered the laboratory.
- The containers should be labelled with the chemical or dye name and the date received. When the bag is opened, the date of opening should be added to the details on the label.
- A file should be kept of each dye type (e.g. Reactron Black B, Reactron Supra Black HFGR) in which the test dyeing samples are stored, to allow comparison of the quality of the dye received.

5.5.4 **Equipment**

Good equipment in the laboratory that best represents the machines on the factory floor greatly improves the frequency of "right first time" dyeing. Additional equipment can be purchased to monitor dyeing efficiency, but in general a good understanding of dye chemistry and good shade matching equipment is likely to be sufficient. On the factory floor, machines that are automated will improve the dyeing process by maintaining the correct time, temperature and pH. Equipment should be kept clean to avoid contamination of samples. Thermometers, pH meters and balances should be checked and calibrated regularly (at least once every six months).

5.5.5 **Preparing inputs**

Weighing fabric, weighing and measuring out chemicals should be considered carefully and if digital weighing machine can be afforded (which is not expensive) will measure the fabric weight more accurately and thus measurement can be optimized.

5.5.6 **Supervision of the process**

Monitoring the process by the machine operator has to be supervised by the dye manager or floor in charge regularly.
6 Changing the Mind Set

Ultimately it was felt that many of these things were easily achievable and offered considerable benefits to the factories, however even though the factory managers and directors acknowledged this limited effort appeared to be made to adopt the changes. It was obvious that a major issue in alternative production is the mind set of the management and the factory staff. The management need to become more aware of the “full economic cost” of dyeing operations and not to narrowly focus their attention on the cost per kilogram of dye. If they begin to do this they will see the value of investing in better equipment, changing to reputable dye suppliers who provide better quality dyes as well as improved technical support, and altering established factory practices. Simple protocols such as checking the quality of dyes when a new order is received, could dramatically improve the efficiency and quality of dyeing, which would reduce costs and pollution.
Annex A: Observations and Recommendations for Factory 25

Factory Profile
Factory 25 is an integrated factory undertaking knitting, dyeing, finishing and garment production. Dyeing is currently limited to cotton although the company in currently building a second dyeing plant for other fabrics. The main dyes used are fibre reactive dyes of vinyl sulphone and mono chloro triazine types from both European suppliers and Asia (India, Pakistan and Taiwan), and a small quantity of sulphur dyes at the request of customers. The plant houses 3 Thesis Jet and 9 atmospheric winch dyeing machines, producing approximately 5000 kg of dyed fabric per day. All machines were controlled by integrated pc control to monitor liquor level, liquor flow rate, fabric transport rate (m/min), dosing and temperature, the winch machines only had temperature controllers and liquor level indicators. Approximately 70 % of dyeing is right first time, although initial transfer of recipes from the laboratory to bulk can cause some problems. Fixation rates are approximately 75 % for pale shades and 65 % for medium and dark shades.

Sampling
In February 2003 process effluent samples were collected for three processes using 100 % knitted cotton fabric:

1. Vermillion red (including pre-treatment)
2. Bleach white (only stages different to pre-treatment)
3. Sulphur black

The samples were analysed in an analytical lab for the following parameters:
- pH
- Chemical Oxygen Demand (COD)
- Biological Oxygen Demand (BOD)
- Sodium
- Sulphate
- Total Dissolved Solids (TDS)
- Total Suspended Solids (TSS)
- Colour (absorbance)

The absorbance values can be used to monitor the material balance (eg. help to calculate the fixation rates) and efficiency of the processes, which in conjunction with observations aid the identification of process modifications with the aim of improving efficiency and reducing pollution.

Results and Recommendations
The results and recipes sampled are given in Appendix 1. Unfortunately, the research team have concerns over the accuracy of some of the results provided by the analytical laboratory, particularly for colour, and initial calculations of efficiency suggest that COD values may also be inaccurate. This is frustrating for both the factory and the research team. The team require
information in which they have confidence before they can provide you with detailed information of the extent of potential savings you could make. Therefore, to provide the factory with accurate results and optimal support, additional sampling will be required, a process we hope you will support. It is intended to conduct these within the next few weeks and to return the results to the factory within a week.

**Calculating Total Efficiency for Textile Dyeing**

The calculation that will be applied to the results in order to determine the exhaustion and fixation, and ultimately the potential for cost savings is as follows:

Exhaustion (E %) = \[
\frac{\text{OD}_0 - \text{OD}_1}{\text{OD}_0} \times 100
\]

Fixation (F %) = \[
\frac{\text{OD}_0 - (\text{OD}_1 + \text{OD}_2 + \ldots + \text{OD}_x)}{\text{OD}_0} \times 100
\]

Where:
- Optical Density (OD) = absorbance
- OD_0 = Start absorbance with all dye in dyebath
- OD_1 = The dyebath at the end of the dyeing (i.e. when the dyebath is dropped)
- OD_2 + OD_2 + \ldots + OD_x are rinses after washing

This can be worked through for an example dyeing to show the potential for cost savings if fixation is increased. If in the example:

\[\begin{align*}
\text{OD}_0 &= 0.4 \\
\text{OD}_1 &= 0.1 \\
\text{OD}_2 &= 0.04 \\
\text{OD}_3 &= 0.02
\end{align*}\]

Then:

Exhaustion % = \[
\frac{0.4 - 0.1}{0.4} \times 100 = 75 \%
\]

Fixation % = \[
\frac{0.4 - (0.1 + 0.04 + 0.02)}{0.4} \times 100 = 60 \%
\]

Assuming that under optimal conditions the maximum possible exhaustion is 80 % and the maximum possible fixation is 77 % (Figure 1), then it is possible to increase the fixation by 17 %.
Increasing the fixation would result in less waste and would provide cost savings. For example, assuming that these figures relate to dyeing 250 kg of fabric with 20 kg Reactron Supra Black HF-GR (8 % on mass of fabric), then the amount of dye wasted is 17 % of 20 kg (3.4 kg). If Reactron Supra Black HF-GR costs TK 350 per kilogram, then the cost of the dye lost in this dyeing is:

\[3.4 \text{ kg} \times \text{TK 350} = \text{TK 1190}\]

This is equivalent to a loss of dye per kilogram of fabric dyed of:

\[
\frac{\text{TK 1190}}{250 \text{ kg}} = \text{TK 4.76 per kg}
\]

Assuming 5000 kg of fabric is dyed daily for 300 days per year, of which 50 % is dyed using Reactron Supra Black HF-GR at 8 % on mass of fabric, then:

\[5000 \text{ kg} \times 300 \text{ days} \times 0.5 = 750000 \text{ kg of fabric is dyed annually.}\]

If fixation is 60 % for all these dyeings, then TK 4.76 is lost for every kilogram of fabric dyed and over a year it is possible to make a total saving of approximately:

\[750000 \text{ kg} \times \text{TK 4.76} = \text{TK 3570000 per year}\]
\[= \$ 67,356 \text{ per year}\]

Whilst at present we are unable to determine the potential percentage improvement in fixation for factory 25, it is likely that low or no cost adaptations will lead to improvements in efficiency and savings (the proposed resampling will enable the research team to determine this accurately). These adaptations can be divided into:
• Good housekeeping;
• Process specific options;
• Selection of raw materials, in particular the chemicals used in dyeing;
• Optimising process and chemical use; and
• Technology change and/or modification;
• Training.

Good Housekeeping
Good housekeeping measures are usually simple and inexpensive, or even free, but can lead to substantial increases in efficiency.

Storage
If reactive dyes are not stored correctly the quality and the concentration of active materials will decline and dyeing will subsequently be affected. Uptake of moisture makes the dyes heavier (this is like a dilution effect) and consequently an incorrect quantity of actual dye will be measured out, which will reduce the effective depth of dyeing and result in the need for reshading, which will extend the dyeing time and increase the energy used. Therefore containers must be tightly shut and kept dry so that the dyes do not absorb moisture. Dyes and auxillaries not supplied in a waterproof and tightly closing container should be transferred to clean, dry containers as soon as they are received. There were examples seen in factory 25 where such modification could be employed.

Moisture via open containers also leads to hydrolysis of the dye (especially if warm – i.e. it is influenced by temperature). Hydrolysis is the process where by the active part of the dye reacts with water. This will render the dye “unreactive” leading to dyeings of poor wet fastness since the dye will remain relatively weakly attached to the fibre through physical forces (as opposed to the much stronger covalent bonding that should occur with reactive dyes) and continually ‘bleed’ during subsequent washing if it is not removed effectively after dyeing. Initial tests on dyes suggest that hydrolysis and some degradation of dyes are taking place as a result of storage conditions. Further tests will be required to calculate the possible effect of this on dyeing efficiency.

Hydrogen peroxide also has a limited shelf life and should be kept dry and ideally cool to prevent it from decomposing, which will subsequently lead to an unsatisfactory level of whiteness of fabrics.

Handling of Chemicals
Clean and dry utensils should be used to measure out each dye to prevent cross-contamination of dyes and production of incorrect shades. For example, if the same utensil is used first for a black dye for one recipe and then a yellow for another, without washing and drying between dyes, the yellow dye will become contaminated from the black dye remaining on the utensil; this will result in a duller yellow shade than required and the need for reprocessing and, depending on the depth of shade of the contaminated dyeing, possible ‘over-dyeing’ to another shade.

Careful weighing with the use of accurate scales is essential to ensure the correct quantities for the recipe are used and that reshading or extra washing are not required. Spillage of dyes was
observed in factory 25, suggesting that dyes and other chemicals are being wasted and that weighing may be inaccurate. The use of a data logger attached to a good pair of scales would provide an accurate record of the actual mass of dye weighed out each time.

Good housekeeping is also essential for the dyeing laboratory. The laboratory is well set up, Good Laboratory Practice (GLP) should also be ensured at all times including for example: cleaning relevant utensils and glassware between use; using appropriate standard methods to make up stock solutions on a regular basis; and regular calibration of equipment such as scales.

**Optimising Processes and Chemical Use**

These include in-factory measures to optimise the dyeing process and use of chemicals to improve efficiency.

**Liquor Ratio**

The correct liquor ratio for the recipe must be maintained (in test dyeings and on large scale dyeings), otherwise incorrect concentrations of dyes and other chemicals will be present in the dyebath and the desired shade may not be achieved first time. To achieve this all water meters should be working accurately and machine operators should carefully monitor water quantities when machines are filled. Machines which have level monitoring tubes, such as those in factory 25 should be regularly changed to ensure that they are clean and that the water level can easily be read.

Consideration of low liquor ratio’s should take place as this will reduce chemical use and increase fixation, both of which should save money and reduce pollution. Performance properties, such as levelness will need to be evaluated. This needs to be tied in with consideration of “agitation” of fabric and circulation of fabric/liquor.

**pH Control**

The pH value must be carefully controlled as it significantly affects the application of dyes and chemicals. For example, in the application of sulphato-ethylsulphone (SES) reactive dyes to cotton (a major dye class used in Factory 25), the dye is initially exhausted onto the fabric under slightly acidic pH conditions, the pH of the dyebath should then be raised to approximately pH 11 to facilitate bonding between the dye and fabric. Exceeding (or not reaching) this pH may cause the dye to hydrolyse (or remain un-reacted) to a greater extent and fixation will be significantly reduced and a large percentage of the dye will be lost in the wastewater. Exceeding the pH also means that alkali is wasted, increasing costs. The correct pH can easily be attained by monitoring the pH of every dyebath (possibly at more than one stage). This can be done in a number of ways, using either a temperature compensating pH meter (costing about Tk 9500 to buy). It is important that the pH meter is temperature adjusting because manually temperature adjusted pH meters can lead to complications and errors, reducing the benefit of pH measurement. Good quality pH strips (costing approximately Tk 7 each to buy) can also be used (although these are not as accurate and may have problems with deep dark colours).

**Temperature Control**

Similarly, if the temperature is too high hydrolysis of the dye may occur and if it is too low then complete reaction with the fibre will not be achieved. In both cases the dye will be lost to the
effluent. Ensuring the automatic temperature monitors are all functioning properly and that
temperature is carefully controlled by the operators will improve fixation and efficiency.
Optimising the temperature (and time) may also reduce the quantity of salt used.

Optimal Dyeing Conditions
Temperature, liquor ratio and pH are dependant on the recipe and dye class used. Experiments
are currently being conducted on the types of dyes used at Factory 25 to try to determine
optimal dyeing conditions. It is expected that it may be possible to reduce chemical
consumption in textile wet processing by 20 – 30%.

Electrolyte Control
The dosing rate and the concentration of electrolyte is important as it will determine the level of
exhaustion and also, therefore, the fixation level. There is need for further consideration of this.

Training
Several of these options can be achieved by training staff so that they understand the dyeing
process and the importance of careful monitoring (and following the dyeing instructions exactly).
It is important to have appropriately trained people working at night (if dyeing is taken place and
the percentage of right first time dyeings is to be increased). It is bad practice to only have one
person trained to carry out a particular job, especially if the job goes on for 24hrs a day.

Health and Safety
A number of practices observed could be easily and inexpensively improved from a health and
safety perspective, for example:

- Pipetting of solutions by mouth should not be practiced, pipette bulbs should be used,
  these are inexpensive and will protect workers and improve accuracy;
- Gloves should always be worn to handle reactive dyes;
- Breathing in dust (from dyes and certain other chemicals) should be avoided. Dust masks
  should be worn if exposure is likely, especially on a large scale operation (includes
  weighing, mixing and transfer of dyes if performed manually).
- Take care with strong alkali’s (corrosive) and wear gloves and protective clothing if
  possible;
- Take care when dealing with liquors at high temperature (risk of burns);
- Take care when lifting/moving heavy loads (eg. large scale, wet fabric) and ideally wear
  protective footwear.

Factory Effluents
The samples analysed from the production process where primarily to provide an understanding
of the process and the chemicals used, to calculate efficiency and to provide a baseline against
which to measure improvements after the introduction of cleaner production options. They are
not specifically intended to be used as a measure of the effluent leaving the factory, however, it
is possible to use them to an extent to calculate this (although end of pipe samples are better for
this purpose). It is the intention of the team to collect an end of pipe composite sample over a
24 hr period to more accurately determine the form and concentration of factory effluent.
However, the results can be used to estimate the pollution levels, their relation to national water quality standards and potential problems (Table 1).

**Table 1: Summary of factory process water quality and national legislative standards**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Maximum</th>
<th>Average over the three processes (estimate)</th>
<th>National waste water quality standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>11.6</td>
<td>8.4</td>
<td>6.5-9*</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>20520</td>
<td>1724</td>
<td>200</td>
</tr>
<tr>
<td>BOD (mg/l)</td>
<td>1302</td>
<td>252</td>
<td>150*</td>
</tr>
<tr>
<td>Sodium (mg/l)</td>
<td>32921</td>
<td>1977</td>
<td>No standard</td>
</tr>
<tr>
<td>Sulphate (mg/l)</td>
<td>14500</td>
<td>1320</td>
<td>No standard</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>55995</td>
<td>6680</td>
<td>2100</td>
</tr>
<tr>
<td>TSS (mg/l)</td>
<td>21584</td>
<td>1158</td>
<td>150</td>
</tr>
</tbody>
</table>

* Standard for textile effluent

The effluent therefore exceeds the standards for pH in some process effluents but it appears that on average it is within the limits. All other parameters measured exceeded the standards for both the maximum value and the average. However the average calculation is extremely rough as the quantity of rinse water used has been estimated and if this is considerably more than the value used in the calculation then the average values could be much lower. To accurately determine the concentrations in the final effluent leaving the factory it is necessary to continuously sample the outflow pipe for a 24 hour period.

Assuming that it is likely that the concentrations are above national standards, and composite sampling in other factories suggests that this is likely, it is necessary to reduce these parameters in the effluent. This can be achieved in the various ways stated above, including:

- Process optimisation - ensuring the best possible conditions are achieved e.g. having a good laboratory with good instruments and working practice; maintaining the correct liquor ratio, pH and temperature time ratio for the dye class.
- Chemical substitution - using for example less toxic or more effective chemicals e.g. heterobifunctional reactive dyes.
- Recycling - for example using final wash-offs as initial wash-offs in the next dyeing.
- Effluent treatment with a biological treatment unit. This could be jointly developed and managed with other factories, which would reduce capital and running costs.

**Summary**

The feedback and options highlighted in this report are based on the initial observations and conclusions drawn from the process water sampling and site visits. The project will provide further suggestions and options in the near future and it is hope that further testing of process water samples and test dyeings of dye samples will be conducted in the near future. It is also intended to run trials of some cleaner production options on a small scale, for example, using less salt or good quality sodium chloride instead of sodium sulphate. The project would bear the costs of the fabric and chemicals used in the trial, and we very much hope that you would consider undertaking some of these trials with us.

Your cooperation in this project is greatly appreciated and it is hoped that as a result of this work the factory will benefit from improved process efficiency and cost savings.
Appendix 1: Process Sampling Results

Vermillion Red, Machine Number 4: Fabric 291 kg, water 2900 l LQ 1:10

Pre-Treatment Cycle

Dyeing Cycle
<table>
<thead>
<tr>
<th>Water (l)</th>
<th>Sample ID</th>
<th>pH</th>
<th>COD (mg/l)</th>
<th>BOD5 (mg/l)</th>
<th>Na (mg/l)</th>
<th>Sulfate (mg/l)</th>
<th>TDS (mg/l)</th>
<th>TSS (mg/l)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>2900</td>
<td>25.4.1a</td>
<td>9.38</td>
<td>156</td>
<td>85</td>
<td>1.9</td>
<td>566</td>
<td>264</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2600</td>
<td>25.4.2c</td>
<td>5.88</td>
<td>2264</td>
<td>132</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2900</td>
<td>25.4.1b</td>
<td>7.99</td>
<td>40</td>
<td>22</td>
<td>1.0</td>
<td>322</td>
<td>54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2900</td>
<td>25.4.1c</td>
<td>6.93</td>
<td>179</td>
<td>52</td>
<td>1.0</td>
<td>304</td>
<td>43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2600</td>
<td>25.4.2</td>
<td>5.88</td>
<td>2264</td>
<td>132</td>
<td>25.5</td>
<td>2319</td>
<td>148</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2900</td>
<td>25.4.3</td>
<td>11.43</td>
<td>5192</td>
<td>402</td>
<td>30.6</td>
<td>9982</td>
<td>643</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2600</td>
<td>25.4.4</td>
<td>10.49</td>
<td>580</td>
<td>272</td>
<td>4.0</td>
<td>1137</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2600</td>
<td>25.4.5</td>
<td>9.04</td>
<td>676</td>
<td>232</td>
<td>2.0</td>
<td>1036</td>
<td>105</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2200</td>
<td>25.4.6</td>
<td>4.87</td>
<td>868</td>
<td>322</td>
<td>1.0</td>
<td>954</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2250</td>
<td>25.4.8</td>
<td>6.84</td>
<td>3420</td>
<td>1700</td>
<td>200</td>
<td>5361</td>
<td>397</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2850</td>
<td>25.4.9</td>
<td>10.41</td>
<td>1120</td>
<td>660</td>
<td>32921</td>
<td>11000</td>
<td>55995</td>
<td>2158</td>
<td></td>
</tr>
</tbody>
</table>

### Pretreatment:

- **PCLF** (detergent) = 1.45 kg (0.5 g/l), Ladiquest (sequester) = 1.45 kg (0.5 g/l), Ciba fluid C 1st = 1.75 kg (0.6 g/l), All together at 40°C for 5 mins

### Acid (granular) DROP

- Soda = 8.73 kg (3 g/l), Caustic = 4.37 kg (1.5 g/l)
- At 40°C for 5 mins, H₂O₂ = 8.73 kg (3 g/l) dosed in at 70°C over 10 – 20 mins, Sepa (stabilizer, Swiss) = 0.873 kg, (0.3g/l) raise to 95°C for 60 mins. DROP

### Cold rinse

- Ladiquest = 0.58 kg (0.2g/l), 20 mins at 40-95°C, cool to 80°C. DROP

### AP = 0.29 kg (0.1g/l), Acetic acid = 2.9 kg (1g/l)

- At 60°C for 20-30 mins

### Cold rinse

- Ladiquest = 0.87 kg (0.3g/l), Ciba C = 1.45 kg (0.5g/l)
- Acetic acid = 0.29 kg (0.1g/l), Raise to 60°C for 10 mins, take pH 5-6, Add dyes:
  - Reactron Supra yellow F3R = 5.529kg (1.90 g/l)
  - Cottofix red ME43L = 10.47 kg (3.6 g/l)
  - Remazol Blue RR = 0.32kg (0.11 g/l) Dose over 30 mins at 40-60°C

### Salt = 198 kg (68 g/l)

- Dose at 60°C for 30 mins and run for 10-15 mins, Soda = 58 kg (20g/l) dose at 60°C for 45-50 m ins then run for 1 hour, Sample fabric, DROP

### Dyes:

- Reactron Supra yellow F3R = 5.529kg (1.90 g/l)
- Cottofix red ME43L = 10.47 kg (3.6 g/l)
- Remazol Blue RR = 0.32kg (0.11 g/l) Dose over 30 mins at 40-60°C

### Salt = 198 kg (68 g/l)

- Dose at 60°C for 30 mins and run for 10-15 mins, Soda = 58 kg (20g/l) dose at 60°C for 45-50 m ins then run for 1 hour, Sample fabric, DROP

### Additional Notes:

- **Dilution:** 1:10
- **Peak Absorbance**
  - 448 nm: 2.690
  - 298 nm: 2.504

<table>
<thead>
<tr>
<th>Peak</th>
<th>λ (nm)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>448</td>
<td>2.690</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>2.504</td>
<td></td>
</tr>
</tbody>
</table>

- **Dilution:** None
- **Peak Absorbance**
  - 300 nm: 2.770

<table>
<thead>
<tr>
<th>Peak</th>
<th>λ (nm)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2.770</td>
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</tr>
<tr>
<td>Description</td>
<td>Date</td>
<td>Time</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>Continuous cold rinse</td>
<td>25.4.10</td>
<td>10.47</td>
</tr>
<tr>
<td>RSK = 1.74 kg (0.6 g/l)</td>
<td>25.4.11</td>
<td>9.27</td>
</tr>
<tr>
<td>Cold rinse for 10 mins</td>
<td>25.4.12</td>
<td>7.77</td>
</tr>
<tr>
<td>Acetic acid = 1.45 kg (0.5 g/l)</td>
<td>25.4.13</td>
<td>4.08</td>
</tr>
<tr>
<td>Cold rinse</td>
<td>25.4.14</td>
<td>5.09</td>
</tr>
<tr>
<td>Fixing Cibafix ECO = 1.75 kg (0.6 g/l)</td>
<td>25.4.15</td>
<td>6.83</td>
</tr>
<tr>
<td>Cold wash for 10 mins</td>
<td>25.4.16</td>
<td>7.02</td>
</tr>
<tr>
<td>Softener = 23.3 kg (8 g/l) at 40°C for 25 mins</td>
<td>25.4.17</td>
<td>7.22</td>
</tr>
<tr>
<td>Parameter</td>
<td>pH</td>
<td>COD (mg/l)</td>
</tr>
<tr>
<td>-----------</td>
<td>----</td>
<td>------------</td>
</tr>
<tr>
<td>PCLF (detergent) = 0.28 kg (0.1%)</td>
<td>2800</td>
<td>25.17.1</td>
</tr>
<tr>
<td>Sequester (HM) = 0.28 kg (0.1%)</td>
<td>All together at 80°C for 15 min DROP</td>
<td></td>
</tr>
<tr>
<td>DROP PCLF (detergent) = 1.14 kg (0.4%)</td>
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</tr>
<tr>
<td>Sequester (HM) = 1.14 kg (0.4%)</td>
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<tr>
<td>Ciba C = 1.7 kg (0.6%)</td>
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<tr>
<td>Caustic Soda = 7.1 kg (2.5%)</td>
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</tr>
<tr>
<td>Soda Ash = 2.84 kg (1.00%)</td>
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<tr>
<td>Stab = 1.0 kg (0.35%)</td>
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</tr>
<tr>
<td>All together dosing at room temp</td>
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</tr>
<tr>
<td>H₂O₂ = 14.2 kg (5.0%)</td>
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<td></td>
</tr>
<tr>
<td>at 45°C and then temp increased to 70°C for 10 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After adding H₂O₂ temp increased to 95°C for 60 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>At 95°C and run 20 – 30 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>add Bluton BVB = 511 gm (0.18%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DROP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recipe: Sulphur Black Fabric 239kg, liquor 2390 l, LQ 1:10</td>
<td>Water (l)</td>
<td>Sample ID</td>
</tr>
<tr>
<td>--------------------------------------------------------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td></td>
<td>2390</td>
<td>25.5.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCLF (0.5%)  = 1.2 kg, Soda (1.00%)  = 24 kg Temp 95 °C for 20 min and then drop</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2400</td>
<td>25.5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ciba (0.5%)  = 1.2 kg, Sodium Sulphite (5%)  = 12 kg, Temp increased from 40°C to 90°C for 10 mins. Add Dye: Sodium Sulphite (1.2%) = 29 kg, Sulphur black (8.5%) = 20.30 kg, dosing time 30 mins, run 10 min. Temp increased to 95°C for 1 ½ hour and add salt (10%) = 24 kg, soda (5%) = 12 kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>25.5.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rinse</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2500</td>
<td>25.5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hot wash: H₂O₂ (1.5%)  = 3.6 kg, Temp 40°C for 30 mins, Soda (1.0%)  = 2.4 kg, PCLF (0.5%)  = 1.2 kg, Temp increased from 40 to 95 °C for 30 mins, Drop</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>3000</td>
<td>25.5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cold wash</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2350</td>
<td>25.5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Softner (SF) (0.5%)  = 1.2 kg, Softner (HCS) (6%)  = 14 kg, Soda (0.2%)  = 0.48 kg Drop</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Peak λ (nm) | Absorbance | 296 0.430 |
| Peak λ (nm) | Absorbance | 312 1.557 |
| Peak λ (nm) | Absorbance | 296 2.143 |
| Peak λ (nm) | Absorbance | 326 1.649 |
| Peak λ (nm) | Absorbance | 292 2.205 |
| Peak λ (nm) | Absorbance | 324 1.802 |
| Peak λ (nm) | Absorbance | 300 2.722 |
| Peak λ (nm) | Absorbance | 236 3.408 |
Annex B: Sample Report Laboratory trial with Bifunctional Dyes

1. Introduction
Prior to bulk dyeing in factory floor, it is essential to develop an optimum production process under controlled condition. The optimum process will most efficiently utilize the ingredients of products and reduce the material that goes to waste water.

Earlier in this project, few studies have been conducted on developing a process with mixed dye type. But, no studies so far have been conducted on developing the process with same dye type. In this study, an attempt has been made to develop a process with similar dye type. The findings of the laboratory trial under controlled condition are discussed in this report.

2. Methodology:
Project and factory method were used in this trial. Project method is widely used and recommended by the dye suppliers and used by this research project. The factory method is used in factory floor for bulk trial. In this trial, these methods were evaluated against time; cost, shade and fixation.

In project method, soda ash is added at 60°C whereas in factory method soda ash is added at 30°C. Literature study suggests that soda ash initiates the hydrolysis of the process. Therefore, there is always a possibility of affecting the rate of fixation in fabric. In the factory method, soda ash is added at earlier stage of the process, so it is expected that the rate of fixation will be depleted in the fabric. Profiles of these methods are given below in Fig 1 and Fig 2.

For both methods, similar types of dyes were used. Dychufix Black GR 150, Dychufix Orange 2RXF 125 and Dychufix Navy Blue 2GL-XF H/C were used to develop a recipe for dark black shade. Note that these dyes were from same group i.e. bifunctional group and the supplier was Dysin. The trial was carried out in two separate days. Same recipes (see Appendix 1) were followed for factory and project method.
Figure 1: Profile of the project method.

Figure 2: Profile of the factory method.

**Equipment:** The Rota Dyer was used for dyeing and absorbance was measured with the HACH Spectrophotometer.

**Calculations:** The following formula was used for calculating the fixation, exhaustion and efficiency

\[
\text{Fixation} \% = \frac{\text{abs. at start of dyeing} - \text{abs. at end of dyeing} - \text{abs. of washes}}{\text{abs at start of dyeing}}
\]

\[
\text{Exhaustion} \% = \frac{\text{abs. at start of dyeing} - \text{abs. at end of dyeing}}{\text{abs. at start of dyeing}}
\]

\[
\text{Total Efficiency} \% = \frac{\text{Exhaustion} \times \text{Fixation}}{100}
\]

Sample 1: Exhaustion \% = \frac{(698-87.7)\times100\%}{698} = 87.4\%

Sample 1: Fixation \% = \frac{(698-87.7-28.35-26.528) \times 100}{698} = 79.57\%

Sample 1: Efficiency = \frac{87.4 \times 79.57}{100} = 69.54
5. Results and discussions

The first time right shade was achieved in the project and factory methods.

In order to find out the difference between the fixation rates of the factory and project method, an independent sample t test was carried out. The result of the test suggests that there was no difference (p>0.05, t= 0.212, df = 14) between the fixation rate of factory and project method. However, these results were found under controlled laboratory conditions. It is possible that fixation with the factory method may not be high during bulk trial as pH and other parameters may not be that accurate.

Table 3 (see Appendix 2) shows that Dysin dyes were less expensive than Atlas dyes. It also shows that the dyes for factory recipe were less expensive than other dyes. If the factory recipe is followed, there is always a risk of redyeing. According to the dye manager of factory 45, factory has to spend Tk 6000 for 300 kg fabric per year for redying dark shades. This cost includes electricity, manpower, dyes, chemical and auxiliaries. Therefore, the cost of dyes for factory recipe is much higher than it was anticipated. It is suggested that to reduce the risk of redying, recipe should be developed from same type of dyes. Results of this study also show that recipe developed from same type of dyes does not require redyeing.

Factory method requires 3 h 5 min and project method requires 2h 45 min. So, there is a clear difference between dyeing time of the two methods. Certainly, project method will be considered better as it requires less dyeing time. Cost wise it will also be considered better as electricity, manpower, water etc. cost will be less.

Recommendation

1. Similar dye type is recommended for developing the recipe.

2. The project method is recommended to follow as it saves time, cost, and gives good fixation rate.
APPENDIX: 1

Recipe 1: Control recipe

7.5% Dychufix Black GR 150  
0.4% Dychufix orange 2RXF 125  
1% Dychufix Navy Blue 2GL-XF H/C  
80g/l Glauber Salt solution(20 w/v %)  
20g/l Soda Ash(20 w/v %)  

Total Volume  
Final Liquor ratio

Note: Duplicate Samples were tested. They were labelled as 1,1a.

Recipe 2 - (Black GR 150 shade percentage was increased 15%, Navy blue shade percentage decreased 10%)

8.625% Dychufix Black GR 150  
0.4% Dychufix orange 2RXF 125  
0.9% Dychufix Navy Blue 2GL-XF H/C  
80g/l Glauber Salt solution(20 w/v %)  
20g/l Soda Ash(20 w/v %)  

Total Volume  
Final Liquor ratio

Note: Duplicate Samples were tested. They were labelled as 2,2a.

Recipe 3 - (Black GR 150 shade percentage was increased 10%, orange shade percentage decreased 10%, and Navy blue shade percentage decreased 10%)

8.25% Dychufix Black GR 150  
0.36% Dychufix orange 2RXF 125  
0.9% Dychufix Navy Blue 2GL-XF H/C  
80g/l Glauber Salt solution(20 w/v %)  
20g/l Soda Ash(20 w/v %)  

Total Volume

Recipe 2, 3, 4 are developed from recipe 1 by increasing or decreasing the shade percentage.
Final Liquor ratio 1:10

Note: Duplicate Samples were tested. They were labelled 3, 3a.

Recipe 4 - (Black GR 150 shade percentage was increased 15%, orange shade percentage decreased 10%, Navy blue shade percentage decreased 15%)

8.625% Dychufix Black GR 150 4.31 ml
0.36% Dychufix orange 2RXF 125 1.80 ml
0.85% Dychufix Navy Blue 2GL-XF H/C 0.85 ml
80g/l Glauber Salt solution (20 w/v %) 20.00 ml
20g/l Soda Ash (20 w/v %) 15.00 ml
Total Volume 41.96 ml

Note: Duplicate Samples were tested. They were labelled 4, 4a.
## Appendix 2

**Table 1: Results obtained from project method**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial absorbance</th>
<th>Absorbance after dyeing</th>
<th>Absorbance after cold wash</th>
<th>Absorbance after hot wash</th>
<th>Exhaustion</th>
<th>Fixation</th>
<th>Total efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>649.50</td>
<td>65.20</td>
<td>26.80</td>
<td>28.74</td>
<td>89.96</td>
<td>81.41</td>
<td>73.24</td>
</tr>
<tr>
<td>1a</td>
<td>605.50</td>
<td>64.30</td>
<td>21.00</td>
<td>27.28</td>
<td>89.38</td>
<td>81.41</td>
<td>72.76</td>
</tr>
<tr>
<td>2</td>
<td>723.75</td>
<td>114.50</td>
<td>42.10</td>
<td>41.12</td>
<td>84.18</td>
<td>72.68</td>
<td>61.18</td>
</tr>
<tr>
<td>2a</td>
<td>687.00</td>
<td>137.90</td>
<td>43.50</td>
<td>35.00</td>
<td>79.93</td>
<td>68.50</td>
<td>54.75</td>
</tr>
<tr>
<td>3</td>
<td>728.75</td>
<td>104.60</td>
<td>37.70</td>
<td>33.12</td>
<td>85.65</td>
<td>75.93</td>
<td>65.03</td>
</tr>
<tr>
<td>3a</td>
<td>800.00</td>
<td>103.70</td>
<td>33.10</td>
<td>44.34</td>
<td>87.04</td>
<td>77.36</td>
<td>67.33</td>
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<tr>
<td>4</td>
<td>906.60</td>
<td>121.00</td>
<td>41.70</td>
<td>48.58</td>
<td>86.65</td>
<td>76.70</td>
<td>66.46</td>
</tr>
<tr>
<td>4a</td>
<td>831.00</td>
<td>108.10</td>
<td>40.35</td>
<td>43.54</td>
<td>86.99</td>
<td>76.90</td>
<td>66.89</td>
</tr>
</tbody>
</table>

**Table 2: Results obtained from factory method**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial absorbance</th>
<th>Absorbance after dyeing</th>
<th>Absorbance after cold wash</th>
<th>Absorbance after hot wash</th>
<th>Exhaustion</th>
<th>Fixation</th>
<th>Total efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>698.00</td>
<td>87.70</td>
<td>28.35</td>
<td>26.52</td>
<td>87.44</td>
<td>79.57</td>
<td>69.58</td>
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<tr>
<td>1a</td>
<td>593.50</td>
<td>95.40</td>
<td>31.35</td>
<td>50.88</td>
<td>83.93</td>
<td>70.07</td>
<td>58.81</td>
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<tr>
<td>2</td>
<td>788.50</td>
<td>95.80</td>
<td>27.40</td>
<td>53.06</td>
<td>87.85</td>
<td>77.65</td>
<td>68.21</td>
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<tr>
<td>2a</td>
<td>740.00</td>
<td>107.80</td>
<td>21.25</td>
<td>50.50</td>
<td>85.43</td>
<td>75.74</td>
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<tr>
<td>3</td>
<td>735.00</td>
<td>101.50</td>
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<td>86.19</td>
<td>75.11</td>
<td>64.74</td>
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<td>90.40</td>
<td>26.15</td>
<td>43.86</td>
<td>88.26</td>
<td>79.17</td>
<td>69.87</td>
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<tr>
<td>4</td>
<td>827.10</td>
<td>116.50</td>
<td>34.15</td>
<td>41.06</td>
<td>85.91</td>
<td>76.82</td>
<td>66.00</td>
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<tr>
<td>4a</td>
<td>718.25</td>
<td>107.10</td>
<td>19.60</td>
<td>63.06</td>
<td>85.09</td>
<td>73.58</td>
<td>62.61</td>
</tr>
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</table>
Table 3: Price of dyes from different dye suppliers and factory for developing the dark black shade

<table>
<thead>
<tr>
<th>Dye supplier</th>
<th>Recipe for dark black shade</th>
<th>Shade%</th>
<th>Cost / kg</th>
<th>Total cost (Tk.)</th>
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</thead>
<tbody>
<tr>
<td>Atlas dye supplier</td>
<td>Reactron Supra Black HFG 100</td>
<td>8.63</td>
<td>320</td>
<td>2760</td>
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<tr>
<td></td>
<td>Reactron orange F2R 125</td>
<td>0.40</td>
<td>480</td>
<td>192</td>
</tr>
<tr>
<td></td>
<td>Supra Navy blue FB</td>
<td>0.90</td>
<td>590</td>
<td>531</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>Total 3483</strong></td>
</tr>
<tr>
<td>Dysin dye supplier</td>
<td>Black GR (150)</td>
<td>8.63</td>
<td>300</td>
<td>2587.5</td>
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<tr>
<td></td>
<td>Navy blue 2GL XF H/C</td>
<td>0.90</td>
<td>575</td>
<td>517.5</td>
</tr>
<tr>
<td></td>
<td>Orange 2RXF 125</td>
<td>0.40</td>
<td>385</td>
<td>154</td>
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<td></td>
<td></td>
<td></td>
<td><strong>Total 3259</strong></td>
</tr>
<tr>
<td>Factory</td>
<td>Reactron Supra Black HFG 100</td>
<td>6.65</td>
<td>320</td>
<td>2126.72</td>
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<tr>
<td></td>
<td>Reactron orange F2R 125</td>
<td>0.42</td>
<td>480</td>
<td>202.56</td>
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<tr>
<td></td>
<td>Reactron Black B</td>
<td>1.74</td>
<td>200</td>
<td>348.6</td>
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<td><strong>Total 2677.88</strong></td>
</tr>
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Note: all the above dyes are bifunctional dye except Reactron Black B.