The Effect of Laundry Detergents and Residual Alkali on the Light Fastness of Reactive Dyes on 100% Cotton

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By

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Declaration

This is to certify that this thesis comprises only the original work of the author, except where due acknowledgement has been made, and has not been previously submitted for assessment for any other degree. This thesis is less than 55,000 words in length exclusive of tables, bibliography and appendices.

Stanley Macarthur Fergusson
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Abstract

This study presents findings on the effect of domestic laundry detergents on the fastness to light of selected fibre reactive dyes applied to cotton. The study was carried out to elucidate the reasons for the accelerated colour loss of cotton garments washed under Australian domestic laundering conditions.

Cotton fabric dyed with commonly used reactive dyes were laundered with water only, several domestic detergents and a laboratory formulated neutral detergent, and then exposed to light for two hours in the wet state. Quantities of detergent used were in accordance with the manufacturers recommendations. Exposures were repeated fifteen times equivalent to 30 hours exposure. Colour loss and colour difference were measured after 5, 10 and 15 wash cycles and 10, 20 and 30 hours exposure.

When the fabric was exposed wet the colour faded more rapidly than when exposed dry to light. Detergents increased the colour loss even when the fabric was not exposed to light. The presence of an oxidizing bleach (sodium perborate) in the detergent increased colour loss during washing and wet exposure to light. Ultraviolet radiation from the light source, heat, moisture, alkali and oxidising bleach during exposure resulted in hydrolysis of the dye-fibre bond causing dye desorption during washing and rinsing. Water alone increased the fading of the dyes most likely due to presence of dissolved oxygen held within the fibre. The combination of ultraviolet radiation and oxidizing bleaches altered the chemistry of the dye and hence its shade. This was particularly evident on the black dye and one of the navy blue dyes.
Abbreviations and Symbols

AS  Australian Standard
BHS  British Home Stores
BS  British Standard
Cell  Cellulose
C.I.  Colour Index
cm  centimetre
CSIRO  Commonwealth Industrial Research Organisation
ΔE  Delta E – a measure of colour difference.
D65  Standard Northern Daylight
EDTA  Ethylene Diamine Tetra Acetic Acid
ETO  Ethylene oxide
g/l  grams per litre
g/m²  grams per square metre
GPR  General Purpose
HCl  Hydrochloric acid
H₂O₂  Hydrogen Peroxide
ICI  Imperial Chemical Industries (UK)
ISO  International Standards Organisation
JIS  Japanese Institute of Standards
K/S  A measure of total colour strength.
M  Molar
MBTF  Mercury Ballasted Tungsten Filament
MOD  Ministry of Defence (UK)
MSDS  Material Safety Data Sheet.
NaBO₃.4H₂O  Sodium perborate tetra hydrate.

NBS  National Bureau of Standards. (USA)

Nm  Nanometer (a measure of wavelength of light)

O  Oxygen

-OH  Hydroxyl group.

r.p.m.  revolutions per minute

TLC  Thin Layer Chromatography.

UK  United Kingdom

U.V.  Ultra Violet
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Chapter 1.
Introduction and Literature Review
1.1 Aims and Objectives
Consumers, retailers, garment and fabric suppliers report instances of unacceptable colour change and colour loss with cotton and cotton rich fabrics. Experience and anecdotal evidence suggests that the problem lies largely with navy blue and black pure cotton garments. The industry experience of the author suggests that the cause of the phenomena may be due to variations in laundry and drying practice. Domestic washing conditions vary widely with time, temperature and detergent type and concentration. Some of these variations in washing have been known to influence the performance and behaviour of a dye during the life cycle of the garment. Current tests for light fading do not provide data on the performance of dyes during domestic washing conditions and exposure to light during drying. Hence the accepted reference standards of dye performance may not necessarily reflect the performance under “real” life use.

This work aims to:
1. Study the effect of domestic laundry detergents and residual alkali remaining in the fabric from those detergents on the light fading properties of navy blue and black reactive dyes on cotton fabric.
2. Investigate the effect of repeated washing and subsequent fading of the dyed fabric that may occur during normal household laundering procedures.
3. Determine the effect of laundry detergent on the washing fastness of specific reactive dyes.

All experiments were to be designed to simulate “real life” domestic washing and drying conditions including selection of dyes and fabric.

This investigation proposes that the findings will be a more useful and reliable guide as to the light fading performance of certain commonly used reactive dyes on cotton fabrics.

1.2 Introduction
This chapter reviews relevant research literature into the problems associated with the light fading of reactive dyes on cotton. The development and chemistry of reactive dyes in relation to cellulose fibres principally cotton is outlined. The importance of the physical and chemical properties of cotton in respect to dyeing using reactive dyes is considered.
The chemical composition and cleaning action of laundry detergents is reviewed and the action of light on dyes in relation to fading explored. Other factors reviewed are the assessment of fastness properties of dyed fabric and light fading mechanisms. Physical and chemical factors affecting the light fading properties of dyed cotton are listed and methods of evaluating light fading summarised.

1.3 Reactive dyes

Reactive dyes, as their name implies, chemically react with the fibre to form a strong linkage that gives rise to high performance to wet treatments such as laundering. Today they are the largest single range of dyes used for the dyeing of cotton fibres and their blends. They are also very important for the printing of regenerated cellulosic fibres such as viscose rayon and lyocell (a special type of regenerated cellulose) where bright shades and high wet fastness is required. The revolution in reactive dye usage has been brought about by a steady reduction in the costs of manufacture; the cost reductions made possible by the production of larger batch sizes and improved yields during the coupling stage of manufacture.

1.3.1. History and Development of Reactive Dyes

The earliest reactive dye (1932) produced was Supramine Orange R [1] (C.I.Acid Orange 30); see Figure 1.1. It was not clearly understood at that time why this particular dye had excellent wet fastness on wool.

\[
\text{Figure 1.1 Supramine Orange R, C.I. Acid Orange 30 [1].}
\]

Subsequent research showed that the high wet fastness was due to the \( \omega \)-chlorine group which formed a covalent bond with the amino (-NH\(_2\)) group in the wool fibre via a nucleophilic substitution reaction according to the scheme given in Figure 1.2.

\[
\text{D -- NHCOCH_2Cl} + \text{NH}_2 -- W -- \text{COOH} \quad \text{Where D= chromophore} \\
\text{W= wool fibre} \\
\rightarrow \text{D -- NHCOCH_2NH -- W -- COOH + HCl}
\]

\[
\text{Figure 1.2. Reaction mechanism between Acid Orange 30 and wool fibre [1]}
\]
In 1937 a German patent was lodged that indicated it was possible to attach dyes to the wool fibre by covalent bonding. Various chemicals had already been tried that could react with the hydroxyl groups in cellulose. However, the very severe reaction conditions that had to be employed led researchers to the then conclusion that the dye-fibre reaction with cellulose was not practical or commercially achievable. Hence the various wool dyes that are capable of forming covalent bonds with cellulose were not considered at that time.

The first truly reactive dyes for cotton were developed by Rattee and Stephens at ICI England in 1955 [2]. These first cotton fibre reactive dyes were based on dichlorotriazine groups. When dyed under alkaline conditions (approximately pH 10.0) the resultant dyeings had excellent wet fastness. The alkalinity caused a reactive chlorine atom on the triazine ring to be substituted by an oxygen atom from the cellulose hydroxyl group. The alkali also caused acidic dissociation of some of the hydroxyl groups in the cellulose allowing the cellulosate ion (Cell — O²⁻) to react with the dye, as illustrated in Figure 1.3.

\[
\text{Cell – OH} + \text{OH}^- \rightarrow \text{Cell – O}²⁻ + \text{H}_2\text{O}
\]

\[
\text{Cell – O}²⁻ + \text{Dye – Cl} \rightarrow \text{Cell—O—Dye} + \text{Cl}⁻
\]

![Figure 1.3. Reaction mechanism between the triazine ring and the cellulose chain [3].](image)

1.3.2 Classification of Reactive Dyes

The dye chromophore is that part of the chemical structure of a dye that gives it colour. In reactive dyes the dye chromophore has at least one fibre reactive group added (refer Figure 1.4). This distinguishes reactive dyes from acid and simple direct dyes. The number and type of the reactive groups present in the dye determines its degree of reactivity and hence the dyeing conditions as shown in Table 1.1.
Table 1.1. Reactive groups and their relative reactivity at corresponding dyeing temperatures [3].

<table>
<thead>
<tr>
<th>Reactive group</th>
<th>Reactivity</th>
<th>Dyeing temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichlorotriazine</td>
<td>High</td>
<td>25 - 40</td>
</tr>
<tr>
<td>Monochlorotriazine</td>
<td>Low</td>
<td>80 - 85</td>
</tr>
<tr>
<td>Monofluorotriazine</td>
<td>Moderate</td>
<td>40 - 60</td>
</tr>
<tr>
<td>Trichloropyrimidine</td>
<td>Low</td>
<td>80 - 95</td>
</tr>
<tr>
<td>Dichloroquinoxaline</td>
<td>Low</td>
<td>50 - 70</td>
</tr>
<tr>
<td>Difluorochloropyrimidine</td>
<td>Moderate to high</td>
<td>30 - 50</td>
</tr>
<tr>
<td>Vinylsulphone</td>
<td>Moderate</td>
<td>40 - 60</td>
</tr>
<tr>
<td>Nicotinyltriazine</td>
<td>Moderate to high</td>
<td>100 – 130</td>
</tr>
</tbody>
</table>

Figure 1.4. Typical fibre – reactive structures in current commercial reactive dyes [3].

The largest single selling reactive dye today is C.I. Reactive Black 5, Figure 1.5, a homobifunctional or double anchor dye bis-β-sulphatoethersulphone introduced in 1957 by Hoechst (DyStar). Sales of 46,000 tonnes were recorded in 2003-4 [4].

Figure 1.5 Chemical structure of C.I.Reactive Black 5 [4].
The two sulphone reactive groups give the dye relatively high fixation and, as such, good economy. It is widely used for the production of black and navy mixture shades, but suffers from relatively poor fastness to light in all but the heaviest of depths. The dye reacts with the hydroxyl groups in the cellulose chain via a nucleophilic (Michaels) addition reaction [5]; see Figure 1.6. Since this particular dye is so widely used it has been selected as one of the dyes to be studied in this work.

\[
\text{D – CH}_2 = \text{CH} + \text{Cellulose – O}^{2–} \rightarrow \text{D – CH}_2\text{CH}_2\text{O – Cellulose}
\]

Where D = chromophore including the bridging group

**Figure 1.6 Michaels nucleophilic addition reaction [5].**

The development of bi-functional or double anchor, homo bi-functional or hetero-bifunctional reactive dyes increases the degree of fixation of the dye onto cellulose. The traditional hetero bi-functional dye consists of a monochlorotriazine group together with a vinyl sulphone group characterised by the Sumifix Supra range as in Figure 1.7. Other hetero-bi-functional dyes make use of fluorotriazine in conjunction with a vinyl sulphone group.

**Figure 1.7. Typical hetero-bi-functional reactive dye structure [3].**

Of the homo bi-functional dyes the most common are those based on bis-monochlorotriazine and bis-monofluorotriazine; the latter being the basis of the Cibacron LS [6] (low salt) though not exclusively, and the former Procion H-E range of dyes as shown in Figure 1.8. Note the two chlorine (Cl) atoms attached to the triazine ring in the centre of the molecule as indicated by the two arrows.
Higher fixation efficiency could possibly be obtained by incorporating additional reactive groups into the dye molecule. However, this can have a detrimental effect on the dyeing properties such as migration and can lead to lower build-up of the final shade. Several patents have been lodged for dyes that contain three reactive groups; in particular that disclosed by Bayer [7], refer Figure 1.9. The fluorine reactive group increases the reactivity of the dye and could therefore increase the dyebath exhaustion of the dye.

This structure with three reactive groups Figure 1.9 is claimed to have high reactivity and excellent fixation yields even when dyed under adverse long dye-liquor to fibre conditions. These developments have resulted in the introduction of more advanced reactive navy blue dyes that offer better overall light fastness properties. The majority of black dyes, however, remain mixtures still based on C.I.Reactive Black 5.

One of the advantages of the vinyl sulphone structure is that it contains a masking group (OSO$_3$Na) attached to the two methyl groups. This masking group increases the dyes resistance to hydrolysis during the early stages of the dyeing process and is not removed or
deactivated until the alkali is added at the fixation stage. It is for this reason that the dyes can be prepared and sold in liquid form which is the requirement for modern digital ink jet direct to fabric printing machines. The use of liquid dyes is very common in modern high speed textile printing factories, as well as in large dye houses where automatic dispensing machines and liquid delivery systems are used to prepare the required dyes for the process.

1.3.3 Factors Affecting Reactive Dye Performance

The various dye manufacturers dye ranges are characterised by their different reactive groups and their degree of reactivity towards the cellulosic fibre as shown in Table 1.1 & Figure 1.4. Environmental legislation, particularly in developed countries, has prompted dye manufacturers to develop and introduce more efficient reactive groups. These new reactive groups reduce both the effect of dye hydrolysis and problems associated with electrolyte contamination (principally sodium sulphate and sodium chloride) in dyehouse effluent. Sodium salts present a particular hazard to sewage treatment authorities as treated effluent containing high concentrations of sodium salts cannot be recycled onto land. Potassium salts are a suitable alternative electrolyte, since potassium is an essential element in the agricultural growth chain. Effluent containing potassium salts can be more readily recycled onto land. However the industry is reluctant to use the potassium salts due to the higher cost and perceived low availability.

Table 1.2 shows that reactive dyes for cellulose and hence cotton have the greatest loss to effluent. A major problem with the reactive dye system is the tendency for the dye to

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<th>Fibre</th>
<th>Estimated loss to effluent percent</th>
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<tbody>
<tr>
<td>Acid</td>
<td>Polyamide</td>
<td>5 – 20</td>
</tr>
<tr>
<td>Basic</td>
<td>Acrylic</td>
<td>0 – 5</td>
</tr>
<tr>
<td>Direct</td>
<td>Cellulose</td>
<td>5 – 30</td>
</tr>
<tr>
<td>Disperse</td>
<td>Polyester</td>
<td>0 – 10</td>
</tr>
<tr>
<td>Metal –complex</td>
<td>Wool</td>
<td>2 – 10</td>
</tr>
<tr>
<td>Reactive</td>
<td>Cellulose</td>
<td>10 – 50</td>
</tr>
<tr>
<td>Sulphur</td>
<td>Cellulose</td>
<td>10 – 40</td>
</tr>
<tr>
<td>Vat</td>
<td>Cellulose</td>
<td>5 - 20</td>
</tr>
</tbody>
</table>
\[ H-\text{OH} \ + \text{Dye} - \text{Cl} \rightarrow \text{Dye} -\text{OH} + \text{HCl} \]

Figure 1.10. Hydrolysis of a typical monochlorotriazine reactive dye.

hydrolyse during the dyeing process. This hydrolysis increases as both the pH and the temperature increase. Dye that has not diffused into the fibre, which is either lying on the fibre surface or in solution in the water, reacts with the hydroxyl (–OH) group in water rather than the cellulose as represented in Figure 1.10.

Once the dye has reacted with water it is not possible for it to react with the hydroxyl groups of cellulose. Hence the hydrolysed dye is disposed to effluent.

1.3.4 Environmental Issues
The loss to effluent is greater for cellulose than other fibres, due to the much lower affinity of the cellulose fibre for dyes dissolved in water. In water, both cotton cellulose and the dyes have a negative charge. Electrolyte is added to the dyebath to induce a positive charge at the fibre surface so that dyes may be absorbed at the surface before diffusion into the swollen fibre. Other dyes for cellulose such as sulphur and vat dyes suffer from other problems; the former using sodium sulphide in both manufacture and application and the latter using sodium dithionite as the reducing agent. Both of these sulphur containing chemicals are harmful to the environment as well as effluent transport and process systems such as concrete pipe work and effluent treatment works. At the concentrations employed sodium sulphide in the effluent stream breaks down yielding hydrogen sulphide gas which is poisonous; sodium dithionite yields sulphur dioxide which is also toxic.

1.4. The Cotton Fibre: An Overview

1.4.1 Sources of Cotton Fibre
Cotton is a natural vegetable fibre from the seedpod of plants in the *Gossypium* family or genus *Hyabiscus*, and is grown in subtropical climates. About 45% of total world wide fibre consumption is represented by cotton. The principle sources of cotton fibre are listed in Table 1.3. Cotton fibres exhibit considerable variability in their chemical and physical
properties, depending on the country of origin and the conditions under which they are cultivated.

Table 1.3. World cotton production 2006/2007 [9].

<table>
<thead>
<tr>
<th>Source</th>
<th>Million Kg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>7,079.90</td>
</tr>
<tr>
<td>India</td>
<td>4,746.30</td>
</tr>
<tr>
<td>USA</td>
<td>4,702.75</td>
</tr>
<tr>
<td>Pakistan</td>
<td>2,155.43</td>
</tr>
<tr>
<td>Brazil</td>
<td>1,524.04</td>
</tr>
<tr>
<td>Uzbekistan</td>
<td>1,175.69</td>
</tr>
<tr>
<td>Turkey</td>
<td>870.88</td>
</tr>
<tr>
<td>African Franc Zone</td>
<td>653.16</td>
</tr>
<tr>
<td>EU – 25</td>
<td>326.58</td>
</tr>
<tr>
<td>Syria</td>
<td>217.72</td>
</tr>
<tr>
<td>Egypt</td>
<td>217.72</td>
</tr>
<tr>
<td>Turkmenistan</td>
<td>261.26</td>
</tr>
<tr>
<td>Australia</td>
<td>239.49</td>
</tr>
<tr>
<td>Others</td>
<td>1,741.76</td>
</tr>
<tr>
<td><strong>World Total</strong></td>
<td><strong>25,930.45</strong></td>
</tr>
</tbody>
</table>

1.4.2 Physical and Chemical Properties of Cotton

Variability can be evident in fibres even from the same seed pod. Hence consistency in fibre sourcing is required to ensure minimal changes in processing characteristics between production lots. This presents a major challenge to the textile manufacturing industry. Figure 1.11. shows the major features in the cross-section of the cotton fibre.

![Cross-section of cotton fibre, showing salient features.](image)

Table 1.4. shows the typical chemical composition of cotton fibres. The cellulose content varies from a low of 88% to a high of about 96.0%. In the natural harvested state the average cotton fibre is approximately 90% pure cellulose. This percentage rises to about 96% after industrial scouring and bleaching. Scouring removes natural occurring waxes, salts and pectins present in the fibre. Pectins are a complex group of substances, the chief constituent being polygalaturonic acid. These pectins appear to be concentrated in the
Table 1.4. Chemical composition of cotton fibres [10].

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Percent (dry weight)</th>
<th>Typical</th>
<th>High</th>
<th>Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>94.9</td>
<td>96.0</td>
<td>88.0</td>
<td></td>
</tr>
<tr>
<td>Protein</td>
<td>1.3</td>
<td>1.9</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Pectins</td>
<td>0.9</td>
<td>1.2</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>1.2</td>
<td>1.6</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Wax</td>
<td>0.6</td>
<td>1.0</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Organic acids, maleic, ciric, etc.</td>
<td>0.8</td>
<td>1.6</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Total sugars</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pigment</td>
<td>Trace</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

primary wall of the fibre. The ash content consists of a range of inorganic compounds principally sodium, calcium and magnesium salts. Bleaching gives the fibre a brighter cleaner colour and serves to reduce imperfections in fibres from different sources. Depending on the method of yarn manufacture, cotton seed or husk may be present in the final yarn. Combed yarns contain less cotton seed as the majority of this is removed during the combing process. Carded yarns however contain more of the seed which is bleached during the bleaching process to give a more uniform fabric appearance.

Cellulose is a polysaccharide of which the repeating unit is $\beta$-glucose. The repeating unit of the molecular chain can be represented as in Figure 1.12. There is strong hydrogen bonding between the hydroxyl groups of the molecular chains, so that the polymer chains do not break easily even when the fibre is saturated with water. Unlike other cellulosic fibres, for example flax, hemp and jute, cotton is unique in that its strength does not decrease when wet. The strength of the cotton fibre increases when wet due to the increased hydrogen bonding. This is because water molecules can easily form hydrogen bonds with the free cellulose hydroxyl groups. The hydrophilic nature of cotton allows moisture to penetrate readily between the fibrils into the non-crystalline regions of the polymer chain. Cotton has a regain of 8.5% at 65% relative humidity and 20°C measured as per Australian Standard AS.2001.7-2005 (BS 4407.1988. MOD). However, at 100% humidity the regain rises to 25 - 26%. Water absorption at high humidity results in the swelling of the secondary cellular wall, which has little effect on the fibre length. This is unusual as when swelling takes place there is normally a reduction in length proportional to the degree of swelling.
1.4.3 Chemical Treatment of Cotton

During the scouring of cotton fabrics prior to dyeing, alkalis such as sodium hydroxide and sodium carbonate are used. This scouring removes waxes and impurities from the fabric and has an influence on the dye uptake depending on the amount of alkali used. Treatment of cotton with higher quantities of alkali i.e. 26% sodium hydroxide (mercerising) has a more marked effect on the physical and chemical properties of the cotton fibre. The average regain of the fibre increases by almost 25% to 10.5% at 65% relative humidity and 20°C. Mercerising also results in physical changes to the cotton fibre that give added value to the final product. If the fabric is under tension during the sodium hydroxide treatment the fibre is prevented from shrinking during the swelling process. Surface lustre is developed, in part due to the changes that take place in the fibre cross-section. The fibre loses its kidney shape and becomes more circular as shown in Figure 1.13., thus increasing the surface reflective properties. Increased hydrogen bonding between the molecular chains also occurs thus giving an increase in fibre strength of approximately 20%. Since the fibre swells dramatically during the treatment, the fibrils in both the crystalline and non-crystalline regions become more accessible to the penetration of moisture. Thus the relative moisture absorbency increases. This increase in moisture absorbency increases the comfort factor of a typical cotton garment. At the same time the dye-ability of the fibre increases, so that a lower quantity of dye is required for a given shade depth. Not all cotton fabrics are mercerised. Therefore the experimental work in this study was restricted to cotton fabrics that had not been mercerised.
Within any given cotton crop a percentage of immature and dead fibres will always be present. The percentage of these fibres depends to a large extent on the conditions during the ripening period of the crop. Figure 1.14 illustrates the variability in the fibre cross section between mature, immature and dead fibres. Immature fibres dye lighter than mature fibres causing colour variation. Dead fibres in a yarn or fabric show as uncoloured or white flecks lowering the appearance of a fabric and thus the final finished quality.

Cotton fibres sourced from different growing regions vary widely in fibre length, fineness and colour. These variations can result in large fibre losses during spinning and wet processing particularly when immature fibres are present. Variations between batches can also result in variable uptake of dye by the fibre giving rise to colour variations.
This is particularly so when scouring using sodium hydroxide. Partial mercerisation of the fibre can occur. For this reason the quantities of chemicals used in scouring and bleaching processes need to be carefully monitored.

1.5. Detergents

Detergents are essential to the cleaning of textile fabrics; in processing and for laundering after wear. Detergents are surface active chemicals that have the ability to emulsify, wet, suspend and remove soily matter from textile materials. They are formulated to have particular performance characteristics to meet a specific customer's end use requirements. Formulations can be made to meet a specific price point. Detergent systems used in textile processing are significantly different to those used within the home environment.
1.5.1. Textile Processing Detergents

Industrial detergents used by textile manufacturers as a general rule do not contain additives such as alkalis, foaming agents or buffers. Textile manufacturers prefer to make specific chemical additions based on local machinery, water conditions, fibre and fabric quality. Because of the types of machinery and pumping systems used in textile wet processing detergents should not foam excessively. The production of foam reduces the efficiency of the pumps used to circulate liquor. Pumping systems in textile processing machines are usually centrifugal impeller pumps. The presence of foam reduces the rate of liquor flow and in extreme cases liquor flow can stop.

1.5.2. Laundry Detergents

Domestic and commercial laundry detergent systems vary widely, some containing more alkali than others; while others contain oxygen generating bleaching compounds such as sodium perborate or sodium percarbonate. An example of a typical domestic powder detergent formulation is represented in Table 1.5.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active detergent (alkyl benzene sulphonate)</td>
<td>23%</td>
</tr>
<tr>
<td>Tri poly phosphate *</td>
<td>30%</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>8%</td>
</tr>
<tr>
<td>Sodium carbonate Na$_2$CO$_3$ *</td>
<td>2%</td>
</tr>
<tr>
<td>Sodium perborate</td>
<td>6%</td>
</tr>
<tr>
<td>Sodium sulphate Na$_2$SO$_4$</td>
<td>- 20%</td>
</tr>
<tr>
<td>Carboxymethyl cellulose</td>
<td>10%</td>
</tr>
<tr>
<td>Foaming agent</td>
<td>2%</td>
</tr>
<tr>
<td>Optical brightening agent</td>
<td>trace</td>
</tr>
</tbody>
</table>

*Current detergent systems have lower phosphate and higher sodium carbonate concentrations.

The phosphate, silicate and sodium carbonate act as “builders” to improve the performance of the detergent as well as assisting in the removal of greases and dirt from the fabric.
Carboxymethyl cellulose acts as an emulsion stabiliser and prevents re-deposition of the suspended dirt particles once removed from the fabric. The addition of a foaming agent is required as the detergent, alkyl benzene sulphonate, does not foam strongly. Sodium sulphate is a by-product from the neutralisation of the sulphonic acid in the detergent. The composition of domestic detergents has changed in most developed countries due to legislation reducing the allowable concentration of phosphates in domestic and industrial effluent. Limits on the amount of phosphates in domestic detergents are now typically about 10%; for example the Material Safety Data Sheets - Unilever Australia Pty. Ltd. (Appendix I).

The ECE Reference Detergent [12] has been developed for testing the washing fastness of dyes. Most laundry detergents now contain optical brightening agents. The type and concentrations of the optical brightener vary with the manufacturer, market and promotion strategies of the product. The ECE reference detergent as formulated does not contain any optical brightening agent.

The ECE Reference Detergent has been adopted as the industry standard for washing fastness tests to overcome the problems associated with optical brightening agents. The composition of the ECE Reference Detergent is shown in Table 1.6, and is used in place of the soap and sodium carbonate combination when carrying out washing fastness tests. While this standardises industry testing practice it does leave open the possibility of “anomalous” or different colour change in the domestic laundry process because of the differences in manufacturer’s formulations.

Professor Derek McKelvie (formally of Marks & Spencer UK) advised the author by email that in the early 1970’s British Home Stores (BHS) recognised that different domestic detergents had different effects on some dyes. This resulted in BHS introducing the “DAZ” test; a test required to be used by suppliers to evaluate whether or not their products met BHS specifications. The “DAZ” test replaced soap and sodium carbonate with a consumer retail home laundry detergent powder in a standard washing fastness test. The conditions, of time and temperature remained the same as in the standard test. “DAZ” was chosen because it was the most severe home laundry detergent then available in the UK. The greatest level of staining against adjacent white fabrics was obtained when this test was used.
1.5.3. Alkali in Laundry Detergents

Alkalis are added to laundry detergents to assist in the removal of oils, fats and waxes. Typically sodium carbonate is used, as this saponifies the animal fats, vegetable oils and waxes to form a soap. This allows easier removal of oily substances. Other alkaline materials such as sodium silicate and sodium polyphosphates can also be included in the formulation to buffer the system particularly if water hardness is a problem. Many laundry detergents also include alkaline salts of ethylene di-amine tetra-acetic acid (EDTA) as water quality improvers. Sodium salts of EDTA are excellent for removing metallic contamination in water and also metal stains on garments. As some reactive dyes are based on metal complexes there is the possibility of the EDTA “de-metallising” the dye resulting in a change in properties.

Water from many sources, particularly sub-surface or bore water, can contain large amounts of dissolved calcium and magnesium salts giving rise to hard water. The presence of the calcium and magnesium salts in the water reduces the efficiency of the detergent system particularly if soap is included in the formulation. Washing additives
such as Calgon (sodium hexa-metaphosphate) can be used to soften hard water and hence improve detergent performance. Water will be made slightly alkaline through the application of water softening chemicals [13].

The affect of alkali retained by fibres after repeated laundering on the stability of dyes to light is not well researched. This research study proposes to assess the effect of residual alkali on the performance of the selected reactive dyes used.

1.5.4 Action of Cleaning

In order to understand the cleaning action of detergents it is appropriate to consider the mode of action of detergents in the laundry process. Mechanical action also plays an important part in the cleaning process, as it facilitates the removal of solid particles of dirt, which must be then suspended within the solvent detergent system.

Water alone is incapable of removing dirt, oils and fats; neither is water a good wetting agent for textile materials. Oils and fats are non-polar and are not attracted to water. Hence detergents become the key element of washing processes. According to Adam [14] cleaning occurs in five stages:

- lowering the surface tension of water;
- wetting of the solid surfaces by the water;
- penetration of water into the porous solid;
- removal and detachment of grease from its adhesion to a solid;
- suspension, dispersion or emulsification of soils, dirt, grease and fatty matter.

In any cleaning process involving water it is essential that there is thorough wetting of the material by water. The reduction of surface tension of water and the wetting of the material are essential factors in the removal of oils, fats and dirt. For water to wet textile materials it is essential that the surface tension of the water is lowered. Detergents are long chain hydrocarbons to which are attached polar and non-polar groups. The polar groups are the water solubilising groups either a sulphonate (-HSO₃) or a sulphate (-SO₄) group. These groups are attracted to the water and the hydrocarbon head or non-polar groups are attracted to the soil in the fabric. The detergent chains then surround the soil and with mechanical action they are detached from the fabric to form groups of micelles that are held either as an emulsion or in suspension until removed by the drain cycle.
Domestic and industrial laundry cleaning processes influence the fading of dyes. Fading is possibly due to exposure to light during drying, and/or to particular chemical reactions which occur in the washing of fabrics and garments. In both cases an understanding of the basic principles of the cleaning process should help clarify how colour losses and colour changes may occur.

1.6 Variables in Domestic and Industrial Laundering
There are a large number of variables in domestic and commercial laundering of fabrics and garments. The most important variables are:

(i) volume of liquor in the machine relative to the weight of fabric being washed i.e. liquor ratio;
(ii) efficiency of the rinsing process e.g. number of rinse cycles and the liquor to fabric ratio;
(iii) type of detergent and alkali plus the presence of other cleaning aids, buffers and additives such as blueing or optical whitening agents;
(iv) pH of the wash liquor;
(v) pH of the final rinse;
(vi) temperature of the washing and rinsing steps;
(vii) degree of mechanical washing action, and the severity of the extraction system.

All of these have an influence on the performance of a dyed fabric, particularly over the life of the garment. Drying conditions will also influence the ultimate performance of a fabric.

1.7 Effect of Light on Dyes.
The fading in light of textiles in general and cotton textiles in particular has been an issue for dyers and technologists well before the discovery by W.H.Perkin of the first synthetic dye (mauveine) in 1856. Textile dyes when applied to fabrics are subject to the action of a range of outside influences for example light, gases such as nitrogen oxides and moisture which may contain dissolved atmospheric chemicals. Reactive dyes have high fastness to wet treatments but the performance of a reactive dye to light is critical. Early studies on light fading (Gebhard [15], 1910) showed that cotton fabrics dyed with direct dyes did not
fade when exposed under vacuum. From these experiments it was concluded that light fading was an oxidative process. Light fading is normally carried out by exposing the dry dyed fabric to a specific light source. The majority of home textiles are often exposed to daylight in a wet condition following laundering. Line drying under sunlight is known to result in accelerated fading. The swelling of the fibre by water is one probable contributing factor. This swelling allows increased diffusion of the oxygen and other chemicals contained in the water to penetrate the fibre microstructure and influence the rate of fading.

Dyes are complex chemical structures. Furthermore, they can contain impurities, isomers of the main structure, as well as un-reacted intermediates. The dye structure may also contain substituent groups that are affected by light in their own right. Many dyes consist of several related structural isomers that can influence a number of the properties of the dye such as build-up, rate of dyeing, colour, fastness properties as well as the degree of fixation on the fibre. The dye may exist in various states of aggregation within the fibre due in part to the differences within the fibre microstructure.

It is also possible that certain chemical structures can combine with oxygen under the action of light to form peroxides. Under these circumstances light has a strong accelerating effect on the formation of peroxides and hence accelerate the rate of fading. This is particularly so with certain anthraquinone vat dye structures. Egerton, in his paper *The Mechanism of the Photochemical Degradation of Textile Materials* [16], raises the hypothesis that hydrogen peroxide is formed on the wet fabric during exposure to light, particularly if the dye is of the sensitising type.

1.8 Assessment of Light Fastness and Wet Fastness Properties of Dyed Fabric

Several reactive dyes exhibit abnormal wet fading when exposed to light under moist alkaline conditions [17]. More recently, however, interest has been directed to the effect of oxygen generating bleaching agents such as sodium perborate and sodium percarbonate as additives to domestic laundry detergents and their effect on the change of shade and wash down effect (oxygen bleach fading) of various dyes on cotton and its blends [18], [19], [20]. However, the effect of such oxygen generating chemicals and their effect on the light fastness of certain dyes after repeated washing and subsequent exposure to light has not been investigated.
The evaluation of the washing fastness of dyes is a subjective process. Change of shade and degree of staining onto adjacent fabrics is assessed using the International Standard Grey Scales. Two series of scales are used, one for assessing the change of shade of the dyed fabric and the other for assessing the staining onto an adjacent white fabric. AS 2001.4.15 - 2006 lists a number of washing conditions that can be used to evaluate the performance of a particular dye under specific conditions. These tests closely mirror those used in ISO 105, Textiles – Tests for Colourfastness, and vary in severity in both temperature and degree of mechanical action that can be introduced.

However these tests do not give the complete picture. They do not provide data as far as the actual performance of the dye is concerned, particularly during subsequent wear and under domestic washing conditions. Domestic laundering conditions vary widely. Samples tested from a particular dye batch of new cotton garments will provide information on whether the dye has been correctly applied, and the general fastness data of the dye under the specific conditions of test. For example, if the adjacent fabrics were heavily stained it would indicate that hydrolysed dye had not been completely removed from the fabric surface during processing, as illustrated by Figure 1.15.

\[
D - \text{CH}_2 = \text{CH}_2 + \text{HO-H} \rightarrow D - \text{CH}_2\text{CH}_2\text{OH}-\text{H}
\]

Figure 1.15. Representation of the hydrolysis of a vinyl sulphone dye.

1.8.1 Tests for Wash Fastness

In the evaluation of the performance of a dyed fabric to washing the most common test solution used is 5.0g/l standard soap together with 2.0g/l sodium carbonate. Other additions such as hydrogen peroxide or sodium hypochlorite may be made to this solution to predict a dye’s ultimate performance. Other detergents systems can also be used and the tests carried out under a range of temperature and time conditions so long as they are specified in the test results. As a general rule only a single test is carried out. Shade change and staining of adjacent fabrics are assessed visually against the International Geometric Grey Scales [21]. The extent of shade change is assessed using a grey scale that shows differences of 0, 1.5, 3, 6, and 12 N.B.S. (National Bureau of Standards) units [22]. The staining on adjacent undyed fabrics is assessed by comparing the pattern with
pairs of grey scales that shows differences of 0, 4, 8, 16 and 32 N.B.S. units. A long liquor ratio of 50:1 is used in all test procedures. This is much longer than that normally found in domestic and industrial machines. At the completion of the washing test the composite specimen (consisting of the original sample together with the specified adjacent fabrics) is rinsed under cold running water for 2 minutes. Here again such conditions do not replicate that found in domestic practice.

1.8.2 Test for Perspiration Fastness

Wet perspiration is also known to influence the light fading of dyes. A number of studies have been published [7], [23] and a specific test developed. This test (ISO/WD 105-B07 part of ISO 105) specifies a method to assess the fastness of dyes when perspiration is present and the sample exposed to a specified light source. Originally the test specified an acid perspiration solution. An alkaline solution was subsequently added to the testing procedure. Subsequent studies showed that there was little difference in the results between the acid and alkaline “perspiration” solutions. The main reagent used for the perspiration solution is L-histidine monohydrochloride monohydrate ($C_6H_9N_3O_2.HCl.H_2O$) in combination with sodium chloride, lactic acid and a suitable phosphate buffer for the acid test at pH 4.3 ± 0.2. The alkaline solution is prepared in a similar manner with an alkaline phosphate buffer to a pH 8.0 ± 0.2. Fading is conducted using a xenon arc lamp against the standard wool blue scales.

1.8.3 Other Tests for Fastness

Various test methods for colour fastness to light, perspiration and water of some reactive dyes have been evaluated by Okada, Sugane et al [24]. They concluded that because of the range of different types of reactive dyes, the fastness results were sometimes contradictory and that various light fading occurred in the cellulose depending on the environmental conditions. It was claimed that there was no practical testing method that could strictly estimate whether the fading was reductive or oxidative. Current test methods were shown to be inadequate to estimate the true stability of a reactive dye particular with regard to its light stability.

Unilever, the global household detergent manufacturer, has studied the mechanism of fading of commercial reactive dyes on cotton [25]. They evaluated the effect of moisture on the rate of fading and found that in the pH range 3-8 wet fabric fades faster than dry.
Larger increases in the rate of fading were noted at pH 2 and pH 9. In their study samples of printed cotton were irradiated in a quartz glass bath filled with water using xenon arc. The paper illustrated that oxygen was required for fading to occur. They also noted that UV (ultra violet light) could be eliminated from the light source if the fabric was treated with a suitable UV absorber. No work has been carried out on the effect of consecutive wet exposure, drying, then washing and wet exposing a number of times using domestic laundry detergents, as would be undertaken in a normal household situation. The rate of fading in both dry and wet states as well as in the presence of artificial perspiration has been evaluated [26]. The authors concluded that in the dry state or in the presence of artificial perspiration the fading mechanism was reductive. However, in the presence of water, fading was caused by oxidation.

A number of workers have studied the fading of reactive dyes in both wet and dry conditions but using cellophane as the substrate [27]. Cellophane is a purer cellulose substrate compared to commercially grown cotton and therefore does not take into consideration the effect of the micro molecular structure of the cotton fibre. The micro molecular structure comprises both crystalline and non-crystalline regions that are not regularly spaced along the molecular chain. This variation could account for some of the problems associated with dyestuff fading during a garments normal life cycle.

1.9 Mechanisms of Fading of Dyes by Light

Light fading of textile dyes has been reviewed [28] and a complex picture of the mechanisms relating to the fading of dyes is evident. The colour of a dye arises from absorption of light in the visible region i.e. 400 – 700nm. The absorption of light raises the dye molecule to an electronically exited state. If enough energy is transferred to the dye molecule the electrons may move to a higher orbital. Once in this higher state the energy is then dissipated in the form of reflected light so that the electrons can return to their original orbital. While in the higher energy state the charge separation of the π-electrons becomes greater and as such could be more easily affected by moisture and detergent additives.

The light fading of reactive dyes on cotton and silk has been investigated by Deepali, Rastogi et al [29]. They concluded that light fastness is influenced by both the nature and degree of dye fibre interaction. They also concluded that the bi-functional reactive dyes
perform better than the mono-functional types due to the formation of fibre–dye-fibre cross-links within the fibre micro structure.

Most dyes can be degraded by photo-oxidation via singlet oxygen. It is the singlet oxygen that initiates the degradation of the dye. Griffiths and Hawkins [30], elucidated the photo-oxidative process of some azo dyes that showed the attack on the singlet oxygen was via unsaturated hydro peroxide intermediate.

If a dye (represented by $^3D$ in the triplet ground state as a free radical) is attacked by singlet oxygen, light fading of the dye can be initiated. This will occur if the dye is sensitive to peroxy-forming products in the wash liquor as shown in Figure 1.16. As previously discussed, it is known that peroxy forming compounds (such as sodium perborate or sodium percarbonate) when added to domestic detergents, can influence the light fading of a sensitive dye.

$$^3D^* + ^3O_2 \rightarrow D + ^1O_2$$

$$^1O_2 + D \rightarrow \text{Decomposed dye}$$

Figure 1.16. Possible peroxy compound formation causing degradation [30].

Dye molecules contain a large number of double bonds. It is this arrangement of alternating double and single bond that gives dyes their colour. Typically there are a number of ways in which light fading can occur:

(a) Breaking of the double bond and molecular rearrangement. If the energy is great enough for the shared electron to be displaced and leave the molecule, resulting in a single bond, then the shape of the molecule and hence the colour changes.

(b) If the bond receives sufficient energy to break completely, this can create two or more different and smaller molecules. As a result a colour change, i.e. fading occurs.

In the production of cotton fabrics dyed with reactive dyes, if latent peroxide from the bleaching process is present, the peroxy compounds can interfere with the bonding mechanism. This interference causes hydrolysis of the dye, resulting in poor exhaustion.
and dye fixation. Thus lower fastness to wet treatments in the final finished fabric can occur. If the dye is sensitising as far as light is concerned an increase in the rate of light fading can occur under subsequent moist alkaline conditions. As the cotton fibre in the moist state is swollen, there is a greater tendency for oxygen and peroxy compounds to enter the fibre micro structure, thus attacking the dye fibre covalent bond.

Light fading may also take place where high energy ultraviolet light is present. The substrate can influence the light fading of the dye to which it is bound, particularly if the substrate contains carbonyl (C=O) groups which can be excited. If the reactive dye is covalently bound to the cellulose rather than physically bound, then the light fastness would be expected to be greater [7].

1.10 Factors Affecting the Light Fastness Properties of Dyed Cotton

The factors that influence the light fading of textiles can be summarised as follows [31]:

a) light source intensity and wavelength distribution;
b) exposure time;
c) surface temperature of the fabric;
d) moisture content of the fabric;
e) composition of the surrounding atmosphere;
f) the chemical and physical structure of the textile fibre;
g) the degree of dye aggregation within the fibre structure;
h) presence of metal ions either bound in the dye or present as impurities on the fibre.

These are generally considered to be the basic parameters. However, recent research [3] has shown that with respect to cellulosic fibres additional factors come to bear such as pH of the sample and residues of additives present in domestic washing detergents.

1.11 Evaluating Light Fastness

The effect of bleaching agents in detergents has been well documented, particularly their effect on the “wash down” or colour loss properties of various dyes [18], [19], [20]. A specific test has now been adopted for the evaluation of colour fastness of textiles to domestic and commercial laundering, ISO 105-C09:2001. In a recent study [26] it was found that the rate of fading of vinyl sulphone dyes was greater under conditions of acid perspiration rather than alkaline perspiration. The study also concluded that the presence of
L-histidine monohydrochloride, lactic acid and DL-aspartic acid have a major effect on the fading of some reactive dyes. The effect of residual alkali retained in cellulosic fibres after domestic washing has not been thoroughly investigated. For some time it has been known that the light fastness of cotton textiles, in particular dark shades such as navy and black, can present problems. Current standard methods of test are all based on exposing a dried sample of fabric to a specific light source, either daylight, xenon arc, carbon arc or MBTF (Mercury Tungsten Filament Lamp). None of these tests take into account the effect of domestic laundry detergents, retained alkali, detergent systems, moisture and their effect on the light fastness of a textile fabric after repeated launderings and wet exposure during drying.

Early evaluation of various accelerated light fading tests rather than daylight were carried out by Cooper & Hawkins [32] of the General Electric Co. Ltd. Research Laboratories in Wembley, England. They compared carbon arc lamps, mercury discharge lamps and tungsten filament lamps. They concluded that of the light sources investigated none had the spectral distribution of sunlight, except for the carbon arc. Carbon arc emitted radiation in the region 300 – 430 nm, approximately the same as noon summer sun in the UK. Typically the wavelength of sunlight is 290 – 1700nm; ultra violet 290 – 400nm, visible 400 – 700nm and infrared 760 – 1700nm. The intensity of the ultraviolet and visible components depends on the season, and time of the day. In the southern states of Australia it is well known that the intensity of the ultraviolet radiation is highest in the months of December to March i.e. during summer time. This intensity is due in part to the depleted ozone layer over Antarctica.

Dark shades such as navy blue and black are the most susceptible to the problem of fading, because changes in shade and tone are more evident. By way of illustration of the problem Figure 1.17 shows a pair of men’s black polyester cellulose washable trousers that have been repeatedly washed in a domestic washing machine then dried on an outside line. The trousers have been hung on the line from the waist; hence the major level of fade has occurred at the waist band. Microscopic examination of the faded area showed only the cellulosic portion has faded; the black polyester appeared to be unchanged. Measurement of the colour difference between faded and un-faded areas was made. (HunterLab, ColorQUEST II Reflectance Spectrophotometer, 10° observer and D65 as the light source) The measurements showed that there had been a loss of depth of 25% in the faded region.
as well as a significant shift in hue. However standard tests used by industry to predict colour fastness would not have identified the potential for this differential fading to occur.

Figure 1.17. Polyester viscose trousers after several domestic washes & wet exposure to sunlight.

It is therefore the principle object of this research to obtain an improved understanding of the variables involved in anomalous fading of cotton garments during home use.

There are a number of internationally recognised standard tests for the evaluation of the light fastness of dyes. The major difference between the methods is the light source. For example the Japanese test method JIS L-0842 uses a carbon arc lamp. The daylight fading method is rarely used, unless there are specific requirements demanded of the end product; for example, military applications. Daylight fading is a relatively long process as it depends to a large extent on the prevailing weather conditions. Other problems that can be encountered are related to atmospheric pollutants such as sulphur dioxide, nitrogen oxides, ozone as well as changes in the relative humidity of the atmosphere. These factors can contribute to undesirable side effects in the light fading process and hence unreliability in the test data.
The Xenon Arc exposure method is widely used in both Europe and the USA for accelerated fading of dyes on textiles. The rate of fading and the degree of the fade is compared against a series of Wool Blue Light Fastness Standards. These are faded alongside the sample to be tested. The Blue Light Fastness Standards consist of a series of eight (8) blue acid dyes dyed onto wool fabric. Standard No. 1 has the poorest fastness to light and Standard No. 8 the greatest fastness. Each standard in the series is approximately twice as fast as the previous standard. According to Giles[33], in the Microscal apparatus fading of the blue standards 1, 2, 3, and 4 occurs after about 5.5, 11, 22 and 49 hours respectively.

A brief description of the method used for daylight fading is as follows:

- the samples to be tested together with the blue standards are mounted on a card;
- a portion of each is covered by a suitable light proof material;
- the samples are mounted under glass at an angle of 45° in a north facing position (south facing if in the northern hemisphere);
- samples are inspected frequently. When a change can be just seen compared to the unexposed portion, the number of the standard showing a similar change is noted;
- exposure is then continued until the contrast between the exposed and the unexposed portion is equal to the contrast between the two grey patterns illustrating Grade 3 of the Geometric Grey Scale for Assessing Change of Shade.

1.12 Summary

Light fading of reactive dyed cotton fabrics and garments that have been worn and washed in a domestic environment is not fully understood. The general conclusion drawn by the majority of researchers is that fading is due to an oxidative process. Domestic detergent formulations contain additives which could contribute to light fading. For example, the presence of an oxygen generating bleach in a domestic detergent could well aggravate light fading.

Furthermore standard laboratory tests do not necessarily predict the performance of a dye to domestic laundering conditions. None of these tests take into account the effect of domestic detergent residues together with moisture after repeated laundering and wet exposure during line drying. This study aims to investigate these issues in the context of light fastness of reactive dyes on one hundred percent cotton.
Chapter 2.
Materials and Methodology
2.1. Introduction
The object of this work was to study the effect of repeated domestic launderings and then exposure to light on reactive dyed navy blue and black cotton fabrics. Black and navy are the two single most predominant colours dyed throughout the world. As noted before approximately 60% of all dyes produced are black and navy blues. It is therefore reasonable to estimate that about 40% of all textiles are dyed either black or navy blue. The percentage of fabrics dyed with these dyes is less than the production figures because navies and blacks are dyed at approximately 50% more by weight of dye. One objective of this study was to determine what effect, if any, residual alkali retained in the fabric after laundering had on the fading behaviour of the dyes. Another objective was to study whether there is a difference in the behaviour of different detergents and home laundry systems on the ultimate light fastness performance properties of the selected dyes.

2.2. Materials

2.2.1 Fabric
The fabric selected was a pure cotton single jersey typically use for the manufacture of upper body garments and sportswear.
The technical details of the fabric were:
Yarn type – Rotor Spun carded cotton - 1/24’s Tex.
Fabric weight – 178g/m^2
Fabric construction – single jersey 13courses/cm, 11wales/cm

2.2.2 Dyestuffs
The dyes chosen represent typical current Australian consumption and are used extensively within the cotton dyeing industries throughout Asia and the Indian sub-continent. Eight (8) dyes were selected based on their usage.
These are:
- Cibacron Navy LS-G, C.I. Reactive Blue 264 (Huntsman Chemicals formally Ciba Specialty Chemicals). This bifunctional dye is known to be possibly based on fluoro triazine with a vinyl sulphone reactive group attached to the triazine ring [6].
- Sumifix Supra Navy 3GF 150% - C.I. Reactive Blue 222 (Sumitomo Chemicals)
- Intracron Dark Blue CDX - C.I. Reactive Blue 222 (Yorkshire)
C.I. Reactive Blue 222; a bifunctional dye based on monochloro triazine together with a vinylsulphone reactive group.

- Levafix Navy Blue E-BNA - C.I. Reactive Blue 225 (Dystar). This dye has 4 reactive groups, three on the triazine ring and one vinyl sulphone group. The three reactive groups on the triazine ring are two fluorines atoms and one chlorine atom. Unlike many newer reactive dyes the structure of this dye has been disclosed in the Colour Index [34].

![Figure 2.1. Structure of C.I.Reactive Blue 225 [34].](image)

- Remazol Navy RGB 150%- C.I. Reactive Blue 250 (Dystar)– the structure of this dye is not disclosed.
- Levafix Navy C-A (Dystar) – this dye is not listed in the Colour Index and assumed to be a mixture.
- Cibacron Dark Blue W-R (Huntsman Chemicals formally Ciba Speciality Chemicals). This dye is not listed in the Colour Index and was assumed to be a mixture.
- Cibacron Super Black R (Huntsman Chemicals formally Ciba Speciality Chemicals). This particular dye has proved to be very popular within Australia being outstandingly economical. It is a mixture and presumed to be based on C.I. Reactive Black 5.

Dyeings at two strengths 1.5% and 3.0% of Remazol Navy RGB 150% were carried out to compare the fastness performance between a medium and a full depth shade.

Material Safety Data sheets of the selected dyes were obtained from the suppliers and are shown in Appendix II.
2.2.2.1 Identification of Constituents in the Dyes Used

As some of the dyes were not listed in the Colour Index it was assumed that they were mixtures of various dyes. Many commercial dyes are mixtures of at least two dyes. Mixtures of dyes are manufactured for a number of reasons; some of these include economy of application, improved dyeing properties such as build up and fixation as well as better exhaustion. To determine the mixture constituents, Thin Layer Chromatography (TLC) was carried out on all the eight dyes used. C.I. Reactive Black 5 was used as the reference standard.

C.I. Reactive Black 5 was chosen as the reference because it is the most common reactive dye in current use and frequently used in the formulation of commercial black and navy blue reactive dye mixtures [4].

Procedure

5g/l solutions in deionised water were prepared for each dye. Standard Merk 233 TLC plates were used.

The plates were prepared as follows: a pencil line was drawn 2cm from the bottom of the plate this being the origin of the chromatograph. The plate was divided into five vertical sections each section being 4cm wide. A small spot approximately 7mm in diameter of each dye solution was placed at the origin using a fine Pasteur pipette. The plates were dried in the laboratory oven @ 40°C. The dried plates were suspended in a glass tank containing the eluent so that only 1cm of the bottom of the plate was immersed in the eluent. The top of the tank was closed with polyethene film to prevent solvent evaporation and a glass plate placed on top of the film. After 6 hours the separation was complete. The plates were removed from the tank and again dried in the oven at 40°C.

An initial TLC eluent was prepared using the following recipes; the quantities being in parts by weight:

- 5pts. n-butyl alcohol
- 5pts. pyridine
- 3pts. water
- 2pts. ammonia 0.880
Several trials were carried out but the results from this eluent did not give clear partition of the components. Other problems with this eluent were the strong odour and the toxic nature of the pyridine.

A further series of TLC’s were carried using a different eluent composition all constituents in parts by weight:

- 6pts. n-propyl alcohol
- 1pt. ethyl ethanoate
- 3pts. Water

This method gave good partition of the dyes.

### 2.2.2.2 Relative Strengths of Dyes Used

The relative strengths of the navy blue dyes used were measured using the Hunterlab ColorQuest II spectrophotometer. It was not necessary to measure the strength of the black because of the large difference in tone. The lighter shade 1.5% depth of Remazol Navy RGB 150% was not included in the measurements because it was exactly half colour strength of the 3.0% shade of Remazol Navy RGB 150%

### 2.2.3 Chemicals

A number of chemicals of GPR grade were used during the experiments. These are listed together with the supplier:

- ammonia 0.880 Science Supplies Pty. Ltd.
- n-butyl alcohol Science Supplies Pty. Ltd.
- pyridine Science Supplies Pty. Ltd.
- n-propyl alcohol Science Supplies Pty. Ltd.
- ethyl ethanoate Science Supplies Pty. Ltd.
- hydrogen peroxide 50% Degussa
- sodium hydroxide Science Supplies Pty. Ltd.
- Dyamul LFA Yorkchem Pty. Ltd.
- Seriquest CMA Yorkchem Pty. Ltd.
- Dispersant AD Yorkchem Pty. Ltd.
2.3 Standardisation of the Base Fabric

As a standard base cloth was required for experimental work the jersey fabric was scoured and bleached in a Werner Mathis mini jet using the formulation below at a liquor ratio of 30:1. The high liquor ratio was necessary to ensure that the fabric ran smoothly in the machine. Under normal production conditions the liquor ratio would be in the order of 10:1. Experience has shown that the best results in the laboratory machine are obtained at this higher liquor to fabric ratio:

- 1.0g/l Commercial Detergent Mixture (Dyamul LFA – Yorkchem)
- 1.0g/l Sequestering agent (methyl phosphonate/ polyacrylate type)
- 5.0g/l Sodium Hydroxide (solid)
- 5.0g/l Hydrogen Peroxide 50%

Chemicals were added at a liquor temperature of 25°C and the temperature raised to 98°C at 3.0°C per minute. The bath was held at top temperature for 45 minutes before cooling to 60°C at 3.0°C per minute. The scoured and bleached fabric was given two rinses at 40°C then neutralised to pH 6.4 using a 10% sulphuric acid solution. Finally the fabric was given a rinse in cold water prior to hydro-extraction and drying in a relaxed state in a drying cabinet.

The commercial detergent used was a mixture of a non-ionic - 9 mole ethylene oxide nonyl phenol condensate surfactant together with sodium lauryl ether sulphate added to raise the cloud point of the non-ionic surfactant.

The sequestering agent fulfils two functions:

(a) to sequester any metallic contamination in the fabric that would result in the formation of oxy cellulose due to the rapid evolution of oxygen from the hydrogen peroxide;

(b) a mild stabiliser for the hydrogen peroxide.

Sodium hydroxide was added to aid the removal of the natural waxes present in the cotton fibre.

2.4 Preparation of Dyed Fabrics

Dyeings were carried out according to the dye manufacturers’ standard method [35], [36], [37], [38], [39] of application to cotton. The percentage of dye applied to the fabric (Table
2.1) aimed to give similar colour strength for all navy blue dyes. The manufacturer of Cibacron Super Black R recommended an application of 5.0%.

Table 2.1. Concentration of dye applied to the fabric.

<table>
<thead>
<tr>
<th>Dyestuff</th>
<th>Percentage of Dye Applied to the Fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cibacron Navy LS-G</td>
<td>4.0%</td>
</tr>
<tr>
<td>Cibacron Dark Blue W-R</td>
<td>3.6%</td>
</tr>
<tr>
<td>Cibacron Super Black R</td>
<td>5.0%</td>
</tr>
<tr>
<td>Intracron Dark Blue CDX</td>
<td>3.6%</td>
</tr>
<tr>
<td>Sumifix Supra Navy 3GF 150%</td>
<td>4.0%</td>
</tr>
<tr>
<td>Levafix Navy Blue E-BNA</td>
<td>4.0%</td>
</tr>
<tr>
<td>Remazol Navy RGB 150%</td>
<td>1.5%</td>
</tr>
<tr>
<td>Remazol Navy RGB 150%</td>
<td>3.0%</td>
</tr>
<tr>
<td>Levafix Navy C-A</td>
<td>4.0%</td>
</tr>
</tbody>
</table>

Table 2.1 above lists the dyes used together with the quantity of dye applied to the fabric. The dyeings were performed in an Ahiba Turbomat machine at a liquor ratio of 8:1. Approximately 65 -70g of fabric was dyed at each dyeing. The fabric was wound onto a perforated cylinder through which the dye liquor was pumped. This method ensured level and consistent dyeings. At the completion of dyeing the dyed fabric was given a thorough rinse with cold water by passing water through the perforated cylinder and thence through the fabric followed by neutralising with acetic acid to pH 7.0. Dyeings were finally soaped at the boil with 1.0g/l Dispersant AD (Yorkchem) to remove unfixed and hydrolysed dye. Dispersant AD is a specially formulated product based on a low molecular weight sodium polyacrylate. This type of product has been found to be more effect than soap or non-ionic detergents for the removal of unfixed and hydrolysed dye. Prior to drying the fabric was given a final rinse in cold water.

2.5 Light Fading Equipment

The study required the samples to be exposed wet and the fabric allowed to dry during the exposure period. An appropriate simple test method consistent with the equipment available needed to be devised. A procedure based on the Mercury Tungsten Filament, Internally Phosphor-Coated (MBTF) lamp as specified in Australian Standard AS2001.4.21.2006 was found to be the most suitable. This equipment is readily available, simple to use and it was possible to mount samples in such a manner as to allow wet exposure to occur while at the same time allowing the exposed samples to dry.
Extensive evaluation of this exposure system has previously been carried out by the Material Research Laboratories of the Australian Department of Defence [40]. They found that of a total of 196 textile samples exposed, 81% of the samples exposed to the MBTF system agreed with the daylight test and the remaining 19% were not greater than 0.5 of a unit (on the blue scale) different. As a consequence of this work the MBTF lamp was adopted as the Australian Standard. One of the major advantages of the MBTF system is cost, not only the capital cost but also the running costs which are significantly lower than either carbon arc or xenon. The system is widely used in both manufacturing industry and in the quality control laboratories of major retailers.

In order to ensure that the MBTF lamp used gave the correct radiation emissions a radiation profile of the lamp was carried out by CSIRO Division of Polymer Science in Clayton as shown in Figure 2.2. The lamp chosen was a 500W Philips HPML.

A comparison of the radiation spectrum of the MBTF lamp and sunlight at noon was also made as shown in Figure 2.3. The resultant graphs Figures 2.2 and 2.3 compare closely with work carried out by Hindson & Southwell [40]. The initial intensity of light is low during the warm-up stage, full intensity being reached after approximately 6 minutes. When compared to noon sunlight, the MBTF lamp has a strong peak at around 550nm.
compared to sunlight at 500nm. There is also a strong peak at 375nm and a further peak at 400 - 410nm though not as strong as that at 375nm. The spectrum differs to that of daylight as the radiation cuts out at about 300nm and the peaks in the nearer UV around 350 – 375nm occur at frequencies to which many dyestuffs are sensitive [40]. The sensitivity of dyes to these frequencies can result in the rupture of the azo (-N=N-) link as well as damage to the covalent bond that attaches the dyestuff to the cotton fibre. This may well be aggravated by the presence of moisture and other chemicals present on the fabric.

![Comparison of Sunlight vs HPM Lamp](image)

**Figure 2.3. Comparison of MBTF Lamp against noon sunlight.**

### 2.6 Dry Fading

As a comparative standard all the dyed fabrics were subjected to fading dry before washing as per Australian Standard AS. 2001.4.21-2006. The loss in colour strength of each dye was measured after 10 hours, 20 hours and 30hours respectively.
2.7 Washing of Dyed Fabrics

2.7.1 Wash and Exposure Cycles
To simulate approximately three to four months domestic laundering of a cotton garment, the dyed samples were washed 15 times with exposure to light, wet, for two hours after each wash. During the exposure the samples dried. After the fifth cycle of washing and drying the reflectance of the samples was measured and the colour difference calculated. This procedure was repeated for ten (10) and fifteen (15) cycles. The fifteen wash and dry cycles described above were carried out for each detergent and machine according to Table 2.2.

Table 2.2. Detergent and machine type.

<table>
<thead>
<tr>
<th>Machine Type</th>
<th>Detergent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Loading</td>
<td>Typical detergent for Top Loading Machines</td>
</tr>
<tr>
<td>Top Loading</td>
<td>Formulated Neutral Detergent</td>
</tr>
<tr>
<td>Top Loading</td>
<td>Water Only</td>
</tr>
<tr>
<td>Front Loading</td>
<td>Typical detergent for Front Loading Machines</td>
</tr>
</tbody>
</table>

The volume of water used for a typical wash load in each type of machine was carefully measured. This was necessary in order to determine the mass of domestic laundry detergent to be used in each case. Current standard washing fastness tests do not take into account the variability within the domestic home laundry. For example, Australian Standard AS.2001.4.15-2006, describes 24 test procedures but all are similar to ISO 105, Textiles – Tests for Colourfastness to Washing; the international standard test method and none are truly representative of domestic practice.

As far as possible the experimental conditions aimed to mirror actual home laundry practice, particularly in relation to the quantity of detergent powder and the volume of water used for a typical wash load.
2.7.2 Liquor to Goods Ratio

Domestic washing conditions vary widely, in particular machine types with varying capacities and degrees of mechanical action. Principally, domestic washing machines are of two types:

1. top-loading machines
2. front-loading machines

Two machines were selected:
- Maytag - Top loading machine
- Hoover Zodiac 12 - Front loading machine

The regular warm wash cycle on both machines was selected as most appropriate for this study.

A series of tests were carried out to determine the liquor volume of the two machines. The volume of liquor for a typical wash cycle for each machine was measured using a flow meter. Typical wash loads will vary depending on the bulk density of the materials being washed. For example a king-sized sheet of approximate area 5.3 m² together with two pillow cases will require more water than a number of smaller articles of greater weight. By evaluating a number of domestic wash loads with articles of differing bulk it was possible to determine the average liquor to goods ratio. The Maytag Top Loading machine required 72 litres of water for a large load of 3.5kg of 100% cotton garments. This equated to a liquor to goods ratio of 20:1 i.e. for every 1kg of material 20 litres of water was required. In the Hoover Zodiac front loading machine the liquor ratio again varies with the bulkiness of the fabrics being washed. The machine used a standard volume of 24.5 litres per wash. A range of differing garment weights and bulk were trialled. It was found that the liquor ratio varied between 12.5:1 and 8:1 depending on the type of fabric being washed. It was therefore decided to use a liquor to goods ratio of 10:1.

2.7.3 Detergent Selection

Two commercial domestic home laundry detergents were chosen for the experimental work:

A. A formulated household detergent system recommended for Top-Loading washing machines. No oxidising bleaches were included in the formulation. [Note: Oxidising bleaches such as sodium percarbonate and sodium perborate are often
included in the detergent formulations particularly if low liquors are used for the wash cycle.]

B. A widely used domestic detergent powder specially formulated for domestic front loading machines. Foam generation can be a problem in front loading machines so the detergent formulations are blended to have much lower foaming propensity. This detergent system contained sodium perborate; an oxygen generating bleaching and whitening additive that can affect the colour fastness of the dyes.

Material safety data sheets for the above detergents were obtained from the manufacturers and are given in Appendix I.

Since detergent systems vary widely in pH, a third and neutral pH detergent was used as a reference standard. The neutral pH detergent was formulated with the following constituents:

- 15.85g Sodium Do-decyl Benzene Sulphonate
- 2.90g Nonyl Phenol ethoxylate, 10 mol ethylene oxide.
- 3.50g Soap
- 77.75g Water
- 100.00g Total

The composition and quantities of the neutral detergent were calculated from the ECE reference detergent as previously discussed in Chapter 1 [12].

2.7.4 Detergent Quantity

Each of the commercial powder detergents was supplied with a measuring cup and the standard application quantity defined on the packaging material. The recommendations were:

- Normal wash 1 cup of detergent.
- Heavy soiled fabrics 1 – 2 cups of detergent

Most top loading washing machines have variable liquor quantities depending on the weight of fabric being cleaned. The actual amount of detergent powder to be used in each wash was determined. One measure cup contained 62.5g of detergent. A typical 3.0kg
load of fabrics at the “hi” liquor level requires 72 litres of water. The quantity of detergent therefore would be 0.87g/litre. The lowest selectable level used 50 litres of water; hence the detergent concentration would be 1.30g/litre. For the purpose of this study the detergent concentration selected was 1.0g/l.

The bulk density of the detergent for the front loading machine was slightly heavier; one scoop weighing 58.2g. The nominal volume of water in the wash cycle of the Hoover Zodiac machine was 24.2litres. In this case a detergent concentration of 2.4g/l was used for each wash cycle as this quantity was equivalent to the manufacturers’ recommendation of 1 scoop.

The neutral laboratory formulated detergent was assessed only in the top loading machine. The concentration used was the same as for the commercial top loading detergent powder, namely 1.0g/l.

2.7.5 Total Alkalinity and Buffer Capacity of Detergents.
Buffer curves of both commercial detergents were prepared by titration of a 1.0g/litre solution of the detergent with 0.05M sulphuric acid. A graph of pH against ml. of 0.05M sulphuric acid was prepared from the results of the experiment.

Total alkali as sodium carbonate of each detergent was determined by titration of a 10.0g/litre sample of the detergent powder with 0.05M sulphuric acid using bromo-thymol blue as indicator.

2.7.6 Washing Conditions
Simulated laboratory washing tests use a series of ball bearings to replicate the mechanical action of a washing machine, at a long liquor ratio. As a number of fabrics were to be washed together (simulating household laundering) a suitable machine giving control of liquor to goods ratio, temperature as well as comparable mechanical action was required. The Werner Mathis multi purpose dyeing machine offered the most appropriate system for the washing trials see Figure 2.4.

The garment dyeing attachment was appropriate for both the top loading and front loading machines refer Figure 2.5. This attachment can be run at variable speeds from 1r.p.m up to 25r.p.m. The tumbler speed was set at 12r.p.m.
Figure 2.4. Werner Mathis multi purpose dyeing machine.

Figure 2.5. Internal mechanics of the Werner Mathis machine.
As the mechanical action in a house hold washer is provided by either a tumbling action in the case of a front loading machine or by the bowl (or central vaned paddle) reciprocating as is the case in the top loading machine this speed was considered to be appropriate. Heating and cooling is by way of a water filled electrically heated jacket surrounding the cylinder. The temperature and process time are controlled with the Datex 2000 electronic controller Figure 2.6.

During the washing cycle the unit is sealed with a door on a mechanical seal so that no liquor leaks from the system during the process. An externally mounted tank is filled with the required volume of water. The pre-weighed and dissolved detergent powder was added by way of an addition device so that no chemicals were lost during the addition phase.

![Figure 2.6. Datex controller.](image)

The nine (9) dyed samples were washed together at the pre-determined liquor to goods ratio together with the requisite quantity of detergent. White fabric was included in initial tests to determine if colour in liquor cross stained to the other fabrics. There was no colour bleeding causing cross staining therefore the nine dyeing were washed together.
The following amounts of detergent were used:

- 1.0g/litre Typical detergent for the Top Loading Machine
- 1.0g/litre Neutral laboratory formulated detergent for the Top Loading Machine
- 2.4g/litre Typical commercial detergent for the Front Loading Machine.

A water insoluble marking pen was used to mark the area to be exposed. Hence only the area exposed to light was measured by the reflectance spectrophotometer. The fabric samples were placed in a suitable polyester net bag, normally used in households for the washing of delicate lingerie fabrics.

### 2.7.7 Wash Procedure for Top Loading Machines.

A set of the nine (9) dyed samples were washed with detergent for top loading machines and a second set of the nine (9) dyed samples were washed with the Neutral detergent formulation, using the conditions for top loading machines. A further set of samples were washed with water only. The pH of the wash liquor and the rinse liquor for both detergents was recorded.

The machine speed was set at 12 rpm and the samples washed in the detergent solution for 10 minutes @ 45°C at a liquor ratio of 20:1. The final pH of the wash liquor was taken at the completion of the wash cycle as the liquor was draining.

A spray rinse equivalent to the volume of water used for the washing was then carried out. The fabrics were then given a single cold rinse for 10 minutes at a liquor ratio of 20:1 and temperature of 27°C. At the completion of the rinse cycle the pH of the rinse water was recorded. As no spin dry cycle was available water was removed to a moisture content of 83% using squeeze rollers.

### 2.7.8 Wash Procedure for the Front Loading Machine

A set of the nine (9) dyed samples were washed with detergent for front loading machines. The machine speed was set at 12 rpm and the samples washed in the detergent solution for 10 minutes @ 45°C at the liquor ratio of 10:1. The pH of the wash liquor was taken as the liquor was draining.
The Hoover Zodiac machine has a series of five (5) rinses each rinse cycle operates for 5 minutes before draining and refilling. Accordingly the dyed samples were given five (5), five (5) minute rinses at a liquor ratio of 10:1. At the end of each rinse cycle the pH of the rinse liquor was recorded. Only one spin dry cycle operates on the Hoover Zodiac Machine; at the end of the final rinse. None of the samples were given a spin dry.

2.8 Drying and Exposure of Samples
After washing and prior to exposure all samples were brought to a constant moisture content by squeezing through a pair of squeeze rollers (laboratory padding mangle). The moisture content of the fabrics prior to drying was 83%. This process removes the unbound water i.e. water that is trapped between the fibre bundles in the yarns. Bound water is that moisture chemically bound to the fibre through hydrogen bonding between the molecular chains. Under domestic conditions the unbound water is normally removed during the centrifuging cycle in both the top loading and front loading machines. Bound water can only be removed by the application of an external force that will induce evaporation from the fabric surface. Typically heat and or air circulation or a combination of both will induce evaporation to take place.

Figure 2.7. Fabric samples under exposure.

The samples of wet fabric were arranged around the circumference of the cylinder see Figure 2.7. The top and bottom of the fabric samples were covered so that only the marked area of the fabric was exposed to the light. The covered areas of the dyed fabrics were used to assess loss of colour strength when the fabric was washed and not exposed to light.
The exposed area lay between 80mm from the top and 80mm from the bottom. In this way the sample areas under assessment were exposed only to the phosphor coated area of the lamp. It was important that exposure did not take place outside the phosphor coated area. The lamp was turned on and the samples exposed for two (2) hours. After the initial warm up period of 6 minutes the temperature of the exposure was measured using a black panel thermometer; the temperature reading was 73°C ± 2.0°C. The samples were then washed again and exposed for a further two (2) hours. This procedure was repeated until the samples had been washed and exposed five times or the equivalent of ten (10) hours exposure. During exposure the samples dried. This simulates the drying of washed articles on an outside line.

2.9 Evaluation of Exposed Samples

After exposure the colour strength of the samples were measured using the HunterLab, ColorQUEST II Spectrophotometer. K/S values and the relative strengths between the exposed and unexposed areas were calculated using Premier Colorsan Software. Measurements were made under the following conditions 10° observer, maximum wavelength 600nm and D65 light source. D65 is the international standard viewing light source and is equivalent to noon northern daylight.

2.9.1 K/S Values [41]

The mathematical basis for all colour measuring software is the Kubleka-Munk series of equations. These equations state that for opaque materials such as textile fabrics, the ratio of total light absorbed and scattered by a mixture of dyes is equal to the sum of the ratios of light absorbed and scattered by the dyes measured separately. If absorption is defined as “K” and scattering defined as “S”, Kubelka-Munk states that:

$$K/S \text{ mixture} = (K/S) \text{ dye 1} + (K/S) \text{ dye 2} + (K/S) \text{ dye 3} + \ldots$$

K/S is not an easily measured quantity, but can be calculated from the reflectance data of a sample –“A”—by the Kubelka –Munk equation that states:

$$K/S = \frac{(1 - R)}{2R}$$

Where R = Reflectance
As an example, if a sample has a reflectance of 20% at a wavelength of 500nm, then the K/S can be calculated as:

\[
\frac{K/S}{2(0.2)} = \frac{1 - 0.2}{2(0.2)} = 1.6
\]

K/S calculations can be used to evaluate the build up of a particular dye. They can also be used to evaluate the change in strength of a dyeing which has been subjected to a particular set of processing conditions. This is because there is a direct relationship between K/S and dye concentration. Significant differences in reflectance can occur at high dye concentrations particularly when dark shades such as blacks and navies are involved. This results in deviations from the linearity of the Kubleka-Munk function mainly due to surface reflection characteristics resulting in lower reflectances.

The washing process and exposure process was repeated a further five (5) times to equate to a total of 20 hours exposure, when measurement was again carried out. A total of 15 washings gave a total of 30 hours wet exposure.

The fabrics were assessed for loss in colour depth and colour change after 5, 10 and 15 washes, which equates to 10, 20 and 30 hours exposure.

A control series of fabrics were exposed dry and measured after 10, 20 & 30 hours exposure to determine the relative effect of dry exposure compared to wet exposure.

**2.9.2 Delta-E ΔE- Colour Difference [42]**

Delta-E is a measure that represents the distance between two colours in a defined colour space. Delta-E is calculated by the equation:

\[
\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}
\]

Where \(\Delta L\) = lightness,

\(\Delta a = \) red - green character of a colour, positive values of red shades and negative values for green shades &

\(\Delta b = \) yellow – blue character of a colour, positive values for yellow shade and negative values for blue shades.
A $\Delta E$ of 1.0 represents the smallest colour difference the human eye can see. Any $\Delta E$ less than 1.0 would not be noticeable, but a $\Delta E$ greater than 1.0 is usually noticeable. However in certain circumstances a $\Delta E$ greater than 1.0 may not be noticeable, for example, two yellows of the same hue may have a $\Delta E$ greater than 1.0 but may not be noticeable. This is because of the saturation of the yellow colour. Green yellows have low saturation and as a self shade it is difficult to see a 10% difference in colour. The colour difference can be seen easily if the yellow is mixed with a blue to give a green. If the colour difference between the two yellows is substantially different in hue then they become noticeable.

Colours that fade off-tone are more easily distinguished than those that fade in-tone. If fading results in a colour change it is very noticeable. By comparison, if the fade is the same hue but simply changes in depth it is more difficult to recognise.

2.10 Residual Alkali in Washed Samples..
Residual alkali present in fabric after washing was measured from the pH of hot and cold aqueous extracts. The extracts were carried out according to test method AS 2001.3.1 – 1998, Chemical tests - Determination of pH of aqueous extract.
Chapter 3.

Results and Discussion
3.1. Introduction
The experimental data was represented in tables and graphs. These were then analysed to
determine how domestic laundering conditions affect the light fading of navy blue and
black reactive dyes on cotton fabrics. The affect of different detergents on dye desorption
and consequent colour change during washing was assessed. Colour change on exposure
to light due to the detergent used and/or retained alkali in the fabric was evaluated. The
influence of oxidative detergent additives such as sodium perborate on dye desorption
and the wet fading were considered.

3.2. Thin Layer Chromatography (TLC) Analysis
Some dyes used in this investigation were not listed in the Colour Index. Therefore Thin
Layer Chromatography (TLC) was carried out to determine if any of the dyes used were
mixtures.

Cibacron Dk.Blue W-R  C.I Reactive Blue 222  C.I Reactive Blue 222  Reactive Black  C.I Reactive Black 5
Intracron Dk. Blue CDX  Sumifix S. Navy 3GF 150%  Cibacron S.Black R

Figure 3.1. TLC plate
The TLC plates Figures 3.1 and 3.2 show the partition of the components of each of the dyes used. C.I.Reactive Black 5 was selected as the standard for TLC comparison because it is the largest single selling reactive dye [4].

Two commercial dyes both cited as C.I.Reactive Blue 222 as shown Figure 3.1 were used in the experiments. One of the C.I.Reactive Blue 222 dyes, Intracron Dark Blue CDX, appears to have been shaded with a red component by the manufacturer in order to give a redder tone to the dye. However there is also the possibility that this pink component could be an isomer or partially reacted intermediate.

The TLC of the other C.I.Reactive Blue 222, Sumifix Supra Navy Blue 3GF 150%, showed a slightly stronger partition compared to the Intracron Dark Blue CDX. This may suggest the presence of a different isomer.

<table>
<thead>
<tr>
<th>C.I.Reactive Black 5</th>
<th>C.I.Reactive Blue 264</th>
<th>C.I Reactive Blue 225</th>
<th>C.I.Reactive Blue 250</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cibacron Navy LS-G</td>
<td>Levafix Navy B. E-BNA</td>
<td>Remazol Navy RGB</td>
<td>Levafix Navy C-A</td>
</tr>
</tbody>
</table>

Figure 3.2. TLC plate
Cibacron Super (S) Black R, Figure 3.1 is similar to C.I.Reactive Black 5 but shaded with red and yellow dyes. Depending on the conditions of manufacture particularly at the coupling stage C.I.Reactive Black 5 can vary in tone from reddish to bluish [4]. It is for this reason manufacturers add toning dyes to produce a product of “standard” colour.

Cibacron Dark Blue W-R (Figure 3.1) is a mixture that has a similar partition to C.I.Reactive Black 5 but contains another blue dye. When compared with the TLC of Remazol Navy RGB 150% (Figure 3.2) the blue component could be similar to that of C.I. Reactive Blue 250.

Levafix Navy C-A (Figure 3.2) is a mixture and appears to be based on the same components as C.I.Reactive Blue 225, Levafix Navy Blue E-BNA. There may also be a small amount of C.I. Reactive Black 5 present in the mixture to give added tinctorial strength. Material Safety Data Sheets (MSDS) were obtained from the manufacturers and copies are included in Appendix II. In some cases the MSDS information includes reference to C.I. Reactive Black 5.

The chromatographic analysis showed none of the dyes in the study were pure chemical entities. Even those considered identical by their Colour Index classification contained other components and isomers. Therefore each of the commercial dyes may well have different wash fastness and light fading behaviour. As a result this must be expected to lead to depth and tonal changes after washing and light exposure.

3.3 Relative Strength of Dyes Used

Table 3.1 shows that all the navy dyes used were within 13% strength of each other. Levafix Navy C-A was the weakest dye used. Cibacron Dark Blue W-R and Remazol Navy RGB 150% were the strongest. Intracron Dark Blue CDX and Sumifix Supra Navy 3GF150% had the same colour strength even though a lower amount of Intracron Dark Blue CDX was applied to the fabric.

Levafix Navy Blue E-BNA was slightly stronger than Cibacron Navy LS-G. As light fading is a function of colour strength, the relative strength of individual dyes provides a parameter for determining their performance.
Table 3.1. Relative strengths of navy blue reactive dyes.

<table>
<thead>
<tr>
<th>Dyestuff</th>
<th>Percentage applied to Fabric</th>
<th>Percentage Strength *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cibacron Navy LS-G</td>
<td>4.0</td>
<td>100</td>
</tr>
<tr>
<td>Cibacron Dark Blue W-R</td>
<td>3.6</td>
<td>87</td>
</tr>
<tr>
<td>Levafix Navy C-A</td>
<td>4.0</td>
<td>103</td>
</tr>
<tr>
<td>Levafix Navy Blue E-BNA</td>
<td>4.0</td>
<td>98</td>
</tr>
<tr>
<td>Remazol Navy RGB 150%</td>
<td>3.0</td>
<td>87</td>
</tr>
<tr>
<td>Intracron Dark Blue CDX</td>
<td>3.6</td>
<td>90</td>
</tr>
<tr>
<td>Sumifix Supra Navy 3GF 150%</td>
<td>4.0</td>
<td>90</td>
</tr>
</tbody>
</table>

*The lower the figure the greater the strength.

3.4 Dry Fading.

To provide a base standard for the impact of wet fading and washing all the dyed fabrics were subjected to fading in the dry form without laundering (Australian standard AS. 2001.4.21-2006). The loss in colour strength of the dyed fabric was measured after 10, 20 and 30 hours respectively.

![Colour Loss of Dyes after Dry Exposure](image)

Figure 3.3. Comparative dry exposures of all dyes

From Figure 3.3 it can be seen that all dyes had the greatest loss of colour during the first 10 hours of exposure. Colour loss slowed between 10 and 30 hours exposure. A possible
reason for this non linear behaviour could be that larger dye aggregates present on the
fabric surface are more easily attacked by the light causing extra fading in the first 10
hours of exposure.

Significant differences in light fading are evident between the notionally identical Sumifix
Supra Navy 3GF150% and Intracron Dark Blue CDX (both listed as C.I. Reactive Blue
222). The different fading behaviour of these two dyes is clearly due to the different
colour entities making up the two commercial dyes. None of the other dyes used in the
study were chemically identical though there may be some chemical similarity.
Differences in their behaviour to both wet and dry light exposure must be expected.

Table 3.2. Percentage colour loss on dry exposure.

<table>
<thead>
<tr>
<th>Number Hours Exposure</th>
<th>10 hours</th>
<th>20 hours</th>
<th>30 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0% Cibacron Super Black R</td>
<td>13.8</td>
<td>14.5</td>
<td>16.8</td>
</tr>
<tr>
<td>3.6% Cibacron Dark Blue W-R</td>
<td>11.3</td>
<td>9.5</td>
<td>9.8</td>
</tr>
<tr>
<td>4.0% Cibacron Navy LS-G</td>
<td>8.0</td>
<td>11.1</td>
<td>15.5</td>
</tr>
<tr>
<td>4.0% Levafix Navy C-A</td>
<td>10.8</td>
<td>14.0</td>
<td>14.9</td>
</tr>
<tr>
<td>4.0% Levafix Navy Blue E-BNA</td>
<td>16.3</td>
<td>17.7</td>
<td>20.6</td>
</tr>
<tr>
<td>3.6% Intracron Dark Blue CDX</td>
<td>9.0</td>
<td>10.4</td>
<td>12.6</td>
</tr>
<tr>
<td>4.0% Sumifix Supra Navy 3GF 150%</td>
<td>9.7</td>
<td>13.6</td>
<td>16.1</td>
</tr>
<tr>
<td>3.0% Remazol Navy RGB 150%</td>
<td>14.0</td>
<td>16.8</td>
<td>20.2</td>
</tr>
<tr>
<td>1.5% Remazol Navy RGB 150%</td>
<td>14.4</td>
<td>19.3</td>
<td>20.3</td>
</tr>
</tbody>
</table>

Cibacron Dark Blue W-R showed a slight increase in depth, approximately 4.0%, after the
initial 10 hours exposure. This could be explained by a tonal change occurring during the
initial fade that shows as an apparent darkening of colour. This tonal change may be due
to the degree of aggregation [43] of the dye molecules within the micro fibre structure.
Instrumental measurements showed that the DL value (the value of lightness) of the shade was darker and its chroma was duller and greener.

When measuring dark shades, particularly deep navies and blacks there is a high degree of absorbance and low levels of reflected light. This can result in a greater degree of experimental error [44].

The maximum loss in colour strength (Figure 3.3. and Table 3.2) of all dyes after 30 hours exposure was 20% for Levafix Navy Blue E-BNA and both Remazol Navy RGB 150% dyeings (1.5% and 3.0%). Cibacron Dark Blue W-R had the least loss in colour strength of slightly less than 10%. Cibacron Navy LS-G, Intracron Dark Blue CDX and Sumifix Supra Navy 3GF150% all showed similar light stability after 10 and 20 hours exposure, but after 30 hours exposure Intracron Dark Blue CDX showed better light stability. The blue scale of light fastness after exposing the standard blue scales to 30 hours continual exposure, produced a grey scale change of shade rating of 3-4.

The loss of colour strength between all dyes appeared to be consistent when exposed under dry conditions, with the exception of Cibacron Dark Blue W-R which appeared to increase in strength after 10 hours exposure.

Light fading can be directly related to the applied colour strength of a dye. In industry it has been the practice of some dyers to use navy blue dyes as the blue component in three colour combinations believing it to be more economical due to the higher colour strength of the navy blue dye. In fact such a situation could prove dangerous as the final shade will fade off-tone in a very short space of time. From Figure 3.4 and Table 3.2 it can be deduced that if Levafix Navy Blue E-BNA or Remazol Navy RGB 150% was used as the blue component in a three colour mixture then a major shade change would occur after only 10 hours of exposure.

Comparison of Intracron Dark Blue CDX with Sumifix Supra Navy 3GF150% shows that during the first 10 hours the rate of fading is similar with both dyes. Between 10 and 30 hours exposure, however Sumifix Supra Navy 3GF150% exhibits a greater degree of fading. Under normal circumstances it would be expected that dyes of same Colour Index number would fade in a similar manner. In this case Sumifix Supra Navy 3GF150% has lost approximately 27% more colour strength than Intracron Dark Blue CDX. Such a result would indicate that even though the two dyes are listed under the same C.I. number,
there are substantial chemical differences between them. Therefore from the TLC analysis
the differences are possibly due to either the shading colours, the different isomers of
reaction or a combination of both. This would account for Intracron Dark Blue CDX
having better stability to light fading under dry conditions.

Dry fading of Cibacron Dark Blue W-R shows an apparent increase in depth after the
initial 10 hour of fading. This apparent increase in depth is possibly due to a shade change
causing the colour to appear darker after the initial exposure. Remazol Navy RGB150% at
a similar depth does not show this apparent increase in depth.

Comparing Levafix Navy Blue E-BNA against Levafix Navy C-A the dry fading of the
two dyes is significantly different. The Levafix Navy C-A has better overall light fastness
after 30 hours exposure relative to Levafix Navy Blue E-BNA. TLC analysis showed that
there are some chemical similarities between the two dyes, the increased resistance to light
fading of the Levafix Navy C-A could be due to surface aggregation of the dye.

3.5 Commercial Detergent Comparison

Buffer capacity is an important requirement in commercial detergents to ensure any acid or
alkaline soil on articles to be washed does not reduce detergent efficiency. Buffer curves
at 1g/litre of each of the commercial top loading and front loading detergents were
determined by titration against 0.05M sulphuric acid. The curves, Figure 3.4 showed
good buffering capacity between pH 9.8 and pH11.3 and between pH5.3 and pH 7.0. (The
steepness of the curve between pH7.0 and pH9.8 and between pH 3.0 and pH 5.3 indicates
a fall off in the capacity of the detergent to buffer the washing system.)

The pH of each of the detergents at 1.0g/l dissolved in de-ionized water was 11.3. On the
basis of this result the total alkali as sodium carbonate (Na₂CO₃) was determined as:

Top Loading Detergent………………21.7%
Front Loading Detergent …………..20.0%

That is, 1.0g of the top loading detergent powder contains 0.217g sodium carbonate alkali
equivalent and 1.0g detergent powder contained 0.20g sodium carbonate equivalent alkali
for the front loading detergent. The measuring cup supplied with the domestic powders
Figure 3.4. Buffer curves of commercial laundry detergents

contained 60.0g; corresponding to 13.02g and 12.0g of sodium carbonate alkali equivalent for the top load and front load detergent respectively. High alkali in the wash could have an effect on the ultimate performance of dyes particularly in respect to front loading machines.

3.6. Influence of Washing Conditions

Cleaning and washing performance is as much dependent on mechanical action as the type and concentration of the detergent being used. The pH of the liquor was measured at each phase of the machine cycle. Normally there are different formulations for top load and front load washing machines. Front loading machines require a detergent that does not foam excessively. Sodium perborate is often added to improve the cleaning action at the lower liquor volume in front loading machines. Consistent pH results were obtained over a number of experiments of the wash and rinse steps in the front loading machine as shown in Figure 3.5.

Even though the pH of 1.0g/litre of the detergent was 11.3 the actual pH at the end of the first wash was 9.8. Five (5) rinse cycles were used that corresponded with the regular wash cycle program on the Hoover Zodiac 12 washing machine. The pH of the final rinse was found to be consistently 7.4 – 7.5. This indicates that the majority of the alkaline material was removed from the water and probably from the fabric.
The results obtained with the top loading machine were different as far as the pH of the rinse step compared to the front loading machine. One rinse cycle with an intermediate spray rinse between the wash and rinse cycles was used to correspond with the regular wash cycle of the Maytag washing machine. The pH of the wash liquor was found to be 9.8 – 9.9, (same as the front loading machine) Figure 3.6. Over a number of trials the rinse liquor pH was consistent at 8.6 – 8.7. This is similar to that obtained after the second rinse on the front loading cycle Figure 3.5.

Because of the high rinse liquor pH’s in the top loading machine compared to the front loading machine aqueous pH extracts of the fabric from the top loading wash were measured after 15 wash cycles.

The following results were obtained:

- cold aqueous extract    pH 7.7
- hot aqueous extracts    pH 7.6

These figures show that there are only small levels of residual alkali remaining in the fabric. However this level of residual alkali could affect the degree of light fading.
As the pH of the final rinse in the front loading machine was 7.5 being close to neutral it was not considered necessary to carry out aqueous pH extracts.

3.7 Evaluation of Wet Fastness Properties
After dyeing and before washing all the dyed samples were tested for Colour Fastness to Water according to AS 2001.4.E01-2001 and Colour Fastness to Washing AS 2001.4.15.2006 Test 3 Moderate. The results of staining and colour change against the “Geometric Grey Scales” are tabulated in Tables 3.3 and 3.4.

Table 3.3. Colour fastness to washing.

<table>
<thead>
<tr>
<th>Dyestuff</th>
<th>Colour Change</th>
<th>Staining</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Nylon 6:6</td>
</tr>
<tr>
<td>3.6% Cibacron Dark Blue W-R</td>
<td>4</td>
<td>3-4</td>
</tr>
<tr>
<td>4.0% Cibacron Navy LS-G</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>3.0% Remazol Navy RGB 150%</td>
<td>4G</td>
<td>4-5</td>
</tr>
<tr>
<td>3.6% Intracron Dark Blue CDX</td>
<td>4G</td>
<td>4-5</td>
</tr>
<tr>
<td>4.0% Sumifix Supra Navy 3GF150%</td>
<td>4R</td>
<td>4-5</td>
</tr>
<tr>
<td>1.5% Remazol Navy RGB 150%</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>5.0% Cibacron Super Black R</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>4.0% Levafix Navy Blue E-BNA</td>
<td>4</td>
<td>4-5</td>
</tr>
<tr>
<td>4.0% Levafix Navy C-A</td>
<td>4-5</td>
<td>4-5</td>
</tr>
</tbody>
</table>
In the colour change column the letters “G” and “R” have been used to indicate that the original fabric sample has undergone a tonal shift, i.e. “G” Greener, “R” Redder.

Fastness to Water test (Table 3.4) showed no significant shade change of the original dyed fabric. The fastness to washing is a more severe test and it would be expected to show significant differences between the dyes if hydrolysed dye were present.

The results show that with the exception of Cibacron Navy LS-G all the dyes had good fastness to both water and washing and that there was only a minimum of hydrolysed dye present on the fabric.

Table 3.4. Colour fastness to water.

<table>
<thead>
<tr>
<th>Dyestuff</th>
<th>Colour Change</th>
<th>Staining Multi-Fibre</th>
<th>Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Wool</td>
<td>Acrylic</td>
</tr>
<tr>
<td>3.6% Cibacron Dark Blue W-R</td>
<td>4-5</td>
<td>4-5</td>
<td>5</td>
</tr>
<tr>
<td>4.0% Cibacron Navy LS-G</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>3.0% Remazol Navy RGB 150%</td>
<td>4-5</td>
<td>4</td>
<td>4-5</td>
</tr>
<tr>
<td>3.6% Intracron Dark Blue CDX</td>
<td>4-5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>4.0% Sumifix Supra Navy 3GF 150%</td>
<td>4</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>1.5% Remazol Navy RGB 150%</td>
<td>4-5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>5.0% Cibacron Super Black R</td>
<td>4</td>
<td>4-5</td>
<td>5</td>
</tr>
<tr>
<td>4.0% Levafix Navy Blue E-BNA</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>4.0% Levafix Navy C-A</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
</tbody>
</table>

3.8 Colour Change

During domestic washing of navy and black coloured garments colour can move from the fabric into the washing water. Loss of colour results in a colour change of the fabric. Colour change can be either tonal i.e. on-tone or the colour may change in hue i.e. off-
tone. Percentage colour loss only shows changes in colour strength. Colour difference Delta E, (ΔE) measurements take into consideration both change in colour and any changes in hue that occur.

Fading of navy blue and black reactive dyed cotton fabrics is usually accompanied by changes in the colour, these changes can be:

- loss in colour strength;
- change in hue resulting in a different colour;
- apparent increase in colour strength due to dulling of the colour.

Fading often results in several changes to colour taking place at the same time, for example loss in colour strength accompanied by a change in hue. These changes can be measured using a reflectance spectrophotometer together with suitable colour software to produce data that can illustrate the changes that have occurred. The data can be represented as:

1. colour strength expressed as percentage against a known standard;
2. colour difference or Delta E (ΔE) value;
3. total colour value against a known standard expressed as K/S value.

These mathematical representations are useful but they do not provide a visual representation of changes in colour. For this reason mathematical measurements of changes in colour have been supported with photographs to illustrate the colour changes.

### 3.8.1 Colour Loss According to Washing System Not Exposed to Light.

Tables 3.5 to 3.8 show the percentage colour loss for all dyes not exposed to light, after 5, 10 and 15 wash cycles with the three detergent types. Clearly the detergent has a significant influence on desorption (colour loss) of dye from the fabric.

Table 3.5 showed front loading washing removed significantly more dye from the fibres than the top loading washings. However, the detergents used in the two top loading washings are different. In turn this suggests that the detergent in the neutral formulation is more effective in removing colour even in the absence of alkali. This observation also highlights the variations in colour loss that can occur as powders, pre-soaking agents and machine types are changed. Interestingly the neutral detergent formulation had a more severe effect on Cibacron Black R and Cibacron Navy LS-G than the commercial top loading detergent.
Table 3.5.  Percentage colour loss not exposed to light

<table>
<thead>
<tr>
<th>Detergent Type</th>
<th>Cibacron Super Black R</th>
<th>Cibacron Dark Blue W-R</th>
<th>Cibacron Navy LS-G</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 Wash Cycles</td>
<td>10 Wash Cycles</td>
<td>15 Wash Cycles</td>
</tr>
<tr>
<td>Neutral Detergent Top Loading</td>
<td>12.4</td>
<td>16.5</td>
<td>20.9</td>
</tr>
<tr>
<td>Commercial Detergent Top Loading</td>
<td>9.0</td>
<td>9.1</td>
<td>16.1</td>
</tr>
<tr>
<td>Commercial Detergent Front Loading</td>
<td>13.8</td>
<td>28.8</td>
<td>37.5</td>
</tr>
</tbody>
</table>

Conventional thinking would suggest that the colour loss should be higher where the pH is higher. Colour loss resulting from the neutral detergent and top loading detergent followed a similar pattern over the 15 wash cycles with all other dyes except Sumifix Supra Navy 3GF 150%. After 5 wash cycles top loading washing showed a colour loss of 3.9% to 8.9% greater than the neutral detergent. After 15 wash cycles a different pattern emerges, colour loss for the neutral detergent exceeds that of the top loading detergent by between 1.1% to 5.9%. The greater colour loss during the first five wash cycles for the top loading detergent could be due to the alkali content resulting in alkaline hydrolysis of the dye – fibre bond [5]. Colour lost from the fabric during the first two or three wash cycles may have been due to the removal of residual hydrolysed dye remaining in the fabric after the dyeing process.

The more severe affect of the neutral detergent in subsequent wash cycles may well be due to the chemistry of the principle detergent component, sodium dodecyl benzene sulphonate. Other additions to the neutral formulation were 3.0% nonyl phenol 10 mol ETO ethoxylate and 3.5% pure soap. No alkali or buffer salts, were present in the neutral detergent and wash cycle pH was consistently 6.9-7.2. The sodium dodecyl benzene sulphonate may be having an effect on the covalently bonded dyestuff, causing the dye to be released from the fibre. This could explain why many reactive dyes on cotton loose colour during domestic washing. Detergents promote fibre swelling and allow greater penetration of washing liquor into the micro structure of the fibre which can result in increased dye desorption.
Results in Table 3.6 show Levafix Navy C-A has a lower colour loss after 15 wash cycles than Levafix Navy Blue E-BNA. This is probably due to an anomalous reflectance reading showing a hue change, resulting in slight darkening of the colour.

**Table 3.6 Percentage colour loss not exposed to light**

<table>
<thead>
<tr>
<th>Detergent Type</th>
<th>Levafix Navy C-A</th>
<th>Levafix Navy Blue E-BNA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 Wash Cycles</td>
<td>10 Wash Cycles</td>
</tr>
<tr>
<td>Neutral Detergent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top Loading</td>
<td>3.8</td>
<td>13.8</td>
</tr>
<tr>
<td>Commercial Detergent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top Loading</td>
<td>9.4</td>
<td>9.0</td>
</tr>
<tr>
<td>Commercial Detergent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Front Load</td>
<td>7.2</td>
<td>21.2</td>
</tr>
</tbody>
</table>

Levafix Navy C-A also illustrates abnormalities with regard to commercial top loading detergent. The colour loss was greatest after 5 wash cycles, the dye then appeared to increase in colour strength marginally after 10 washes with greater gain in colour after 15 wash cycles. K/S values Figure 3.7 after 5, 10 and 15 wash cycles showed the effect on colour indicating an increase in depth. This abnormality is most probably due to a change in hue.

![Figure 3.7 K/S values for Levafix Navy C-A after washing](image-url)
Table 3.7 showed Sumifix Supra Navy 3GF 150% had a high colour loss of approximately 18.5% for all three detergents after 5 wash cycles. The colour loss resulting from top loading detergent and neutral detergent was effectively the same after 10 and 15 washes (21.4% and 22.0% respectively). The front loading wash system caused higher colour loss; 24.0% after 10 wash cycles and 29.9% following 15 wash cycles.

**Table 3.7 Percentage colour loss not exposed to light**

<table>
<thead>
<tr>
<th>Detergent Type</th>
<th>Intracron Dark Blue CDX</th>
<th>Sumifix Supra Navy 3GF150%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 Wash Cycles</td>
<td>10 Wash Cycles</td>
</tr>
<tr>
<td>Neutral Detergent Top Loading</td>
<td>8.0</td>
<td>13.4</td>
</tr>
<tr>
<td>Commercial Detergent Top Loading</td>
<td>13.8</td>
<td>14.3</td>
</tr>
<tr>
<td>Commercial Detergent Front Load</td>
<td>10.5</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Intracron Dark Blue CDX consistently showed better fastness properties compared to Sumifix Supra Navy 3GF150%. This further confirms that the chemistry of the two dyes is not identical (refer Figure 3.1. TLC Analysis). The neutral detergent formulation has a more severe effect on the Sumifix Supra Navy 3GF150% than on the Intracron Dark Blue CDX were there was no measurable difference in colour loss between the neutral detergent and commercial formulation when washing in the top loading machine.

**Table 3.8 Percentage colour loss not exposed to light**

<table>
<thead>
<tr>
<th>Detergent Type</th>
<th>3.0% Remazol Navy RGB 150%</th>
<th>1.5% Remazol Navy RGB 150%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 Wash Cycles</td>
<td>10 Wash Cycles</td>
</tr>
<tr>
<td>Neutral Detergent Top Loading</td>
<td>6.8</td>
<td>20.1</td>
</tr>
<tr>
<td>Commercial Detergent Top Loading</td>
<td>15.7</td>
<td>21.2</td>
</tr>
<tr>
<td>Commercial Detergent Front Load</td>
<td>22.8</td>
<td>34.4</td>
</tr>
</tbody>
</table>
In the case of Remazol Navy RGB 150% (Table 3.8), both dyeings show similar performance to the three detergent systems. Front loading washing caused very high colour loss at all stages of washing.

The above results show that the most severe colour loss was obtained with the front loading machine. The average colour loss for all dyes after 15 wash cycles was 34.5% for front load wash, verses 21.2% for the neutral wash and 17.5% for the top load commercial detergent. 1.5% Remazol Navy RGB150% showed the greatest colour loss of 47.9% after 15 wash cycles.

The following factors could each have contributed to the more severe colour loss caused by the front loading detergent:

- presence of sodium perborate;
- higher detergent concentration;
- lower liquor to fabric ratio;
- more severe mechanical action.

Again this illustrates the complexity of the home laundering process and its effect on the fastness of any given dye. Sodium perborate present in detergents results in the formation of active oxygen in the form of the peroxy ion

$$\text{NaBO}_3.4\text{H}_2\text{O} \rightarrow \text{Na}^+ + \text{BO}_2^- + \text{OH}^- + \text{O}_2^-$$

The presence of the active alkaline peroxy ion can result in hydrolysis of the dye-fibre bond under the alkaline conditions of the detergent. This is more likely to occur with those dyes based on a vinyl sulphone reactive group [5].

The higher concentration of detergent recommended by the manufacturer is a probable cause of increased colour loss. Detergent concentration for the front loading machine was 2.4 times that recommended for a top loading machine. The volume of liquor compared to fabric is lower in the front loading machine. This lower volume of liquor relative to fabric results in more severe mechanical action which could also increase colour loss.

As a base for the colour loss with the neutral detergent formulation a series of dyeings were washed in water only at 45°C. Table 3.9 shows that both the neutral detergent and water had an effect on dyestuff desorption from the fibre. In all cases the presence of detergent increased the dye desorption after 15 washes.
Table 3.9. Percentage colour loss water vs. neutral detergent not exposed to light

<table>
<thead>
<tr>
<th></th>
<th>Water Only</th>
<th>Neutral Detergent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Wash Cycles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top Load Machine</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Cibacron Super Black R</td>
<td>17.6</td>
<td>20.9</td>
</tr>
<tr>
<td>Cibacron Navy LS-G</td>
<td>22.6</td>
<td>32.8</td>
</tr>
<tr>
<td>Levafix Navy Blue E-BNA</td>
<td>10.1</td>
<td>20.8</td>
</tr>
<tr>
<td>Sumifix Supra Navy 3GF 150%</td>
<td>21.0</td>
<td>22.0</td>
</tr>
<tr>
<td>3.0% Remazol Navy RGB 150%</td>
<td>17.3</td>
<td>23.9</td>
</tr>
<tr>
<td>1.5% Remazol Navy RGB 150%</td>
<td>23.4</td>
<td>27.5</td>
</tr>
</tbody>
</table>

The possible causes for dye desorption by both neutral detergent formulation and water only are most likely to be:

- presence of hydrolysed dye not removed from the fibre;
- destabilization of the bond between the dye and the fibre by the warm water;
- mechanical action of washing cycle.

Hydrolysed dye is difficult to remove from the fibre particularly at low liquor ratios. Electrolyte present in the dyebath during the soaping stage inhibits the removal of hydrolysed dyes, due to the positive ionic charge induced on the fibre surface by the electrolyte. Every precaution was taken to ensure that the presence of hydrolysed dye was at a minimum by soaping at the boil.

Mechanical action during the washing system will facilitate the removal of both hydrolysed dye if present and dye that has been released due to the destabilisation of the dye-fibre bond.
It is unlikely that the bond between the dye and the fibre would be destabilized by warm water alone, unless there was some other factor involved. The only other possible cause could be the heat from the lamp affecting the unexposed portions of the fabric. Rattee and So [45] found that heating during drying had a major effect on the hydrolysis of the dye-fibre bond. The presence of dissolved oxygen in the fibre in conjunction with heat could result in dye–fibre bond hydrolysis. Unexposed portions of the fabric were covered with cardboard to protect the fabric from light exposure (refer Figure 2.7). Some heat would have been transferred to the covered samples from the lamp. De-stabilisation of the dye-fibre bond may occur due to the presence of the neutral detergent as previously indicated. The reasons for this are not clear but may be caused by the presence of residual detergent in the fibre coupled with the heat from the lamp creating a suitable environment for hydrolysis of the dye-fibre bond to occur. [Refer to Figure 2.7 showing how the unexposed fabric is protected from the light source but subject to heat from the lamp.]

3.8.2 Colour Difference According to Washing System Not Exposed to Light
Loss of colour due to dye desorption is only a part of the problem encountered during domestic washing. There can also be a colour change or colour difference accompanying the loss in colour strength. This colour difference is measured as the ΔE (Delta E) value and ΔE >1.0 is usually detectable by an average observer. Table 3.10 shows the colour difference obtained on the washed unexposed samples of fabric after a total of 15 wash cycles.

Cibacron Super Black R, Cibacron Navy LS-G and 1.5% Remazol Navy RGB 150% showed greater colour difference with water only and neutral detergent than with top loading detergent. With all dyed samples other than Sumifix Supra Navy 3GF 150% the front loading detergent resulted in almost double the colour difference compared with the top loading detergent. The concentration in g/l of detergent in the front loading machine was 2.4 times greater than in the top loading machine.

This may well have contributed to the higher colour difference. Sodium perborate present in the front loading detergent will also have had an influence on the colour difference. The manufacturers recommended quantity for the front loading machine is 1 scoop for normal wash and 1.5 scoops for heavily soiled garments.
Table 3.10 Colour difference ∆E not exposed to light

<table>
<thead>
<tr>
<th>Number of Wash Cycles</th>
<th>Water only</th>
<th>Neutral Detergent</th>
<th>Top Loading Detergent</th>
<th>Front Loading Detergent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cibacron Super Black R</td>
<td>3.6</td>
<td>4.1</td>
<td>3.0</td>
<td>6.5</td>
</tr>
<tr>
<td>Cibacron Navy LS-G</td>
<td>2.7</td>
<td>3.6</td>
<td>2.6</td>
<td>5.3</td>
</tr>
<tr>
<td>Levafix Navy Blue E-BNA</td>
<td>1.2</td>
<td>1.7</td>
<td>2.3</td>
<td>4.3</td>
</tr>
<tr>
<td>Sumifix Supra Navy 3GF 150%</td>
<td>2.6</td>
<td>3.0</td>
<td>3.3</td>
<td>3.9</td>
</tr>
<tr>
<td>3.0% Remazol Navy RGB 150%</td>
<td>1.8</td>
<td>2.3</td>
<td>2.2</td>
<td>5.4</td>
</tr>
<tr>
<td>1.5% Remazol Navy RGB 150%</td>
<td>2.5</td>
<td>2.9</td>
<td>2.3</td>
<td>6.5</td>
</tr>
</tbody>
</table>

The quantity of detergent used for the front loading machine was 2.4g/l, compared to the quantity recommended for the top loading machine of 1.0g/l., (refer to 2.7.4 Detergent Quantity).

![Cibacron Super Black R - Colour Difference on Washing](image)

Figure 3.8. Effect of water and detergents on colour difference

Colour difference can be substantial, black is particularly susceptible to the effect of colour change as evidenced by Cibacron Super Black R. Remazol Navy RGB 150%, also showed
marked colour difference being similar to the black particularly at the lighter depth of 1.5%.

Several dyes showed a greater colour change with water only and the neutral detergent formulation compared to the top loading detergent. Figure 3.8 illustrates the ΔE changes with Cibacron Super Black R. Cibacron Super Black R showed the largest colour difference after washing without light exposure. Table 3.11 shows the colour difference of all the dyes after 5, 10 and 15 wash cycles. Of the navy dyes 1.5% Remazol Navy RGB 150% showed the greatest amount of colour change after 15 wash cycles.

Table 3.11 Colour difference ΔE not exposed to light

<table>
<thead>
<tr>
<th></th>
<th>Neutral Detergent</th>
<th>Top Loading Detergent</th>
<th>Front Loading Detergent</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>No. of Wash Cycles</strong></td>
<td><strong>5</strong></td>
<td><strong>10</strong></td>
<td><strong>15</strong></td>
</tr>
<tr>
<td>Cibacron Super Black R</td>
<td>1.7</td>
<td>3.6</td>
<td>4.1</td>
</tr>
<tr>
<td>1.5% Remazol Navy RGB 150%</td>
<td>1.3</td>
<td>2.1</td>
<td>2.9</td>
</tr>
<tr>
<td>3.0% Remazol Navy RGB 150%</td>
<td>0.9</td>
<td>2.0</td>
<td>2.3</td>
</tr>
<tr>
<td>Cibacron Navy LS-G</td>
<td>1.3</td>
<td>2.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Levafix Navy Blue E-BNA</td>
<td>1.3</td>
<td>3.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Cibacron Dark Blue W-R</td>
<td>0.4</td>
<td>1.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Sumifix Supra Navy 3GF 150%</td>
<td>2.7</td>
<td>2.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Intracron Dark Blue CDX</td>
<td>1.4</td>
<td>1.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Levafix Navy C-A</td>
<td>1.3</td>
<td>1.7</td>
<td>1.9</td>
</tr>
</tbody>
</table>

In the majority of cases the neutral detergent and the top loading detergent gave similar results for colour difference. After 5 wash cycles the neutral detergent showed slightly less colour difference than the top loading detergent. Following 10 wash cycles the colour difference with the neutral detergent had increased compared with the top loading detergent. The front loading detergent showed the greatest colour difference after 10 and 15 wash cycles. Levafix Navy C-A showed anomalous results after 15 wash cycles with the top loading detergent. This result could be due to a hue change giving rise to a false reflectance reading.
Thin Layer Chromatographs showed some similarities between Levafix Navy C-A and Levafix Navy Blue E-BNA. However, the MSDS for Levafix Navy Blue E-BNA shows that this dye contains 2-5% C.I.Reactive Black 5. It was appropriate to critically compare their colour loss and colour change on washing. Figures 3.9 and 3.10 illustrate the colour difference due to the detergent type for Levafix Navy C-A and Levafix Navy Blue E-BNA. The results indicate that the former dye had better stability to desorption in the presence of all detergents except the neutral detergent after 15 wash cycles. Levafix Navy Blue E-BNA showed the largest colour difference after 5, 10, and 15 wash cycles with the front loading detergent.

Figure 3.9 Effect of detergents on colour difference

Figure 3.10 Effects of detergents on colour difference
Both the neutral detergent and the top loading detergent had a greater affect on the colour difference of the Levafix Navy C-A after five wash cycles compared to the front loading detergent. The lower colour difference for Levafix Navy C-A after 15 washes with the top loading detergent is anomalous due to a dulling of the sample.

Figures 3.11 and 3.12 illustrate the loss in colour strength attributable to the type of detergent being used.
It can be assumed therefore that the loss in strength is on-tone rather than off-tone. Figure 3.12 shows how much lower the resistance to desorption Levafix Navy Blue E-BNA is compared to Levafix Navy C-A Figure 3.11; losing almost 13% more colour after 15 wash cycles.

### 3.9 Influence of Washing System on the Light Fading of Dyes

Wet exposure to light of the dyed fabrics again showed significant differences between the detergents and machine systems. Wet exposure also highlighted the differences in performance of dyes of supposed similar chemical structure.

Sumifix Supra Navy 3GF 150% and Intracron Dark Blue CDX are of a similar chemical type and were dyed at the same tinctorial strength. Therefore a strict comparison is appropriate. There are significant differences between the behaviour of these two dyes during fading. It was assumed that after the initial 5 washes the majority of the dye lost would be from desorption of hydrolysed dye. Loss in colour strength of the dye after the first five washes was deducted from the subsequent washes to account for the loss of hydrolysed dye. This correction factor was then added back to the strengths of the exposed samples. Therefore it can be assumed that the wet fading compared to the dry fade was due to the presence of residual detergent, alkali and water.

Figures 3.13 and 3.14 show the front loading detergent has the greatest loss in colour strength.
The neutral detergent and the front load detergent caused greater loss in colour strength for Intracron Dark Blue CDX compared to Sumifix Supra Navy 3GF 150% over the three exposure periods. While the graphs show the effect on colour loss they do not show the severe effect on the shade of the fabric after 30 hours wet exposure.

The actual shade shift is more critical in the overall context of the performance of the dye. Dry exposure of the two dyes show similar results (Figures 3.13 vs.3.14); the detergent type has an effect on wet fading of Intracron Dark Blue CDX, and there is a much greater loss in depth. Visually there was significant tonal shift.
Figure 3.15 shows the total loss in colour strength of Intracron Dark Blue CDX comparing wet fading against dry fading. K/S values give total colour loss including the loss due to dye desorption as well as light fading. On comparing Figures 3.15 and 3.16 Sumifix Supra Navy 3GF 150% has a much higher colour loss after 30 hours wet fading. Both graphs show that the front loading detergent has the greater effect on total colour loss when faded in the wet state.

Figure 3.16 K/S values vs. hours of exposure

ΔE (Delta E) values represent total colour difference and show the colour difference between samples rather than loss in colour strength. Figure 3.17 shows the Delta E values

Figure 3.17 Colour difference comparison on dry exposure
between Intracron Dark Blue CDX and Sumifix Supra Navy Blue 3GF 150% on dry exposure. Sumifix Supra Navy 3GF150% showed a greater colour difference after 30 hours exposure. When the results for colour difference after 10 hours exposure are compared to the percentage colour loss as illustrated in Figures 3.13 and 3.14 there is a distinct correlation between the fading and colour difference.

The colour difference i.e. shade change is greater than that indicated by the loss in colour strength as shown by the K/S values. Delta E (ΔE) values of the two dyes are tabulated illustrating the colour difference due to wet light fading Table 3.12.

Table 3.12. Colour difference ΔE - wet light exposure.

<table>
<thead>
<tr>
<th>Hours Wet Exposure</th>
<th>Sumifix Supra Navy 3GF 150%</th>
<th>Intracron Dark Blue CDX</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔE Values</td>
<td>ΔE Values</td>
</tr>
<tr>
<td></td>
<td>Neutral Detergent</td>
<td>Top Load Detergent</td>
</tr>
<tr>
<td>10</td>
<td>2.7</td>
<td>3.4</td>
</tr>
<tr>
<td>20</td>
<td>3.6</td>
<td>4.3</td>
</tr>
<tr>
<td>30</td>
<td>4.6</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Intracron Dark Blue CDX shows better stability to wet light fading after washing in the presence of detergents compared to Sumifix Supra Navy Blue 3GF 150%.. Visual examination of the faded samples also show differences in both tone and brightness of shade after 30 hours wet light fading. Table 3.13 records skilled observer assessments of the shade change after wet exposure. The differences are based on comparing the wet exposed sample to the unexposed original sample under standard D65 lighting conditions.

Table 3.13 Comparative visual examination.

<table>
<thead>
<tr>
<th>Hours Wet Exposure</th>
<th>Sumifix Supra Navy 3GF 150% Visual Examination</th>
<th>Intracron Dark Blue CDX Visual Examination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Neutral Detergent</td>
<td>Top Load Detergent</td>
</tr>
<tr>
<td>30</td>
<td>Lighter Bluer Brighter</td>
<td>Lighter Bluer Brighter</td>
</tr>
</tbody>
</table>
This table also illustrates the difficulties encountered when describing the actual colour differences occurring during light fading. It also demonstrates the difficulty faced with instrumental systems when measuring dark shades [44].

The effect of wet exposure on the colour change of fabrics washed with detergents is of special significance for black dyes based on C.I.Reactive Black 5 such as Cibacron Super Black R. Figure 3.18 shows the significant differences between the detergents and water after wet fading compared to dry exposure.

![Cibacron Super Black R - Colour Difference Comparisons](image)

*Figure 3.18 Colour difference - dry exposure vs. water and detergents exposed wet*

Colour difference for all wash systems after 10 hours wet exposure was less than the dry exposure. A significant increase in colour difference occurred between 10 and 30 hours wet exposure. The detergent for front loading machines showed the greatest colour difference. The samples of fabric show an even more dramatic change of shade attributable to the front loading detergent, see Figure 3.19.
Figure 3.19 Cibacron Super Black R – visual colour change.

Figure 3.20 shows the effect of the different detergents on the loss in colour strength of Cibacron Super Black R after wet fading.

<table>
<thead>
<tr>
<th></th>
<th>Original dyed fabric</th>
<th>15 wash cycles</th>
<th>15 wash cycles &amp; wet exposed 30 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water only</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Front Loading Detergent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top Loading Detergent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutral Detergent</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.14 compares percentage colour loss of dry fade with wet fade of fabrics washed with each detergent. In all cases the greatest percentage colour loss occurred with the front loading detergent. The corrected percentages were calculated as described in section 3.8, paragraph 1.

The greatest percentage loss in colour had occurred with the front loading detergent.
Examination of the colour loss between dry fading and wet fading using corrected figures shows the neutral detergent has a greater affect on the percentage colour loss compared to the top loading detergent. The presence of detergent has a significant effect on the fading of dyes after 20 hours exposure. After 15 washes and 30 hours exposure the front loading detergent had the greatest effect on all dyes.

Table 3.15 compares the colour difference of dry light fading with wet light fading of the selected dyes. At commencement of exposure to light the fabric was wet. At the end of the two hour exposure period the fabric samples were dry. Table 3.15 shows that water alone had a significant effect on the colour difference compared to the samples exposed to light in a dry condition. The results of colour difference for the three detergents indicate that these products are influencing the fading of the dyes in question. The possible cause for this effect is the hydrolysis of the covalent bond. This hydrolysis is brought about by the incident UV radiation from the lamp at 350 -375nm. At these particular wavelengths some azo dyes are sensitive [40]. Further to this the fading may be increased by the formation of a localized peroxy compound as discussed in Chapter 1[31].
### Table 3.15 Colour difference $\Delta E$ dry exposure vs. water and detergents exposed wet.

<table>
<thead>
<tr>
<th></th>
<th>Dry Exposure</th>
<th>Wet Exposure Water Only</th>
<th>Wet Exposure Neutral Detergent</th>
<th>Wet Exposure Top Load Detergent</th>
<th>Wet Exposure Front Load Detergent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hours of Exposure</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Cibacron Super Black R</td>
<td>3.1</td>
<td>4.7</td>
<td>5.8</td>
<td>4.3</td>
<td>8.3</td>
</tr>
<tr>
<td>Cibacron Navy L-SG</td>
<td>1.4</td>
<td>3.2</td>
<td>4.8</td>
<td>3.9</td>
<td>6.6</td>
</tr>
<tr>
<td>Levafix Navy Blue E-BNA</td>
<td>1.9</td>
<td>1.6</td>
<td>3.5</td>
<td>4.1</td>
<td>6.1</td>
</tr>
<tr>
<td>Sumifix Supra Navy 3GF 150%</td>
<td>1.5</td>
<td>3.5</td>
<td>4.7</td>
<td>5.2</td>
<td>5.2</td>
</tr>
<tr>
<td>3.0% Remazol Navy RGB 150%</td>
<td>1.9</td>
<td>3.2</td>
<td>3.9</td>
<td>4.2</td>
<td>6.5</td>
</tr>
<tr>
<td>1.5% Remazol Navy RGB 150</td>
<td>2.1</td>
<td>4.2</td>
<td>5.4</td>
<td>5.1</td>
<td>10.1</td>
</tr>
</tbody>
</table>

The influence of water only on the fading of dyes is shown in Table 3.16. In all cases the percentage strength loss was greater after 20 and 30 hours wet exposure compared to dry exposure. Under these circumstances the presence of water in the fabric together with detergent residues is compounding the effect of covalent dye-fibre bond hydrolysis. Increased swelling of the fibre during wet fading allowed more rapid and deeper penetration of dissolved oxygen into the microstructure of the fibre.

### Table 3.16 Comparative percentage colour loss dry exposure vs. water exposed wet.

<table>
<thead>
<tr>
<th></th>
<th>Dry exposure</th>
<th>Water only Wet faded</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Hours Exposure</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>1.5% Remazol Navy RGB 150%</td>
<td>14.3</td>
<td>19.3</td>
</tr>
<tr>
<td>3.0% Remazol Navy RGB 150%</td>
<td>14.0</td>
<td>17.0</td>
</tr>
<tr>
<td>Cibacron Navy LS-G</td>
<td>8.0</td>
<td>11.0</td>
</tr>
<tr>
<td>Levafix Navy Blue E-BNA</td>
<td>16.3</td>
<td>17.8</td>
</tr>
<tr>
<td>Cibacron Super Black R</td>
<td>13.8</td>
<td>14.6</td>
</tr>
<tr>
<td>Sumifix Supra Navy 3GF 150%</td>
<td>9.8</td>
<td>13.6</td>
</tr>
</tbody>
</table>
As drying takes place moisture migrates from the internal fibre regions. This migration may carry detergent and alkali to the surface of the fabric where they concentrate. This concentration of residues leads to increased chemical activity around the dye molecules aggregated at the fibre surface and hence accelerate colour loss. Migration may also bring hydrolysed dye to the surface which is then removed during the next washing cycle.

Remazol Navy RGB 150% has some similarities to C.I.Reactive Black 5. C.I.Reactive Black 5 is listed as one of the components in the MSDS for this dye. The principle intermediate for C.I.Reactive Black 5 is “H” acid (1-amino-8-hydroxy-naphthalene-3,6-disulphonic acid) [46]. Compared with dry exposure of Cibacron Super Black R, it can be seen that 3.0% Remazol Navy RGB150% fades in a similar manner (Table 3.16). The graph (Figure 3.21) and illustrations (Figure 3.22) show that the lighter depth of shade 1.5% Remazol Navy RGB 150% has a greater loss in colour after 30 hours wet exposure when washed with the front loading detergent.

![Graph showing colour loss comparison](image)

**Figure 3.21 Colour loss – dry exposure vs. water and detergents exposed wet.**
The greater loss in colour strength for the weaker 1.5% Remazol Navy RGB 150% would be expected since fastness to light is a function of colour depth [47]. Colour difference results for this dye are significant, particularly for the lighter depth (Table 3.15) when washed with the front loading detergent. The poor light and washing fastness performance of a garment would present consumer problems if this dye was used as the blue component in a three colour mixture.

**Figure 3.23 Colour loss – dry exposure vs. water and detergents exposed wet.**
Figure 3.24 3.0% Remazol Navy RGB150% -visual colour change
Figure 3.23 compares the dry fading with wet fading of 3.0% Remazol Navy RGB150%. Moisture present on the fabric does increase the degree of fading, but the detergents further increase the fade as can be seen in the illustration Figure 3.24. Water alone has only a minor effect on the loss of colour. The neutral detergent and the top loading detergent significantly increased colour loss and shade difference.

Figure 3.25 Colour difference comparisons on wet exposure.

Figure 3.25 compares the colour difference between Cibacron Super Black R and the two dyeings of Remazol Navy RGB 150% after 30 hours wet fading when washed with the front loading detergent. A similar level of change of colour difference is evident between Cibacron Super Black R and Remazol Navy RGB150% in the fabric illustrations.
The dyeing of Cibacron Dark Blue W-R Figure 3.26 is approximately 13% stronger than that of Cibacron Navy LS-G refer Table 3.1.

![Cibacron Dark Blue W-R - Comparison Detergents Against Dry Fade](image)

Figure 3.26 Colour loss – dry exposure vs. detergents exposed wet.

The results show that Cibacron Dark Blue W-R has a greater tolerance to the front loading detergent than Cibacron Navy LS-G Figure 3.27. Note that on dry fading the two dyes show similar colour loss after 30 hours fading.

![Cibacron Navy LS-G _ Comparison Wet Fade Against Dry Fade](image)

Figure 3.27 Colour loss – dry exposure vs. detergents exposed wet.
Cibacron Navy LS-G shows a greater loss in colour strength with the top loading detergent compared to the Cibacron Dark Blue W-R. The neutral and top loading detergents have a pronounced effect on the fading of both of these dyes.

It seems likely therefore that the main component of the neutral formulated detergent (sodium dodecyl benzene sulphonate) is promoting the hydrolysis of the dye–fibre bond during the drying stage of exposure. As the top loading machine has only a single rinse cycle, detergent residues are retained by the fibre. The long chain alkyl benzene residues are held within the fibre bundles, and therefore are in intimate contact with the dye-fibre bond. During drying and exposure to light these detergent residues migrate to the fabric surface. The concentration of chemicals at the fabric surface increases as the fabric dries. The effect of heat and ultraviolet from the lamp results in hydrolysis of the dye–fibre covalent bond increasing the level of fading.

3.10 Summary – Dye–Fibre Bond Hydrolysis
The factors affecting hydrolysis of reactive dyes during industrial dyeing and finishing are well known [43]. Key initiators of dye-fibre bond hydrolysis are alkali, oxygen, UV radiation and heat. The process of dye-fibre bond hydrolysis can be ongoing as more dye-fibre bonds are broken.

The results of this study strongly indicate that hydrolysis is a key factor in the on-going rate of colour loss and shade change as a result of laundering and drying during use.

The results suggest;

- dye loss can occur when washing in water only, this is most likely due to the presence of dissolved oxygen;
- dye loss increases if the detergent contains an oxygen generating additive such as sodium perborate;
- detergents increase the rate of colour loss;
- different detergent have different effects on the rate of colour loss;
- activation by ultra violet radiation;
- wet exposure to light increases the rate of dye-fibre bond hydrolysis.

The factors affecting colour loss and colour change are cumulative.
Chapter 4.
Conclusions and Recommendations
4.1 Introduction

This study has demonstrated that significant colour change can occur during domestic laundering of cotton fabrics dyed with navy blue and black reactive dyes. Colour loss occurred on exposure to light alone but increased with washing and subsequent wet exposure to light when drying. The colour changes were due to a reduction in colour strength as well as changes in hue. The results showed that detergents, home laundry systems and wet exposure to light all influenced the performance of the selected dyes in respect to fading.

TLC analysis showed that none of the dyes in the study were pure chemical entities; even those considered identical contained other components and isomers. Consequently each dye had a different fading behaviour. Significant colour loss and colour difference were found when laundering with a front loading detergent system. Lower but visually observable levels of fade were found on washing with top loading and neutral detergent systems.

4.2 Colour Change Without Light Exposure.

Reactive dyes are fixed to cotton via covalent bonding to the hydroxyl group of the cellulose molecules. This fixation is achieved in the presence of an alkali, usually sodium carbonate, after diffusion of the dye into the fibre microstructure. Upon the addition of the alkali, dye, either on the fibre surface or in the water, reacts with the hydroxyl group of water giving rise to unfixed or hydrolysed dye. Colour change occurs when double bonds within the dye chromophore are broken by some external force. On completion of dyeing the fabric was treated to remove hydrolysed dye. However it is difficult to remove all unfixed dye as some remain trapped within the fibre structure. Consequently a percentage of the colour change during the first two or three wash cycles was probably due to hydrolysed dye diffusing out.

The desorption of dyes from cotton has been studied [48] and it was found that the presence of detergent, increased temperature and pH accelerated the rate of desorption of direct dyes. If the dye –fibre covalent bond is ruptured then the reactive dye behaves in a similar manner to direct dyes and can be desorbed from the fibre. For both top loading and front loading detergent laundry systems the wash liquor was at a temperature of 45°C and
at approximately pH 10.00. This combination of temperature and alkali can cause hydrolysis of the covalent dye – fibre bond [5] and hence result in a colour change.

No alkali or buffer salts were present in the neutral detergent formulation. After 15 wash cycles the degree of colour change for the neutral and top loading detergents were similar. This suggests that the main neutral detergent component, sodium dodecyl benzene sulphonate, was contributing to colour change. The absence of the buffer salts in the neutral detergent possibly contributed to colour change.

The largest colour change for all the dyes during washing occurred with the front loading detergent laundry system. This is ascribed to the presence of sodium perborate. It is known that vinyl sulphone dyes undergo bond cleavage under alkaline hydrolysis [5]. The severe shade change after washing in the presence of sodium perborate is believed to be due to cleavage of the dye–fibre bond in addition to cleavage of the azo link in the dye. All the dyes used had at least one vinyl sulphone reactive group in the molecule in particular those that are bifunctional. The cleavage of the vinyl sulphone bond would account for the colour loss under the conditions of test.

Other variables that could have contributed to colour loss and colour difference for the front loading detergent were:

1. lower ratio of water to fabric, (10:1 vs. 20:1);
2. more severe mechanical action due to the lower liquor volume;
3. higher concentration of detergent in washing liquor (2.4g/l vs. 1.0g/l).

It is most likely that all these factors contributed to the colour changes found.

4.3 Colour Change On Wet Exposure to Light
On exposure to light the additive affect of dye loss and light fading with the front loading detergent resulted in substantially more colour change compared to the top loading and neutral detergents. Evidence suggested that the light fading of the reactive dyes used in the study, particularly when washed with a detergent containing sodium perborate, was caused by oxidation due to excitation by UV radiation. The MBTF lamp used had a strong peak at about 550nm and a very strong peak at 350nm in the near UV at which many dyes
are sensitive [40]. The covalent dye-fibre bond was broken during light exposure thus causing dye to be desorbed from the fibre.

The above conclusion is supported by Georgio et al [49] who found that the colour of C.I. Reactive Black 5 was completely destroyed in the presence of as little as 0.1g/l hydrogen peroxide (H₂O₂) and ultraviolet radiation of wavelength 200-280nm with an exposure of 1 hour. This system generates hydroxyl radicals (OH⁻) which are highly powerful oxidising species. Hydroxyl radicals can oxidise organic compounds. UV/H₂O₂ systems have led to complete degradation of many organic compounds. This evidence was derived from work on aqueous solutions of dye exposed to hydrogen peroxide and ultraviolet light [49] it directly correlates with the results encountered in the work undertaken.

Other research showed azo reactive dyes can be decolourised in aqueous solution by UV/H₂O₂ oxidation [50]. Light fading on cotton could be due to the role of singlet molecular oxygen [51]. That study found that the dyes investigated produced singlet oxygen possibly by energy transfer on excitation at 514nm. The reported yields of singlet oxygen were low. The role of singlet oxygen [31] was discussed in Chapter 1, section 1.9. The large colour differences which occurred when fabrics were washed with the front loading detergent and then wet faded were most likely due to oxidative hydrolysis caused by the presence of oxygen and ultraviolet light.

Dyeings washed with the top loading and neutral detergents also suffered from lower fastness to light when exposed wet. Top loading machines have a less efficient rinse cycle therefore more detergent and alkali residues remain on the fabric. These residues migrate to and concentrate on the fabric surface during drying. The presence of residual alkali during wet exposure to light in the presence of oxygen increases the degree of light fading due to heat from the light source.

It was concluded that the heat from the light source was a contributing factor in the fading process. [All the dyed samples were exposed using the same light source and at the same temperature.] Heat and light are involved in the rupture of the dye – fibre bond [52]. The relative humidity of the samples exposed dry was lower thus the presence of dissolved oxygen on the fabric was minimal. Samples that were treated with water only, faded to a
greater extent than the dry samples indicating that the moisture content of the fabric is contributing to the rate of fading on exposure to light.

4.4 Limitations
Time constraints imposed a number of limitations on this study:

- only two of the numerous domestic laundry detergents on the market were considered;
- the effect of optical brightening agents on the wet fade of the dyes was not considered;
- only two basic washing machines were considered.

Detergents of formulations different to those used may have resulted in different rates of fading. Optical brightening agents could affect the fading rate of some of the dyes studied. Many modern washing machines have features additional to those of the basic models used.

4.5 Recommendations
This study showed that navy and black cotton fabrics dyed with reactive dyes experience significant colour change during domestic laundering. Detergent formulation and dye structure both contributed to the rate of fading.

The presence of oxidizing bleaches in detergent formulations significantly increased levels of fading of the dyes studied. Therefore this study recommends further investigation into developing a detergent formulation for front loading machines that does not contain oxygen generating bleaches.

This study recommends that dyes with improved stability to residual alkali and detergent additives be a topic for future investigation.
References


[41] www.techexchange.com/thelibrary/colourmatching2.html


Appendix I
# MATERIAL SAFETY DATA SHEET

## 1. IDENTIFICATION OF THE PRODUCT

<table>
<thead>
<tr>
<th>Product Name/s:</th>
<th>Variant/s</th>
<th>Manufacturer's Product Codes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Omomatic/ Persil Low Suds Concentrate Powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Finished Goods Code: 6023-06</td>
</tr>
</tbody>
</table>

**Recommended Use:** Laundry detergent  
**Supplier:** Unilever Australasia  
**A.B.N:** 66 004 050 828  
**Telephone:** +61 2 9871 9200 (Australia) +64 4 5666949 (NZ)  
**Facsimile:** +61 2 9872 4966 (Australia) +64 4 5683396 (NZ)  
**Emergency Telephone:** 1 800 227 200 (Australia) 0 800 108 806 (NZ)  
**Consumer Relations Department**  
Mon-Fri 9.00am-5.00pm

## 2. HAZARDS IDENTIFICATION

<table>
<thead>
<tr>
<th>Hazard Category:</th>
<th>XI: Irritant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Risk Phrase(s):</td>
<td>R36/38 Irritating to eyes and skin.</td>
</tr>
</tbody>
</table>
| Safety Phrase(s):| S2 Keep out of reach of children.  
S22 Do not breathe dust.  
S24 Avoid contact with skin.  
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. |

**Class:** None Allocated

## 3. COMPOSITION INFORMATION ON INGREDIENTS

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>CAS No.</th>
<th>Proportion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Carbonate</td>
<td>497-19-8</td>
<td>10-&lt;30%</td>
</tr>
<tr>
<td>Anionic surfactant</td>
<td></td>
<td>&lt;10%</td>
</tr>
<tr>
<td>Nonionic surfactants</td>
<td></td>
<td>&lt;10%</td>
</tr>
</tbody>
</table>
4. FIRST AID MEASURES

Ingestion: Remove product from mouth. Drink 1 or 2 glasses of water (or milk). If large amount swallowed or symptoms develop obtain medical attention.

Eye contact: Hold eyes open, flood with water for at least 15 minutes and see a doctor.

Skin contact: Wash accidental spillage from skin. Remove contaminated Clothing. Obtain medical attention if symptoms develop.

Inhalation: Remove from source of exposure to fresh air. Obtain medical attention immediately.

Symptoms: Symptoms may vary depending on the level of exposure

Notes to physician: Symptomatic and general supportive treatment should be given.

Treatment: Treat Symptomatically

5. FIREFIGHTING MEASURES

Suitable extinguishing media: Extinguish with water, CO₂, foam or dry chemical. Fire fighters should wear self-contained breathing apparatus for risk of exposure to decomposition products.

Specific hazards: Not flammable but may give off toxic fumes if involved in a fire.

Hazards from decomposition products: Burning can produce CO₂, CO, water vapour, and sulphur oxide.

6. ACCIDENTAL RELEASE MEASURES

Small spills: For spills during personal use, rinse with plenty of water. Normal good housekeeping practices required.

Large spills: For major spills of bulk product, protective clothing consisting of overalls, safety glasses and impervious gloves should be worn. Spills should be contained and absorbed to prevent drain or sewer contamination, and then collect for disposal. For major spills of bulk product, protective clothing consisting of overalls, safety
glasses and gloves should be worn. Shovel or vacuum up spill, avoiding the formation of dust, and collect in suitable containers for disposal. Wash or vacuum any remaining powder. Compressed air must not be used to clean up spills.

It is essential to avoid crushing or grinding the powder, as this could break open the coating surrounding the encapsulated enzyme and generate enzyme dust.

People with a history of respiratory problems must not be employed in the clean up of sizeable spills.

7. HANDLING AND STORAGE

This product is covered by the Workcover Code of Practice for the Safe Handling and Storage of Enzymatic Detergent Powders and Liquids [4th April, 1994] (Australia).

Precautions for Handling: When handling bulk product wear safety glasses and protective gloves. Avoid prolonged contact with skin. Avoid excessive inhalation.

Precautions for Storage: An eyewash station should be installed next to where bulk product is made or stored.

8. EXPOSURE CONTROLS/PERSOAL PROTECTION

National occupational exposure limits: No exposure standards allocated for finished product.

The blanket recommendation for DUSTS: 10 mg/m³

Engineering measures: When handling bulk product, ensure adequate ventilation. Avoid breathing dust.

Personal protection equipment: When handling bulk product wear safety glasses and protective gloves. Avoid prolonged contact with skin. Avoid excessive inhalation.

Manufacturing, packaging and transport: Not defined as a Dangerous Good by the Australian Code for Transport of Dangerous Goods by Road or Rail.

Preparation and use of product: Keep away from foodstuffs and drinks. Wash hands before breaks and at end of shifts.

9. PHYSICAL AND CHEMICAL PROPERTIES

Form/Colour/Odour: White powder with blue speckles

Specific Gravity (20°C): 0.8

Boiling Point (°C): Not applicable
Rel Vapour Density (air=1): Not applicable
Melting Range (C): Not applicable
Vapour Pressure (20C): Not applicable
Flash Point (C): Not applicable
Flammability Limits (%): Not available
pH: 10.0 - 11.0 (1% solution)
Autoignition Temp (C): Not applicable
% Volatile by volume: Not applicable
Solubility in water (mg/l): Not applicable

10. STABILITY AND REACTIVITY
Stability: Product is stable when stored and used in accordance with manufacturers directions.

11. TOXICOLOGICAL INFORMATION
ACUTE EFFECTS
Ingestion: Unlikely to be harmful unless an excessive amount is swallowed
Eye contact: Irritating to eyes.
Skin contact: Irritating to skin.
Inhalation: May cause irritation.
Long Term Effects: No specific chronic effects expected.
Acute Toxicity/Chronic Toxicity: Acute oral toxicity assessed to be greater than 2000 mg/kg body weight.

12. ECOLOGICAL INFORMATION
Aquatic toxicity: Not available
Terrestrial toxicity: Not available
Environmental fate: Not available

13. DISPOSAL CONSIDERATIONS
Refer to State Land Waste Management Authority. Empty cartons can be rinsed and disposed through council recycling service if this type of packaging is accepted.
14. TRANSPORT INFORMATION

UN Number: None Allocated
Proper shipping name: None Allocated
Class: None Allocated
Subsidiary Risk 1: None Allocated
Packing group: None Allocated
Hazchem code: None Allocated
EPG: None Allocated
Segregation Dangerous Goods: None Allocated
Marine Transport: None Allocated
Air Transport: None Allocated

15. REGULATORY INFORMATION

SUSDP Poisons Schedule Number: None Allocated
Prohibition/Licensing Requirements: There are no applicable prohibition or notification, licensing requirements, including for carcinogens under Australian Commonwealth, State or Territory legislation.
Industrial Chemicals (Notifications and Assessment) Act 1989: All ingredients are listed on or exempt from the Australian inventory of Chemical Substances (AICS).

16. OTHER INFORMATION

Date of Revision: 30th October, 2006

Contact Point
Title / Position: Quality Assurance Manager
Section: Quality Assurance, Unilever Australasia
Telephone: (02) 9871 9316
Poison Information Centre 24 Hour Telephone: AUS 131126 - NZ 0800 764 766

DISCLAIMER
This information is based on our current knowledge and is intended to describe the product for the purpose of health, safety and environmental requirements only. Since Unilever Australasia cannot anticipate or control
the conditions under which the product may be used, each user must, prior to usage, review this MSDS in the context of how the user intends to handle and use the product.
MATERIAL SAFETY DATA SHEET

1. IDENTIFICATION OF THE PRODUCT

<table>
<thead>
<tr>
<th>Product Name/s:</th>
<th>Variant/s</th>
<th>Manufacturer's Product Codes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Omo/Persil</td>
<td>High Performance Concentrate Powder</td>
<td>6030-09 6038-05</td>
</tr>
</tbody>
</table>

Recommended Use: Laundry detergent
Supplier: Unilever Australasia
A.B.N: 66 004 050 828
Telephone: +61 2 9871 9200 (Australia) +64 4 5666949 (NZ)
Facsimile: +61 2 9872 4966 (Australia) +64 4 5683396 (NZ)
Emergency Telephone: 1 800 227 200 (Australia) 0 800 108 806 (NZ)
Consumer Relations Department Mon-Fri 9.00am-5.00pm

2. HAZARDS IDENTIFICATION

HAZARDOUS SUBSTANCE – NON-DANGEROUS GOOD

Hazard Category: Xi: Irritant
Risk Phrase(s): R36/38 Irritating to eyes and skin.
Safety Phrase(s): S2 Keep out of reach of children.
S22 Do not breathe dust.
S24 Avoid contact with skin.
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
Class: None Allocated

3. COMPOSITION/INFORMATION ON INGREDIENTS

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>CAS No.</th>
<th>Proportion %</th>
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<td>10-&lt;30%</td>
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<tr>
<td>Anionic surfactant</td>
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</tr>
<tr>
<td>Nonionic surfactants</td>
<td></td>
<td>&lt;10%</td>
</tr>
</tbody>
</table>
102

4. FIRST AID MEASURES

Ingestion: Remove product from mouth. Drink 1 or 2 glasses of water (or milk). If large amount swallowed or symptoms develop obtain medical attention.

Eye contact: Hold eyes open, flood with water for at least 15 minutes and see a doctor.

Skin contact: Wash accidental spillage from skin. Remove contaminated Clothing. Obtain medical attention if symptoms develop.

Inhalation: Remove from source of exposure to fresh air. Obtain medical attention immediately.

Symptoms: Symptoms may vary depending on the level of exposure

Notes to physician: Symptomatic and general supportive treatment should be given.

Treatment: Treat Symptomatically

5. FIREFIGHTING MEASURES

Suitable extinguishing media: Extinguish with water, CO₂, foam or dry chemical. Fire fighters should wear self-contained breathing apparatus for risk of exposure to decomposition products.

Specific hazards: Not flammable but may give off toxic fumes if involved in a fire.

Hazard from decomposition products: Burning can produce CO₂, CO, water vapour, and sulphur oxide.

6. ACCIDENTAL RELEASE MEASURES

Small spills: For spills during personal use, rinse with plenty of water. Normal good housekeeping practices required.

Large spills: For major spills of bulk product, protective clothing consisting of overalls, safety glasses and impervious gloves should be worn. Spills should be contained and absorbed to prevent drain or sewer contamination, and then collect for disposal. For major spills of bulk product, protective clothing consisting of overalls, safety
glasses and gloves should be worn. Shovel or vacuum up spill, avoiding the formation of dust, and collect in suitable containers for disposal. Wash or vacuum any remaining powder. Compressed air must not be used to clean up spills.

It is essential to avoid crushing or grinding the powder, as this could break open the coating surrounding the encapsulated enzyme and generate enzyme dust.

People with a history of respiratory problems must not be employed in the clean up of sizeable spills.

7. HANDLING AND STORAGE

This product is covered by the Workcover Code of Practice for the Safe Handling and Storage of Enzymatic Detergent Powders and Liquids [4th April, 1994] (Australia).

Precautions for Handling: When handling bulk product wear safety glasses and protective gloves. Avoid prolonged contact with skin. Avoid excessive inhalation.

Precautions for Storage: An eyewash station should be installed next to where bulk product is made or stored.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

National occupational exposure limits: No exposure standards allocated for finished product.

The blanket recommendation for DUSTS: 10 mg/m³

Engineering measures: When handling bulk product, ensure adequate ventilation. Avoid breathing dust.

Personal protection equipment: When handling bulk product wear safety glasses and protective gloves. Avoid prolonged contact with skin. Avoid excessive inhalation.

Manufacturing, packaging and transport: Not defined as a Dangerous Good by the Australian Code for Transport of Dangerous Goods by Road or Rail.

Preparation and use of product: Keep away from foodstuffs and drinks. Wash hands before breaks and at end of shifts.

9. PHYSICAL AND CHEMICAL PROPERTIES

Form/Colour/Odour: White powder with blue speckles

Specific Gravity (20°C): 0.8

Boiling Point (°C): Not applicable
10. STABILITY AND REACTIVITY

Stability: Product is stable when stored and used in accordance with manufacturers directions.

11. TOXICOLOGICAL INFORMATION

ACUTE EFFECTS

Ingestion: Unlikely to be harmful unless an excessive amount is swallowed
Eye contact: Irritating to eyes.
Skin contact: Irritating to skin.
Inhalation: May cause irritation.

Long Term Effects: No specific chronic effects expected.

Acute Toxicity/Chronic Toxicity: Acute oral toxicity assessed to be greater than 2000 mg/kg body weight.

12. ECOLOGICAL INFORMATION

Aquatic toxicity: Not available
Terrestrial toxicity: Not available
Environmental fate: Not available

13. DISPOSAL CONSIDERATIONS

Refer to State Land Waste Management Authority. Empty cartons can be rinsed and disposed through council recycling service if this type of packaging is accepted.
14. TRANSPORT INFORMATION

UN Number: None Allocated
Proper shipping name: None Allocated
Class: None Allocated
Subsidiary Risk 1: None Allocated
Packing group: None Allocated
Hazchem code: None Allocated
EPG: None Allocated
Segregation Dangerous Goods: None Allocated
Marine Transport: None Allocated
Air Transport: None Allocated

15. REGULATORY INFORMATION

SUSDP Poisons Schedule Number: None Allocated
Prohibition/Licensing Requirements: There are no applicable prohibition or notification, licensing requirements, including for carcinogens under Australian Commonwealth, State or Territory legislation.
Industrial Chemicals (Notifications and Assessment) Act 1989: All ingredients are listed on or exempt from the Australian inventory of Chemical Substances (AICS).

16. OTHER INFORMATION

Date of Revision: 30th October 2006

Contact Point
Title / Position: Quality Assurance Manager
Section: Quality Assurance, Unilever Australasia
Telephone: (02) 9871 9316 NZ 04 566 6949
Poison Information Centre 24 Hour Telephone: AUS 131126 - NZ 0800 764 766

DISCLAIMER
This information is based on our current knowledge and is intended to describe the product for the purpose of health, safety and environmental requirements only. Since Unilever Australasia cannot anticipate or control
the conditions under which the product may be used. Each user must, prior to usage, review this MSDS in the context of how the user intends to handle and use the product.
Appendix II
Huntsman Textile Effects

MATERIAL SAFETY DATA SHEET


Edition from 03.10.2006

Distribution date 31.01.2007

TRADE NAME

CIBACRON DARK BLUE W-R

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKING

Identification of the substance or preparation

Other names Mixture of azo dyes

Recommended use

Textile dye

Company/undertaking identification

Product responsibility Huntsman Textile Effects CH-4057 Basel

Responsible department Product EHS Fax 0041 61 636 7996

Supplier Huntsman Textile Effects (Australia) Pty. Ltd.

235 Settlement Road

Thornastown

Victoria Australia 3074

Tel: +61 3 9282 0600

Fax: +61 3 9465 9070

Emergency telephone SOS 1800 786 152

2. HAZARDS IDENTIFICATION

Overall statement HAZARDOUS SUBSTANCE, NON-DANGEROUS GOODS

Classified as hazardous according to the criteria of ASCC

R-Phrases R42/43: May cause sensitisation by inhalation and skin contact

S-Phrases S22: Do not breathe dust

S24: Avoid contact with skin
3. COMPOSITION / INFORMATION ON INGREDIENTS

<table>
<thead>
<tr>
<th>Information on ingredients</th>
<th>Content</th>
<th>CAS-No.</th>
<th>Symbol</th>
<th>R-Phrases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium 4-Amino-5-hydroxy-3,6-bis[[4-[[2-(sulfoxy)ethyl]sulfonyl]phenyl]azo]-2,7-naphthalenedisulfonate</td>
<td>50-60 %</td>
<td>17095-24-8</td>
<td>Xn</td>
<td>42/43</td>
</tr>
<tr>
<td>EC No. 241-164-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. FIRST-AID MEASURES

Inhalation  Move to fresh air. Seek medical attention if you feel unwell or if exposure prolonged.
Skin contact Remove contaminated clothing. Wash affected skin with soap and plenty of water.
Eye contact Rinse immediately with plenty of water for at least 10 minutes.
Ingestion Wash out mouth with water. Drink plenty of water.
Advice for the doctor Symptomatic treatment
Further information See section 16 of MSDS

5. FIRE-FIGHTING MEASURES

Fire extinguishing agents Waterspray, foam, powder, carbon dioxide.
Restrictions No restrictions.
Fire/explosion hazard None
Main combustion gas Carbon, nitrogen and sulfur oxides
Personal protection Self contained breathing apparatus.
HAZCHEM Code Not applicable

6. ACCIDENTAL RELEASE MEASURES

Personal protection Gloves, respiratory protection.
Environmental precautions No special precautions
Spillage procedure Damp down. Avoid dust. Scoop into marked containers for disposal as chemical waste. Flush residues away with water.

7. HANDLING AND STORAGE

Handling
Occupational hygiene Avoid ingestion, inhalation, skin and eye contact. Handle in accordance with good industrial hygiene practice and any
8. EXPOSURE CONTROLS AND PERSONAL PROTECTION

National exposure standards

Components with occupational exposure limits
None. Ensure adequate ventilation

Exposure Controls

Occupational exposure controls

General Personal Protection
Gloves, respiratory protection.

Respiratory protection
Respiratory protection, filter P3

Hand protection
Chemical resistant protective gloves (EN 374).
Recommended: permeation time >30 min. (level 2), material e.g. butyl or neopren.
Observe glove manufacturers instructions.

Engineering controls
Use local exhaust ventilation

9. PHYSICAL AND CHEMICAL PROPERTIES

General information

Appearance

Form
Powder

Colour
Black

Odour
None

Important health safety and environmental information

pH
6 - 6.5

Boiling point
Not applicable

Flash point
Not applicable

Oxidising properties
None

Solubility in water
100 g/l

at 30 °C

100 g/l

at 90 °C
Other information

Bulk density 700 kg/m³
Decomposition temperature > 200 °C
Ignition temperature > 500 °C BAM

10. STABILITY AND REACTIVITY

Conditions to avoid None.
Materials to avoid None
Hazardous decomposition products None under normal storage conditions
Chemical stability Material is stable under ambient conditions.

11. TOXICOLOGICAL INFORMATION

Acute toxicity
- LD₅₀ oral > 5000 mg/kg Rat
Primary irritation
(Skin) Non-irritant Rabbit OECD 404
(Eye) Non-irritant Rabbit OECD 405
Skin sensitisation Sensitizing Guinea Pig OECD 406
Adverse effects in man See 16 in MSDS
Additional information The toxicological data is based on the known properties of the components.

12. ECOLOGICAL INFORMATION

Ecotoxicity
Bacterial toxicity

<table>
<thead>
<tr>
<th></th>
<th>IC₅₀</th>
<th>&gt; 100 mg/l</th>
<th>3 h</th>
<th>OECD 209</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish toxicity LC₅₀</td>
<td>&gt; 1000 mg/l</td>
<td>96 hour Zebra fish</td>
<td>OECD 203</td>
<td></td>
</tr>
<tr>
<td>Daphnia toxicity EC₅₀</td>
<td>&gt; 100 mg/l</td>
<td>48 h</td>
<td>OECD 202</td>
<td></td>
</tr>
</tbody>
</table>

Summary Not toxic or harmful to aquatic organisms

Persistence and degradability
Bioelimination 20-30%, TOC/DOC Analysis, OECD 303A
Summary Partially eliminated by adsorption on effluent treatment sludge
Behaviour in treatment plants No inhibition. No nitrification inhibition known

Additional Ecology Data
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD5</td>
<td>0 mgO2/g</td>
</tr>
<tr>
<td>COD</td>
<td>ca. 800 mgO2/g</td>
</tr>
<tr>
<td>Nitrogen content</td>
<td>7.5 %</td>
</tr>
<tr>
<td>Phosphorus content</td>
<td>0.3 % as phosphate</td>
</tr>
<tr>
<td>Organohalogen content</td>
<td>0 %</td>
</tr>
<tr>
<td>Metal content</td>
<td>0.92 % Copper as organo-metal complex</td>
</tr>
<tr>
<td>Tested material</td>
<td>Based on known data of the components</td>
</tr>
</tbody>
</table>

13. DISPOSAL CONSIDERATIONS

Product disposal: Incineration, landfill. Observe local regulations.

Contaminated packaging: Contaminated, empty containers must be disposed of as chemical waste.

14. TRANSPORT INFORMATION

KEEP AWAY FROM FOODSTUFFS

Not classified as dangerous goods

HAZCHEM Code: Not applicable

15. REGULATORY INFORMATION

Industrial Chemical (Notification and Assessment) Act 1989: Inventory of Chemical Substances

SUSDP: Not applicable, product is for industrial applications only

Agricultural and Veterinary Chemicals Act 1988: This product does not require registration under the above act.

16. OTHER INFORMATION

Cases of respiratory sensitisation have been observed with reactive dyes.

Care should be taken to avoid inhalation.

Should an individual become sensitized a physician should be consulted and all contact with reactive dyes must cease immediately.

Recommended restrictions on use

Huntsman textile, paper and leather dyes and chemicals are technical grade and unless otherwise stated or agreed are recommended only for industrial use in applications involving the pretreatment dyeing or finishing of textiles, paper or leather. Other intended uses
including their use in consumer products governed by specific legislation or standards should be referred to the manufacturer. The data contained in the SDS apply only to Huntsman products sold under the stated trade names. Technical information in support will be provided by Huntsman at the request of competent authorities.

member of ETAD
Huntsman Textile Effects

MATERIAL SAFETY DATA SHEET


Edition from 23.10.2006

Distribution date 05.02.2007

TRADE NAME

CIBACRON SUPER BLACK R

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKING

Identification of the substance or preparation

Other names  Mixture of azo dyes

Recommended use  Textile dye

Company/undertaking identification

Product responsibility  Huntsman Textile Effects CH-4057 Basel

Responsible department  Product EHS Fax 0041 61 636 7996

Supplier  Huntsman Textile Effects (Australia) Pty. Ltd.

Thomastown

Victoria Australia 3074

Tel: +61 3 9282 0600

Fax: +61 3 9465 9070

Emergency telephone  SOS 1800 786 152

2. HAZARDS IDENTIFICATION

Stains the eyes

Overall statement  HAZARDOUS SUBSTANCE, NON-DANGEROUS GOODS

Classified as hazardous according to the criteria of ASCC

R-Phrases  R41 : Risk of serious damage to eyes

R42/43 : May cause sensitisation by inhalation and skin contact
S-Phrases
S22 : Do not breathe dust
S24 : Avoid contact with skin
S26 : In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S37/39 : Wear suitable gloves and eye/face protection

3. COMPOSITION / INFORMATION ON INGREDIENTS

<table>
<thead>
<tr>
<th>Information on ingredients</th>
<th>Content</th>
<th>CAS-No.</th>
<th>Symbol</th>
<th>R-Phrases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium 4-Amino-5-hydroxy-3,6-bis[[4-[[2-sulfooxy)ethyl]sulfonyl]phenyl]azo]-2,7-naphthalenedisulfonate</td>
<td>70-80 %</td>
<td>17095-24-8</td>
<td>Xn</td>
<td>42/43</td>
</tr>
<tr>
<td>EC No. 241-164-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. FIRST-AID MEASURES

Inhalation
Move to fresh air. Seek medical attention if you feel unwell or if exposure prolonged.

Skin contact
Remove contaminated clothing. Wash affected skin with soap and plenty of water.

Eye contact
Rinse immediately with plenty of water for at least 10 minutes. Seek medical attention.

Ingestion
Wash out mouth with water. Drink plenty of water.

Advice for the doctor
Symptomatic treatment

Further information
See section 16 of MSDS

5. FIRE-FIGHTING MEASURES

Fire extinguishing agents
Waterspray, foam, powder, carbon dioxide.
Restrictions: No restrictions.
Fire/explosion hazard: None
Main combustion gas: Carbon, nitrogen and sulfur oxides
Personal protection: Self contained breathing apparatus.
HAZCHEM Code: Not applicable

6. ACCIDENTAL RELEASE MEASURES

Personal protection: Goggles, gloves, respiratory protection.
Environmental precautions: No special precautions
Spillage procedure: Damp down. Avoid dust. Scoop into marked containers for disposal as chemical waste. Flush residues away with water.

7. HANDLING AND STORAGE

Handling
Occupational hygiene: Avoid ingestion, inhalation, skin and eye contact. Handle in accordance with good industrial hygiene practice and any legal requirements.

Storage
Fire precautions: No special measures required
Storage facilities: Store in a cool, dry area with adequate ventilation
Segregation: No special precautions.
Storage conditions: Keep containers closed.

8. EXPOSURE CONTROLS AND PERSONAL PROTECTION

National exposure standards
Components with occupational exposure limits: None. Ensure adequate ventilation

Exposure Controls
Occupational exposure controls
General Personal Protection: Goggles, gloves, respiratory protection.
Hand protection: Chemical resistant protective gloves (EN 374).
Recommended: permeation time >30 min. (level 2), material e.g. butyl or neopren.
Observe glove manufacturers instructions.
Eye protection: Tightly fitting safety goggles
Engineering controls: Use only in a well ventilated area
9. PHYSICAL AND CHEMICAL PROPERTIES

General information

Appearance
Form Granular
Colour Black
Odour None

Important health safety and environmental information
pH 5.5 - 6
Boiling point Not applicable
Flash point Not applicable
Oxidising properties None
Solubility in water 100 g/l at 30 °C

Other information
Bulk density 611 kg/m3

10. STABILITY AND REACTIVITY

Conditions to avoid None.
Materials to avoid None
Hazardous decomposition products None under normal storage conditions
Chemical stability Material is stable under ambient conditions.

11. TOXICOLOGICAL INFORMATION

Acute toxicity
- LD50 oral > 2000 mg/kg Rat

Primary irritation
(Skin) Non-irritant Rabbit OECD 404
(Eye) Stains the eyes Rabbit
Skin sensitisation Sensitizing Guinea Pig OECD 406
Adverse effects in man See 16 in MSDS
Additional information The toxicological data is based on the known properties of the components.

12. ECOLOGICAL INFORMATION

Ecotoxicity

Bacterial toxicity
Persistence and degradability

Bioelimination 20-30%, DOC Analysis, OECD 302B

Summary Partially eliminated by adsorption on effluent treatment sludge

Behaviour in treatment plants No inhibition. No nitrification inhibition known

Additional Ecology Data

BOD5 0 mgO2/g
COD ca. 850 mgO2/g
Nitrogen content ca. 7 %
Phosphorus content ca. 0.1 % as phosphate
Organohalogen content 0 %
Metal content Metal content under the ETAD recommended limits
Tested material Based on known data of the components

13. DISPOSAL CONSIDERATIONS

Product disposal Incineration, landfill. Observe local regulations.
Contaminated packaging Contaminated, empty containers must be disposed of as chemical waste.

14. TRANSPORT INFORMATION

KEEP AWAY FROM FOODSTUFFS

Not classified as dangerous goods

HAZCHEM Code Not applicable

15. REGULATORY INFORMATION

Industrial Chemical (Notification and Assessment) Act 1989 A component or components in this product is/are not listed on the Australian Inventory of Chemical Substances.
SUSDP Not applicable, product is for industrial applications only
Agricultural and Veterinary This product does not require registration under the above
16. OTHER INFORMATION

Cases of respiratory sensitisation have been observed with reactive dyes.
Care should be taken to avoid inhalation.
Should an individual become sensitized a physician should be consulted and all contact with reactive dyes must cease immediately.

Recommended restrictions on use

Huntsman textile, paper and leather dyes and chemicals are technical grade and unless otherwise stated or agreed are recommended only for industrial use in applications involving the pretreatment dyeing or finishing of textiles, paper or leather. Other intended uses including their use in consumer products governed by specific legislation or standards should be referred to the manufacturer. The data contained in the SDS apply only to Huntsman products sold under the stated trade names. Technical information in support will be provided by Huntsman at the request of competent authorities.

member of ETAD

MSDS Changes

3. COMPOSITION / INFORMATION ON INGREDIENTS

Information on ingredients

9. PHYSICAL AND CHEMICAL PROPERTIES

Form
pH

12. ECOLOGICAL INFORMATION

Daphnia toxicity
Huntsman Textile Effects

MATERIAL SAFETY DATA SHEET


Edition from 19.10.2006

Distribution date 01.02.2007

TRADE NAME

CIBACRON NAVY LS-G HC

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKING

Identification of the substance or preparation

Other names Azo dye preparation

Recommended use Textile dye

Company/undertaking identification

Product responsibility Huntsman Textile Effects CH-4057 Basel

Responsible department Product EHS Fax 0041 61 636 7996

Supplier Huntsman Textile Effects (Australia) Pty. Ltd.

Thomastown

Victoria Australia 3074

Tel: +61 3 9282 0600

Fax: +61 3 9465 9070

Emergency telephone SOS 1800 786 152

2. HAZARDS IDENTIFICATION

Stains the eyes

Overall statement HAZARDOUS SUBSTANCE, NON-DANGEROUS GOODS

Classified as hazardous according to the criteria of ASCC

R-Phrases

R41 : Risk of serious damage to eyes

R43 : May cause sensitisation by skin contact

S-Phrases

S22 : Do not breathe dust
S24: Avoid contact with skin
S26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S37/39: Wear suitable gloves and eye/face protection

3. COMPOSITION / INFORMATION ON INGREDIENTS

<table>
<thead>
<tr>
<th>Information on ingredients</th>
<th>Content</th>
<th>CAS-No.</th>
<th>Symbol</th>
<th>R-Phrases</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-(4-Amino-5-hydroxy-3-(4-(2-sulfoxyethylsulfonyl)phenylazo)-2,7-disulfonaphth-6-ylazo)-6-{3-(4-amino-5-hydroxy-3-(4-(2-sulfoxyethylsulfonyl)phenylazo)-2,7-disulfonaphth-6-ylazo)phenylcarbonylamino}benzenesulfonic acid, sodium salt</td>
<td>70-80 %</td>
<td>161935-19-9</td>
<td>Xi</td>
<td>41-43</td>
</tr>
<tr>
<td>EC No. 417-640-5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. FIRST-AID MEASURES

Inhalation: Move to fresh air. Seek medical attention if you feel unwell or if exposure prolonged.

Skin contact: Remove contaminated clothing. Wash affected skin with soap and plenty of water.

Eye contact: Rinse immediately with plenty of water for at least 10 minutes. Seek medical attention.

Ingestion: Wash out mouth with water. Drink plenty of water.

Advice for the doctor: Symptomatic treatment

Further information: See section 15 of MSDS

5. FIRE-FIGHTING MEASURES

Fire extinguishing agents: Waterspray, foam, powder, carbon dioxide.

Restrictions: No restrictions.

Fire/explosion hazard: None

Main combustion gas: Carbon, nitrogen and sulfur oxides

Personal protection: Self contained breathing apparatus.

HAZCHEM Code: Not applicable

6. ACCIDENTAL RELEASE MEASURES

Personal protection: Goggles, gloves, respiratory protection.
Environmental precautions | No special precautions
---|---
Spillage procedure | Damp down. Avoid dust. Scoop into marked containers for disposal as chemical waste. Flush residues away with water.

7. HANDLING AND STORAGE

Handling

Occupational hygiene | Avoid ingestion, inhalation, skin and eye contact. Handle in accordance with good industrial hygiene practice and any legal requirements.

Storage

Fire precautions | No special measures required
Storage facilities | Store in a cool, dry area with adequate ventilation
Segregation | No special precautions.
Storage conditions | Sensitive to heat over 40 °C. Keep containers closed.

8. EXPOSURE CONTROLS AND PERSONAL PROTECTION

National exposure standards

Components with occupational exposure limits | None. Ensure adequate ventilation

Exposure Controls

Occupational exposure controls

General Personal Protection | Goggles, gloves, respiratory protection.
Hand protection | Chemical resistant protective gloves (EN 374).
| Recommended: permeation time >30 min. (level 2), material e.g. butyl or neopren.
| Observe glove manufacturers instructions.
Eye protection | Tightly fitting safety goggles
Engineering controls | Use only in a well ventilated area

9. PHYSICAL AND CHEMICAL PROPERTIES

General information

Appearance

Form | Granular
Colour | Black
Odour | None
Important health safety and environmental information

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6 - 7 20 g/l</td>
</tr>
<tr>
<td>Flash point</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Oxidising properties</td>
<td>None</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>&lt; 0.000001 Pascal at 25 °C</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>80 g/l at 30 °C</td>
</tr>
<tr>
<td>Partition coefficient</td>
<td>&lt; -2</td>
</tr>
</tbody>
</table>

Other information

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>&gt; 330 °C</td>
</tr>
<tr>
<td>Bulk density</td>
<td>530 kg/m3</td>
</tr>
<tr>
<td>Decomposition temperature</td>
<td>&gt; 200 °C</td>
</tr>
<tr>
<td>Auto-ignition</td>
<td>&gt; 430 °C DIN 51794</td>
</tr>
<tr>
<td>Ignition temperature</td>
<td>&gt; 500 °C BAM</td>
</tr>
</tbody>
</table>

10. STABILITY AND REACTIVITY

Conditions to avoid: None.
Materials to avoid: None
Hazardous decomposition products: None under normal storage conditions.
Chemical stability: Material is stable under ambient conditions.

11. TOXICOLOGICAL INFORMATION

Acute toxicity

- LD50 oral                        > 2000 mg/kg Rat
- LD50 dermal                      > 2000 mg/kg Rat
Sub-acute toxicity                 NOEL 200 mg/kg/28d 28 d Rat

Primary irritation

(Skin) Non-irritant Rabbit OECD 404
(Eye) Stains the eyes Rabbit OECD 405
Skin sensitisation Sensitizing Guinea Pig OECD 406

Adverse effects in men See 16 in MSDS
Additional information The toxicological tests were carried out on the active component.

12. ECOLOGICAL INFORMATION

Ecotoxicity
Bacterial toxicity

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Time</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC50</td>
<td>&gt; 100 mg/l</td>
<td>0.5 h</td>
<td></td>
</tr>
<tr>
<td>LC0</td>
<td>100 mg/l</td>
<td>96 h</td>
<td>Rainbow trout</td>
</tr>
<tr>
<td>LC50</td>
<td>&gt; 100 mg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daphnia toxicity</td>
<td>EC50</td>
<td>&gt; 100 mg/l</td>
<td>48 h</td>
</tr>
<tr>
<td>Algae toxicity</td>
<td>NOEC</td>
<td>&gt; 100 mg/l</td>
<td>72 h</td>
</tr>
</tbody>
</table>

Summary: Not toxic or harmful to aquatic organisms

Persistance and degradability

Bioelimination: <10% OECD 301E

Summary: 10-20%, DOC Analysis, OECD 302B

Behaviour in treatment plants: Poorly eliminated by adsorption on effluent treatment sludge

Additional Ecology Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD5</td>
<td>7.5 mgO2/g</td>
</tr>
<tr>
<td>COD</td>
<td>930 mgO2/g</td>
</tr>
<tr>
<td>Nitrogen content</td>
<td>8.8 %</td>
</tr>
<tr>
<td>Phosphorus content</td>
<td>&lt; 0.5 %  as phosphate</td>
</tr>
<tr>
<td>Organohalogen content</td>
<td>0 %</td>
</tr>
<tr>
<td>Metal content</td>
<td>Metal content under the ETAD recommended limits</td>
</tr>
<tr>
<td>Tested material</td>
<td>Active component</td>
</tr>
</tbody>
</table>

Additional information

13. DISPOSAL CONSIDERATIONS

Product disposal: Incineration. Observe local regulations.

Contaminated packaging: Contaminated, empty containers must be disposed of as chemical waste.

14. TRANSPORT INFORMATION

KEEP AWAY FROM FOODSTUFFS

Not classified as dangerous goods

HAZCHEM Code: Not applicable

15. REGULATORY INFORMATION

Industrial Chemical (Notification All components of this product are listed on the Australian
SUSDP
Agricultural and Veterinary Chemicals Act 1988

16. OTHER INFORMATION

Cases of respiratory sensitisation have been observed with reactive dyes.

Care should be taken to avoid inhalation.

Should an individual become sensitized a physician should be consulted and all contact with reactive dyes must cease immediately.

Recommended restrictions on use

Huntsman textile, paper and leather dyes and chemicals are technical grade and unless otherwise stated or agreed are recommended only for industrial use in applications involving the pretreatment dyeing or finishing of textiles, paper or leather. Other intended uses including their use in consumer products governed by specific legislation or standards should be referred to the manufacturer. The data contained in the SDS apply only to Huntsman products sold under the stated trade names. Technical information in support will be provided by Huntsman at the request of competent authorities.

member of ETAD

MSDS Changes

9. PHYSICAL AND CHEMICAL PROPERTIES

Form

Bulk density
Safety Data Sheet

LEVAFIX NAVY BLUE E-BNA Gran.

1. Identification of the Chemical/Mixture and the supplier

Product Name: LEVAFIX NAVY BLUE E-BNA Gran.
Other Names: Textile dyeing. Reactive dye
Supplier's Code: DYECEM INDUSTRIES Pty. Ltd.
ABN: 16267780439
Street Address: 60 – 62 Kytta Road
Heidelberg West VIC 3081 Australia
Telephone: +61 (0)3 9457-5311
Facsimile: +61 (0)3 9457-5164
Emergency Numbers: +61 (0)3 9457-5311 (Monday – Friday, 8:00am – 5:00pm) | Transport & Spill emergencies only

2. Hazards Identification

HAZARDOUS CHEMICAL / NON-DANGEROUS GOODS
according to criteria of ASCC / ADG

GHS -
• Hazard Class/Category: SENSITISATION - RESPIRATORY Category 1
SENSITISATION - SKIN Category 1
• Signal Word: DANGER
• Hazard Statements: May cause allergy or asthma symptoms or breathing difficulties if inhaled. H34
May cause an allergic skin reaction H317

Precautionary Statements:
Prevention – P261 Avoid breathing dust / mist.
P285 In case of inadequate ventilation wear respiratory protection (dust mask with particle filter).
P272 Contaminated work clothes should not be allowed out of the work place.
P280 Wear protective gloves.
Response – P304 + P341 - IF INHALED: If breathing is difficult, remove to fresh air and keep at rest in a position comfortable for breathing.
P342 + P311 - If experiencing respiratory symptoms: Call a POISON CENTRE or doctor/physician.
P302 + P352 – IF ON SKIN: wash with plenty of soap & water.
P333 + P313 – If skin irritation or rash occurs: Get medical attention.
P363 – Wash contaminated clothing before reuse.
Disposal – P501 – Dispose of contents/container to authorised special waste disposal site or incineration plant.

NOHSC: 1008 -
• Hazard Category: Xn Harmful
• Risk Phrases: R42 May cause sensitisation by inhalation.
R43 May cause sensitisation by skin contact.
SDS - Ramazol Navy Blue E-BNA Gran.  
Date of Revision: 27/08/2007  
Replaces Version: 29/07/2002

- Safety Phrases:  
  S2   Keep out of reach of children.  
  S22  Do not breathe dust.  
  S24  Avoid contact with skin.  
  S28  After contact with skin, wash immediately with plenty of soap and water  
  S35/37 Wear suitable protective clothing and gloves.  
  S45  In case of accident or if you feel unwell, seek medical advice immediately

ADG -  
- Class: None allocated  
- Subsidiary Risk 1: None allocated  
- Packing Group: None allocated  
- Poisons Schedule: Not scheduled

3. Composition/Information on ingredients

<table>
<thead>
<tr>
<th>Chemical Identity</th>
<th>CAS No.</th>
<th>Proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 2,7-Naphthalenedisulfonic acid, 4-amino-6-[[5-[[5-chloro-2,6-difluoro-4-pyrimidinyl]amino]-2-sulfophenyl]azo]-5-hydroxy-3-[[4-[[2-(sulfoxoy) ethyl]sulfonyl]phenyl]azo]-, lithium sodium salt</td>
<td>108624-00-6</td>
<td>75 - 85%</td>
</tr>
<tr>
<td>- 2,7-Naphthalenedisulfonic acid, 4-amino-5-hydroxy-3,6-bis[[4-[[2-(sulfoxoy)ethyl]sulfonyl]phenyl]azo]-, tetrasodium salt</td>
<td>17095-24-8</td>
<td>2 - 5%</td>
</tr>
<tr>
<td>- Other ingredients determined to be non-hazardous</td>
<td></td>
<td>to 100%</td>
</tr>
</tbody>
</table>

Proportion (% weight per weight): VHIGHT >60, HIGH 30-60, MED 10-30, LOW 1-9, VLLOW <1

4. First Aid Measures

DESCRIPTION OF NECESSARY MEASURES ACCORDING TO ROUTES OF EXPOSURE
For Scheduled Poisons, Poison Information Centres in each State capital city can provide additional assistance. Phone Australia 13 12 26

Swallowed: If the product is swallowed, the patient must immediately drink water repeatedly, if possible with the addition of activated carbon. If the patient feels unwell, seek medical advice.

Eye Contact: Contamination of the eyes must be treated by thorough irrigation with water for 15 minutes, with the eyelids held open. A doctor (or eye specialist) should be consulted immediately.

Skin Contact: Remove all contaminated clothing immediately. Thoroughly wash with plenty of water and soap, or other non-irritating cleansing agents.

Inhalation: Upon inhalation of dust, take the patient into the fresh air. If there is difficulty in breathing, medical advice is required.

Advice to Doctor: Treat symptomatically

5. Fire-fighting Measures

Suitable Extinguishing Media: Water jet, Foam, Powder, CO2

For safety reasons, do not use CO2

Specific Hazards: If burning, may produce oxides of sulphur and nitrogen and carbon monoxide.

Hazchem Code: None allocated

Flammability: Combustible solid


Fire residues and contaminated firefighting water must be disposed of in accordance with local regulations.
6. Accidental Release Measures

Persons responding to accidental spills or release of this product are advised to wear personal protective equipment as given in Section 8 of this SDS.

**Spills:**
- Risk of dust explosion. Eliminate all sources of ignition. Do not breathe dust.
- Do not allow product to enter drains, sewers or waterways.
- Avoid formation and deposition of dust. Take up spilled product with dust-binding material or suitable vacuum cleaner.
- Fill into labelled, sealable containers.

**Disposal:**
- Unusable recovered product should be placed in sealed, labelled containers for disposal in accordance with instructions in section 13.
- Wash away remaining traces with water.

7. Handling and Storage

**Industrial Hygiene:**
- Keep away from food and drink stuffs.
- Wash hands after use and before eating, drinking, smoking or using toilet.
- Remove contaminated clothing and protective equipment before entering eating areas.

**Precautions for Safe Handling:**
- Observe the usual precautionary measures required for chemicals with dust-explosive properties.
- Do not breathe dust.
- Wear personal protective equipment as given in Section 8 of this SDS.
- In filling operations take precautionary measures against static discharges.

**Conditions for Safe Storage:**
- Avoid formation and deposition of dust. Keep containers tightly closed.
- Store in a cool, dry place, out of direct sunlight.
- Store away from oxidising agents.

8. Exposure Controls / Personal Protection

Do not breathe dust. Avoid contact with eyes and skin.
Remove all contaminated clothing immediately.

**NOTICE:** GRANULATE DYE-STUFFS ARE FREE-FLOWING, SPECIALLY DEDUSTED REACTIVE DYE-STUFF PREPARATIONS. BY CAREFUL HANDLING DUSTING CAN BE SUPPRESSED ALMOST COMPLETELY.

Inhalation of dust & aerosols MUST be prevented by either adequate ventilation or by a suitable mask.
Reactive dyestuff.
- People with chronic respiratory problems should not work with reactive dyestuff powders.
- If symptoms such as tightness in the chest or asthma occur while handling reactive dyestuff powders, a physician should be consulted as soon as possible.
- If hypersensitivity is confirmed, all contact with reactive dyestuff powders must cease immediately.

**Occupational Exposure Limits for this specific chemical**

**EXPOSURE STANDARDS**
- Allocated by the ASCC: No exposure standard allocated.
  However, NOHSC:3008 (1995) lists a value of 10mg/m^3 for inspirable dust containing no asbestos and <1% crystalline silica.
- Allocated by other organisations: Not known

**BIOLOGICAL LIMIT VALUES**
- Allocated by the ASCC: No value allocated
- Allocated by other organisations: Not known

**Occupational Exposure Limits for Ingredients**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>TWA</th>
<th>STEL</th>
<th>BLV</th>
<th>Notices</th>
</tr>
</thead>
</table>

Page 3 of 8
TWA – the Time Weighted Average airborne concentration over an eight-hour working day, for a full working week over an entire working life.

STEL - (Short Term Exposure Limit) – the average airborne concentration over a 15 minute period which should not be exceeded at any time during a normal, eight-hour, working day. According to current knowledge, these concentrations should neither impair the health of, nor cause undue discomfort to nearly all workers.

BLV - Biological Limit Value

'SK' notice – absorption through the skin may be a significant source of exposure. The exposure standard is invalidated if such contact should occur.

These exposure standards are guides to be used in the control of occupational health hazards. All atmospheric contamination should be kept to as low a level as is workable. Exposure standards should not be used as the dividing lines between safe and dangerous concentrations of chemicals. They are not a measure of relative toxicity.

If the directions for use on the product label are followed, exposure of individuals using the product should not exceed the above standard. The standard was created for workers who are routinely, potentially exposed during product manufacture.

**Engineering Controls**

Ensure adequate ventilation to control airborne exposure. Good general ventilation should be sufficient; otherwise, provision of local exhaust ventilation is recommended.

Engineering controls, such as provision of local exhaust ventilation or containment, should always be implemented before personal protection equipment is necessary.

**Personal Protection**

**Eye / Face Protection:** Wear safety glasses with eye shields or chemical goggles. Final choice of appropriate eye/face protection will vary according to individual circumstances.

Eye protection devices should conform to AS/NZS 1337 - Eye Protectors for Industrial Applications.

**Respiratory Protection:** Wear dust mask with particle filter.

Wear an approved respirator if engineering controls and dust mask are not effective in controlling airborne exposure.

For guidance on the selection, use and maintenance of Respiratory Protection Devices, refer to AS/NZS 1715 & AS/NZS 1716.

**Gloves:** Wear impervious PVC or nitrile rubber gloves. If necessary, test gloves before use.

**Clothing:** Wear suitable protective clothing such as overalls closed at neck and wrists.

**9. Physical and Chemical Properties**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Colour / Form:</strong></td>
<td>dark blue granules.</td>
</tr>
<tr>
<td><strong>Odour:</strong></td>
<td>Odourless</td>
</tr>
<tr>
<td><strong>pH:</strong></td>
<td>5.0 - 6.0 (100g/l)</td>
</tr>
<tr>
<td><strong>Melting Point:</strong></td>
<td>Not available</td>
</tr>
<tr>
<td><strong>Freezing Point:</strong></td>
<td>Not applicable</td>
</tr>
</tbody>
</table>
10. Stability and Reactivity

Reactivity: Will not react or polymerise.
As with all dusty organic chemicals, the possibility of a dust explosion should be considered.

Chemical Stability: Stable under normal ambient and anticipated storage and handling conditions of temperature and pressure.

Conditions to Avoid: Avoid temperatures above 100°C.

Incompatible Materials: Strong alkalis, oxidising agents and reducing agents destroy the product.

Hazardous Decomposition Products: At temperatures above 150°C, may liberate toxic gases consisting of oxides of sulphur and nitrogen, and carbon monoxide.

11. Toxicological Information

Toxicity Data (PRODUCT = Chemical identified in Section 1)

- **ACUTE TOXICITY**
  - Product: ORAL LD50 > 5,000 mg/kg (rat)
  - Ingredients: CAS 17095-24-8: ORAL LD50 > 2,000 mg/kg (rat) (1)

- **SKIN CORROSION / IRRITATION**
  - Product: non-irritant (rabbit)
  - Ingredients: non-irritant (rabbit) (1)

- **SERIOUS EYE DAMAGE / IRRITATION**
  - Product: non-irritant (rabbit eye)
  - Ingredients: non-irritant (rabbit eye) (1)

- **RESPIRATORY OR SKIN SENSITISATION**
  - Product: No data available
  - Ingredients: CAS 17095-24-8: Possible respiratory sensitisier (1)
  - Ingredients: CAS 108624-00-6: Possible respiratory sensitisier (2)

- **GERM CELL MUTAGENICITY**
  - Product: No data available
  - Ingredients: In Vitro Ames Test (with and without metabolic activation)
    Result: Negative
    Species: salmonella typhimurium
    Concentration: 4 - 5,000 micrograms (1)
- CARCINOGENICITY - Product : No data available
  - Ingredients: No data available

- REPRODUCTIVE TOXICITY - Product : No data available
  - Ingredients: Teratogenicity: NOEL = 1,000mg/kg (rat) (1)

- STOT: SINGLE EXPOSURE - Product : No data available
  - Ingredients: No data available

- STOT: REPEATED EXPOSURE - Product : No data available
  - Ingredients: No data available

- ASPIRATION HAZARD - Product : No data available
  - Ingredients: No data available

Product test results derived from test results of a similarly composed product

HEALTH EFFECTS - ACUTE

Swallowed: May cause mild irritation of digestive tract if ingested in large quantities.
Eye Contact: Non-Irritant. May cause temporary redness / mild irritation.
Skin Contact: Non-Irritant. May cause temporary redness / mild irritation.
Inhalation: High dust concentration may result in irritation of the mucous membranes (eyes or respiratory tract.).

HEALTH EFFECTS - CHRONIC:

Repeated exposure to high dust concentration of some reactive dyestuffs may very occasionally cause respiratory hypersensitivity.
Repeated exposure to high dust concentration of some reactive dyestuff POWDERS containing this dyestuff has very sporadically caused respiratory hypersensitivity.

12. Ecological Information

The following data is derived from test results of an analogous product.

Environmental Fate: No data available
Ecotoxicity: Fish toxicity : LC50 > 100 mg/l (48 h, Leuciscus idus)
  Range Finding Test
  Bacteria toxicity : 100 mg/l Method : 50 % - inhibitory effects:
  Test procedure: Respiratory inhibition of activated sludge organisms according to D. Brown et al., Chemosphere, 10(3), 245-261 (1981), and conforming to OECD Guideline 209
  Chemical oxygen demand (COD) : 590 mg/g
  Biochemical oxygen demand (BOD5): 20 mg/g

Persistence / Degradability:
  Biodegradability : < 10 % Method : evaluated from the components
Bioaccumulative Potential: No data available
Mobility: No data available
Other Data: Product may add max. 2.0 % to the AOX-value of the sewage. (DIN 38409)
The product does not contain heavy metals in concentrations of concern for waste water.
The product does not release nitrogen which can contribute to eutrophication.
The product does not contain phosphates or organophosphorus compounds.
13. Disposal Considerations

If utilisation or recycling of product is not possible, product should be disposed of in accordance with local regulations, at an authorised incineration plant or special waste disposal site.

Contaminated packaging should be emptied as much as possible and may be re-used after appropriate cleaning. Packaging that cannot be cleaned should be disposed of as for product.

14. Transport Information

<table>
<thead>
<tr>
<th>UN Number</th>
<th>None allocated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proper Shipping Name</td>
<td>None allocated</td>
</tr>
<tr>
<td>ADG Class</td>
<td>None allocated</td>
</tr>
<tr>
<td>Subsidiary Risk 1</td>
<td>None allocated</td>
</tr>
<tr>
<td>Packing Group</td>
<td>None allocated</td>
</tr>
<tr>
<td>Hazchem Code</td>
<td>None allocated</td>
</tr>
<tr>
<td>EPG</td>
<td>None allocated</td>
</tr>
<tr>
<td>Segregation Dangerous Goods</td>
<td>None allocated</td>
</tr>
<tr>
<td>Marine Transport</td>
<td>None allocated</td>
</tr>
<tr>
<td>Air Transport</td>
<td>None allocated</td>
</tr>
<tr>
<td>ADR / RID</td>
<td>Non-hazardous / Non-hazardous</td>
</tr>
</tbody>
</table>

15. Regulatory Information

All the constituents of this chemical are listed on the Australian Inventory of Chemical Substances (AICS).

Water Hazard Class (Ger.): WGK 2 - impairment of water quality
WGK = Classification in accordance with the German Water Resources Act
Annex 2 VwWfS (Germany) dated May, 17th 1999

16. Other Information

Prepared in accordance with:

Draft National Code of Practice for the Preparation of Safety Data Sheets - December 2006
including hazard categories and statements (see Section 2 of this SDS) according to NOHSC:2011(2003).

Date of Preparation: 27/08/2007
Date of Revision: 27/08/2007
Reason(s) for Issue:
- Change of SDS format
- Update data in Sections 11

Safety Data Sheets are updated frequently. Please ensure that you have a current copy.

Literary References / Data Sources:
- Supplier SDS: Levafix Navy Blue E-BNA Gran. (Dystar GmbH) - unless otherwise noted.
- (1) European Chemicals Bureau - IUCLID Dataset
- (2) ESIS (Cas No. 108624-00-5)

Legend to Abbreviations and Acronyms:

- < less than
- > greater than
- ºC degrees Celsius
- ACGIH American Conference of Governmental Industrial Hygienists
- ADN European Agreement concerning the International Transport of Dangerous Goods by Inland Waterways.
- ADR European Agreement concerning the International Carriage of Dangerous Goods by Road.
- AIChE Australian Inventory of Chemical Substances
- approx. approximately
- AS Australian Standard
- ASCC Australian Safety and Compensation Council (succeeded NOHSC 7/02/2005)
- BLV Biological Limit Value
End of SDS
Safety Data Sheet

SUMIFIX SUPRA NAVY 3GF 150% gran.

1. Identification of the Chemical/Mixture and the supplier

Product Name: SUMIFIX SUPRA NAVY 3GF 150% gran.
Other Names:
Supplier's Code: Textile dye.
Recommended Use: DYECHEM INDUSTRIES Pty. Ltd.
ABN: 16287780439
Street Address: 60 – 62 Kytta Road
Heidelberg West VIC 3081 Australia
Telephone: +61 (0)3 9457-5311
Facsimile: +61 (0)3 9457-5164
Emergency Numbers: +61 (0)3 9457-5311 (Monday – Friday, 8:00am – 5:00pm)
+61 (0)407-822-236 (After hours)
Transport & Spill emergencies only

2. Hazards Identification

NON-HAZARDOUS CHEMICAL / NON-DANGEROUS GOODS
according to criteria of ASCC / ADG

GHS -
• Hazard Class/Category: None allocated
• Signal Word: None allocated
• Hazard Statements: None allocated

Precautionary Statements:
Prevention – None allocated
Response – None allocated
Disposal – None allocated

NOHSC :1008 -
• Hazard Category: None allocated
• Risk Phrases: None allocated
• Safety Phrases: None allocated

ADG -
• Class: None allocated
• Subsidiary Risk 1: None allocated
• Packing Group: None allocated
• Poisons Schedule: Not scheduled

3. Composition/Information on ingredients

<table>
<thead>
<tr>
<th>Chemical Identifier</th>
<th>CAS No.</th>
<th>Proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azo Reactive dyestuff (C.I. Reactive Blue 222)</td>
<td>EC# 401-310-2</td>
<td>VHIGH</td>
</tr>
</tbody>
</table>
4. First Aid Measures

DESCRIPTION OF NECESSARY MEASURES ACCORDING TO ROUTES OF EXPOSURE
For Scheduled Poisons, Poison Information Centres in each State capital city can provide additional assistance. Phone Australia 13 12 26

Swallowed: If the product is swallowed, the patient must immediately drink water repeatedly, if possible with the addition of activated carbon. If the patient feels unwell, seek medical advice.

Eye Contact: Contamination of the eyes must be treated by thorough irrigation with water for 15 minutes, with the eyelids held open. A doctor (or eye specialist) should be consulted immediately.

Skin Contact: Remove all contaminated clothing immediately. Thoroughly wash with plenty of water and soap, or other non-irritating cleansing agents.

Inhalation: Upon inhalation of dust, take the patient into the fresh air. If there is difficulty in breathing, medical advice is required.

Advice to Doctor: Treat symptomatically

5. Fire-fighting Measures

Suitable Extinguishing Media: Water jet, Foam, Powder, CO2

For safety reasons, do not use CO2

Specific Hazards: If burning, may produce oxides of sulphur and nitrogen, carbon monoxide and hydrogen chloride.

Hazchem Code: None allocated

Flammability: Not flammable, but may burn if involved in a large fire.

Fire-fighting advice: Fire-fighters should wear protective boots, overalls, gloves and goggles. In the case of large fires, fire-fighters are advised to wear self-contained breathing apparatus.

Fire residues and contaminated firefighting water must be disposed of in accordance with local regulations.

6. Accidental Release Measures

Persons responding to accidental spills or release of this product are advised to wear personal protective equipment as given in Section 8 of this SDS.

Spills: Risk of dust explosion. Eliminate all sources of ignition. Do not breathe dust. Do not allow product to enter drains, sewers or waterways.

Avoid generating dust. Take up spilled product with dust-binding material or suitable vacuum cleaner.

Disposal: Unusable recovered product should be placed in sealed, labelled containers for disposal in accordance with instructions in section 13. Wash away remaining traces with water. Prevent washings from entering drains, sewers and waterways.

7. Handling and Storage

Industrial Hygiene: Wash hands after use and before eating, drinking, smoking or using toilet. Remove contaminated clothing and protective equipment before entering eating areas.

Precautions for Safe Handling: Observe the usual precautionary measures required for chemicals with dust-explosive properties. Avoid formation and deposition of dust.
Do not breathe dust.
Wear personal protective equipment as given in Section 8 of this SDS.
In filling operations take precautionary measures against static discharges.

Conditions for Safe Storage:
Keep containers closed. Store in a cool, dry place, out of direct sunlight.

8. Exposure Controls / Personal Protection

Do not breathe dust. Avoid contact with eyes and skin.
Reactive dyestuff.
People with chronic respiratory problems should not work with reactive dyestuff powders.
If symptoms such as tightness in the chest or asthma occur while handling reactive dyestuff powders, a physician should be consulted as soon as possible.
If hypersensitivity is confirmed, all contact with reactive dyestuff powders must cease immediately.

Occupational Exposure Limits for this specific chemical

EXPOSURE STANDARDS

- Allocated by the ASCC: No exposure standard allocated.
  However, NOHSC:3008 (1995) lists a value of 10mg/m3 for
  inspirable dust containing no asbestos and <1% crystalline
  silica.

- Allocated by other organisations: HSE (UK) - Total Inhalable Dust = 10 mg/m3

BIOLOGICAL LIMIT VALUES

- Allocated by the ASCC: No value allocated

- Allocated by other organisations: Not known

Occupational Exposure Limits for Ingredients

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>TWA</th>
<th>STEL</th>
<th>BLV</th>
<th>Notices</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm</td>
<td>mg/m³</td>
<td>ppm</td>
<td>mg/m³</td>
</tr>
<tr>
<td>No Data Available</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

TWA – the Time Weighted Average airborne concentration over an eight-hour working day, for a five-day working week over an entire working life.

STEL - (Short Term Exposure Limit) – the average airborne concentration over a 15 minute period which should not be exceeded at any time during a normal, eight-hour, working day. According to current knowledge, these concentrations should neither impair the health of, nor cause undue discomfort to nearly all workers.

BLV - Biological Limit Value

'Sk' notice – absorption through the skin may be a significant source of exposure. The exposure standard is invalidated if such contact should occur.

These exposure standards are guides to be used in the control of occupational health hazards. All atmospheric contamination should be kept to as low a level as is workable. Exposure standards should not be used as fine dividing lines between safe and dangerous concentrations of chemicals. They are not a measure of relative toxicity. If the directions for use on the product label are followed, exposure of individuals using the product should not exceed the above standard. The standard was created for workers who are routinely, potentially exposed during product manufacture.

Engineering Controls

Ensure adequate ventilation to control airbourne exposure. Provision of local exhaust ventilation is recommended.
Engineering controls, such as provision of local exhaust ventilation or containment, should always be implemented before personal protection equipment is necessary.

Personal Protection

Eye / Face Protection:

Wear safety glasses with eye shields or chemical goggles.
Final choice of appropriate eye/face protection will vary according to individual circumstances.
Eye protection devices should conform to AS/NZS 1337 - Eye Protectors for Industrial Applications.
Respiratory Protection: Wear dust mask with particle filter. Wear an approved respirator if dust mask & engineering controls are not effective in controlling airborne exposure. For guidance on the selection, use and maintenance of Respiratory Protection Devices, refer to AS/NZS 1715 & AS/NZS 1716.

Gloves: Wear impervious PVC or nitrile rubber gloves. If necessary, test gloves before use.

Clothing: Wear suitable protective clothing such as overalls closed at neck and wrists.

9. Physical and Chemical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour / Form</td>
<td>dark blue granules.</td>
</tr>
<tr>
<td>Odour</td>
<td>odourless</td>
</tr>
<tr>
<td>pH</td>
<td>4.5 - 6.5 @ 25°C (30g/l)</td>
</tr>
<tr>
<td>Melting Point</td>
<td>Not available</td>
</tr>
<tr>
<td>Freezing Point</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Initial Boiling Point / Boiling Range</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Flash Point</td>
<td>Not available</td>
</tr>
<tr>
<td>Evaporation Rate</td>
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</tr>
<tr>
<td>Flammability</td>
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<tr>
<td>Flammability Limits</td>
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<tr>
<td>Vapour Pressure</td>
<td>Not available</td>
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<td>Vapour Density</td>
<td>Not available</td>
</tr>
<tr>
<td>Relative Density</td>
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</tr>
<tr>
<td>Solubility</td>
<td>&gt;100g/l @ 25°C</td>
</tr>
<tr>
<td>Partition Co-efficient</td>
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</tr>
<tr>
<td>Auto-Ignition Temperature</td>
<td>470°C</td>
</tr>
<tr>
<td>Decomposition Temperature</td>
<td>Not available</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Not applicable</td>
</tr>
</tbody>
</table>

10. Stability and Reactivity

Reactivity: Will not react or polymerise. As with all dusty organic chemicals, the possibility of a dust explosion should be considered.

Chemical Stability: Stable under normal ambient and anticipated storage and handling conditions of temperature and pressure.

Conditions to Avoid: Avoid temperatures above 120°C.

Incompatible Materials: Strong oxidizing agents, reducing agents and alkalis destroy the product.
11. Toxicological Information

Toxicity Data (PRODUCT = Chemical identified in Section 1)

- **ACUTE TOXICITY**
  - Product: ORAL LD50 > 5,000 mg/kg (mice)
  - Ingredients: No data available

- **SKIN CORROSION / IRRITATION**
  - Product: non-irritant (rabbit)
  - Ingredients: No data available

- **SERIOUS EYE DAMAGE / IRRITATION**
  - Product: non-irritant (rabbit eye)
  - Ingredients: No data available

- **RESPIRATORY OR SKIN SENSITISATION**
  - Product: Repeated exposure to high dust concentration of some reactive dyestuffs may very occasionally cause respiratory hypersensitivity. A sensitisation by this dyestuff has not yet been observed.
  - Ingredients: No data available

- **GERM CELL MUTAGENICITY**
  - Product: No data available
  - Ingredients: No data available

- **CARCINOGENICITY**
  - Product: No data available
  - Ingredients: No data available

- **REPRODUCTIVE TOXICITY**
  - Product: No data available
  - Ingredients: No data available

- **STOST; SINGLE EXPOSURE**
  - Product: No data available
  - Ingredients: No data available

- **STOST; REPEATED EXPOSURE**
  - Product: No data available
  - Ingredients: No data available

- **ASPIRATION HAZARD**
  - Product: No data available
  - Ingredients: No data available

**HEALTH EFFECTS - ACUTE**

Swallowed: May cause irritation of digestive tract if ingested in large quantities.

Eye Contact: Non-Irritant. May cause temporary redness / mild irritation.

Skin Contact: Non-Irritant. May cause temporary redness / mild irritation.

Inhalation: High dust concentration may result in irritation of the mucous membranes.

**HEALTH EFFECTS - CHRONIC:**

Repeated exposure to high dust concentration of some reactive dyestuffs may very occasionally cause respiratory hypersensitivity. A sensitisation by this dyestuff has not yet been observed.
12. Ecological Information

Environmental Fate: No data available
Ecotoxicity: Fish toxicity - LC50: >1,000 mg/l (96 hours, killfish)
Persistence / Degradability: No data available
Bioaccumulative Potential: No data available
Mobility: No data available

13. Disposal Considerations

If utilisation or recycling of product is not possible, it should be disposed of in accordance with local regulations, at an authorised incineration plant or special waste disposal site.

Contaminated packaging should be emptied as much as possible and may be re-used after appropriate cleaning. Packaging that cannot be cleaned should be disposed of as for product.

14. Transport Information

UN Number: None allocated
Proper Shipping Name: None allocated
ADG Class: None allocated
Subsidiary Risk 1: None allocated
Packing Group: None allocated
Hazchem Code: None allocated
EPG: None allocated
Segregation Dangerous Goods: None allocated
Marine Transport: Non-hazardous
Air Transport: Non-hazardous

15. Regulatory Information

All the constituents of this chemical are listed on the Australian Inventory of Chemical Substances (AICS).

16. Other Information

Prepared in accordance with:
Draft National Code of Practice for the Preparation of Safety Data Sheets - December 2006 including hazard categories and statements (see Section 2 of this SDS) according to NOHSC:2011(2003).

Date of Preparation: 05/09/2007
Date of Revision: 05/09/2007
Reason(s) for Issue: Change in SDS format

Safety Data Sheets are updated frequently. Please ensure that you have a current copy.

Literary References / Data Sources:

Supplier SDS - Sumifix Supra Navy 3GF 150 gran. (Sumitomo Chemical Asia - Singapore)
Legend to Abbreviations and Acronyms:

less than
> greater than
°C degrees Celsius
ACGIH American Conference of Governmental Industrial Hygienists
ADN European Agreement concerning the International Transport of Dangerous Goods by Inland Waterways.
ADR European Agreement concerning the International Carriage of Dangerous Goods by Road.
AICS Australian Inventory of Chemical Substances
AOX Adsorbable Organic Halides
approx. approximately
Australian Standard
ASC Australian Safety and Compensation Council (succeeded NOHSC 7/02/2005)
BLV Biological Limit Value
BOD Biological Oxygen Demand
CAS Number Chemical Abstracts Service number is a unique identifier assigned to chemicals by this organisation
CO2 Carbon Dioxide
COD Chemical Oxygen Demand
DOC Dissolved Organic Carbon
EC50 Effective Concentration 50%, amount of a chemical in water, which causes a biological effect in 50% of a group of test animals.
EC/E No CAS and EC No refer to the unique seven-digit code allocated by the Commission of the European Communities. EINECS and ELINCS are older designations for EC#. Similar in function to, & often cross-referenced to, CAS Number.
ESIS European Chemical Substance Information System
g gram
g/cc grams per cubic centimetre
g/l grams per litre
GHS Globally Harmonised System
HCIS Hazardous Chemical Information Service
HSE Health and Safety Executive (United Kingdom)
HSIS Hazardous Substance Information Service
IATA-DGR International Air Transport Association - Dangerous Goods Regulations
ICAO-TI International Civil Aviation Organisation - Technical Instructions on Safe Transport of Dangerous Goods by Air.
IC50 Inhibition Concentration 50%, amount of a chemical in water, which inhibits growth (or other parameter) of 50% of a population of test organisms.
IMDG International Maritime Dangerous Goods Code.
kg kilogram
kg/m3 kilograms per cubic metre
LC50 LC stands for “Lethal Concentration”. LC50 is the concentration of a chemical in air which causes the death of 50% (1/2) of a group of test animals. The chemical is inhaled over a set period of time, usually 1 or 4 hours.
LD50 LD stands for “Lethal Dose”. LD50 is the amount of chemical, given all at once, which causes the death of 50% (1/2) of a group of test animals.
mg milligram
mg/kg milligrammes per gram
mg/l milligrammes per litre
mg/m3 milligrams per cubic metre
mm millimetre
NICNAS National Industrial Chemicals Notification and Assessment Scheme (Australia)
NOHSC National Occupational Health and Safety Commission (succeeded by ASCC)
NZS New Zealand Standard
ppm parts per million
PVC polyvinyl chloride
RID European Agreement concerning the International Carriage of Dangerous Goods by Rail.
R Phrase Risk phrase
S Phrase Safety phrase
STOT Specific Target Organ Systemic Toxicity
UN United Nations (number)
w/v Weight by volume
w/w Weight by weight

This SDS summarizes our best knowledge of the health and safety hazard information of the product and how to safely handle the product in the workplace. Each user should read this SDS and consider the information in the context of how the product will be handled and used in the workplace, including its use in conjunction with other substances.

We have reviewed any information contained herein, which was received from sources outside DYECHEM INDUSTRIES Pty Ltd. However, no warranty or recommendation, expressed or implied, is made as to the accuracy or completeness of the data and information contained in this data sheet.

Health and safety precautions and environmental advice noted in this data sheet may not be accurate for all individuals and/or situations. It is the user's obligation to evaluate and use this product safely and to comply with all applicable laws and regulations. No statement made in this data sheet shall be construed as a permission, recommendation or authorization, given or implied, to practise any patented invention without a valid licence.

DYECHEM INDUSTRIES Pty Ltd shall not be responsible for any damage or injury resulting from: abnormal use of the chemical; any failure to adhere to recommendations; any hazards inherent in the nature of the chemical.

DYECHEM INDUSTRIES Pty Ltd expressly disclaims that the SDS is a representation or guarantee of the chemical specifications for the product.

END of SDS
Safety Data Sheet

REMAZOL NAVY RGB 150% Gran.

1. Identification of the Chemical/Mixture and the supplier

Product Name: REMAZOL NAVY RGB 150% Gran.
Other Names: 
Supplier's Code: 
Recommended Use: Textile dyeing. Reactive dye
Supplier: DYECHEM INDUSTRIES Pty. Ltd.
ABN: 18287780439
Street Address: 60 – 62 Kylta Road
Heidelberg West VIC 3081 Australia
Telephone: +61 (0)3 9457-5311
Facsimile: +61 (0)3 9457-5184
Emergency Numbers: +61 (0)3 9457-5311 (Monday – Friday, 8:00am – 5:00pm) Transport & Spill emergencies only
+61 (0)407-822-236 (After hours)

2. Hazards Identification

HAZARDOUS CHEMICAL / NON-DANGEROUS GOODS according to criteria of ASCC / ADG

GHS -
- Hazard Class/Category: SENSITISATION - RESPIRATORY Category 1
SENSITISATION - SKIN Category 1
- Signal Word: DANGER
- Hazard Statements:
  May cause allergy or asthma symptoms or breathing difficulties if inhaled. H334
  May cause an allergic skin reaction. H317

Precautionary Statements:
Prevention – P261 Avoid breathing dust / mist.
P265 In case of inadequate ventilation wear respiratory protection (dust mask with particle filter).
P272 Contaminated work clothes should not be allowed out of the work place.
P280 Wear protective gloves.

Response – P304 + P341 - IF INHALED: If breathing is difficult, remove to fresh air and keep at rest in a position comfortable for breathing.
P342 + P311 - If experiencing respiratory symptoms: Call a POISON CENTRE or doctor/physician.
P302 + P352 – IF ON SKIN: wash with plenty of soap & water.
P333 + P313 – If skin irritation or rash occurs: Get medical attention.
P363 – Wash contaminated clothing before reuse.

Disposal – P501 – Dispose of contents/container to authorised special waste disposal site or incineration plant.

NOHSC :1008 -
- Hazard Category: Xn Harmful
- Risk Phrases: R42 May cause sensitisation by inhalation.
R43 May cause sensitisation by skin contact.
• Safety Phrases:
  S20/21 When using, do not eat drink or smoke.
  S22 Do not breathe dust.
  S24 Avoid contact with skin.
  S28 After contact with skin, wash immediately with plenty of soap and water.
  S35/37 Wear suitable protective clothing and gloves.
  S45 In case of accident or if you feel unwell, seek medical advice immediately.

ADG -
• Class: None allocated
• Subsidiary Risk 1: None allocated
• Packing Group: None allocated
• Poisons Schedule: Not scheduled

### 3. Composition/Information on ingredients

<table>
<thead>
<tr>
<th>Chemical Identity</th>
<th>CAS No.</th>
<th>Proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,7-Naphthalenedisulfonic acid, 4-amino-5-hydroxy-3,6-bis[[4-[[2-(sulfoxy)ethyl]sulfone]phenyl]azo]-, tetrasodium salt</td>
<td>17095-24-8</td>
<td>LOW VHIGH</td>
</tr>
<tr>
<td>Other ingredients determined to be non-hazardous</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Proportion (% weight per weight): VHIGH >60, HIGH 30–60, MED 10–<30, LOW 1–8, VLOW <1

### 4. First Aid Measures

DESCRIPTION OF NECESSARY MEASURES ACCORDING TO ROUTES OF EXPOSURE For Scheduled Poisons, Poison Information Centres in each State capital city can provide additional assistance. Phone Australia 13 12 26

Swallowed: If the product is swallowed, the patient must immediately drink water repeatedly, if possible with the addition of activated carbon. If the patient feels unwell, seek medical advice.

Eye Contact: Contamination of the eyes must be treated by thorough irrigation with water for 15 minutes, with the eyelids held open. A doctor (or eye specialist) should be consulted immediately.

Skin Contact: Remove all contaminated clothing immediately. Thoroughly wash with plenty of water and soap, or other non-irritating cleansing agents.

Inhalation: Upon inhalation of dust, take the patient into the fresh air. If there is difficulty in breathing, medical advice is required.

Advice to Doctor: Treat symptomatically

### 5. Fire-fighting Measures

Suitable Extinguishing Media: Water jet, Foam, Powder, CO2
For safety reasons, do not use CO2

Specific Hazards: If burning, may produce oxides of sulphur and nitrogen and carbon monoxide.

Hazchem Code: None allocated

Flammability: Combustible solid


Fire residues and contaminated firefighting water must be disposed of in accordance with local regulations.
6. Accidental Release Measures

Persons responding to accidental spills or release of this product are advised to wear personal protective equipment as given in Section 8 of this SDS.

**Spills:**
- Risk of dust explosion. Eliminate all sources of ignition. Do not breathe dust.
- Do not allow product to enter drains, sewers or waterways.
- Avoid formation and deposition of dust. Take up spilled product with dust-binding material or suitable vacuum cleaner.
- Fill into labelled, sealable containers.

**Disposal:**
- Unusable recovered product should be placed in sealed, labelled containers for disposal in accordance with instructions in section 13.
- Wash away remaining traces with water.

7. Handling and Storage

**Industrial Hygiene:**
- Keep away from food and drink stuffs.
- Wash hands after use and before eating, drinking, smoking or using toilet.
- Remove contaminated clothing and protective equipment before entering eating areas.

**Precautions for Safe Handling:**
- Observe the usual precautionary measures required for chemicals with dust-explosive properties.
- Do not breathe dust.
- Wear personal protective equipment as given in Section 8 of this SDS.
- In filling operations take precautionary measures against static discharges.

**Conditions for Safe Storage:**
- Avoid formation and deposition of dust. Keep containers tightly closed.
- Store in a cool, dry place, out of direct sunlight.
- Store away from oxidising agents.

8. Exposure Controls / Personal Protection

Do not breathe dust. Avoid contact with eyes and skin.
Remove all contaminated clothing immediately.

**NOTICE:** GRANULATE DYESTUFFS ARE FREE-FLOWING, SPECIALLY DEDUSTED REACTIVE DYESTUFF PREPARATIONS. BY CAREFUL HANDLING DUSTING CAN BE SUPPRESSED ALMOST COMPLETELY.

Inhalation of dust & aerosols MUST be prevented by either adequate ventilation or by a suitable mask.

Reactive dyestuff.
People with chronic respiratory problems should not work with reactive dyestuff powders.
If symptoms such as tightness in the chest or asthma occur while handling reactive dyestuff powders, a physician should be consulted as soon as possible.
If hypersensitivity is confirmed, all contact with reactive dyestuff powders must cease immediately.

**Occupational Exposure Limits for this specific chemical**

**EXPOSURE STANDARDS**
- Allocated by the ASCC: No exposure standard allocated.
  However, NOHSC:3008 (1995) lists a value of 10mg/m³ for inspirable dust containing no asbestos and <1% crystalline silica.
- Allocated by other organisations: Not known

**BIOLOGICAL LIMIT VALUES**
- Allocated by the ASCC: No value allocated
- Allocated by other organisations: Not known

**Occupational Exposure Limits for Ingredients**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>TWA</th>
<th>STEL</th>
<th>BLV</th>
<th>Notices</th>
</tr>
</thead>
</table>

143
TWA – the Time Weighted Average airborne concentration over an eight-hour working day, for a five-day working week over an entire working life.

STEL – (Short Term Exposure Limit) – the average airborne concentration over a 15 minute period which should not be exceeded at any time during a normal, eight-hour, working day. According to current knowledge, these concentrations should neither impair the health of, nor cause undue discomfort to, nearly all workers.

BLV – Biological Limit Value.

'SK' notice – absorption through the skin may be a significant source of exposure. The exposure standard is invalidated if such contact should occur.

These exposure standards are guides to be used in the control of occupational health hazards. All atmospheric contamination should be kept to as low a level as is workable. Exposure standards should not be used as fine dividing lines between safe and dangerous concentrations of chemicals. They are not a measure of relative toxicity.

If the directions for use on the product label are followed, exposure of individuals using the product should not exceed the above standard. The standard was created for workers who are routinely potentially exposed during product manufacture.

**Engineering Controls**
Ensure adequate ventilation to control airborne exposure. Good general ventilation should be sufficient; otherwise, provision of local exhaust ventilation is recommended.

Engineering controls, such as provision of local exhaust ventilation or containment, should always be implemented before personal protection equipment is necessary.

**Personal Protection**

**Eye / Face Protection:**
Wear safety glasses with eye shields or chemical goggles. Final choice of appropriate eye/face protection will vary according to individual circumstances.

Eye protection devices should conform to AS/NZS 1337 - Eye Protectors for Industrial Applications.

**Respiratory Protection:**
Wear dust mask with particle filter. Wear an approved respirator if engineering controls and dust mask are not effective in controlling airborne exposure.

For guidance on the selection, use and maintenance of Respiratory Protection Devices, refer to AS/NZS 1715 & AS/NZS 1716.

**Gloves:**
Wear impervious PVC or nitrile rubber gloves. If necessary, test gloves before use.

**Clothing:**
Wear suitable protective clothing such as overalls closed at neck and wrists.

**9. Physical and Chemical Properties**

<table>
<thead>
<tr>
<th>Colour / Form</th>
<th>dark blue granules.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odour</td>
<td>Odourless</td>
</tr>
<tr>
<td>pH</td>
<td>4.5 - 5.0 (100g/l)</td>
</tr>
<tr>
<td>Melting Point</td>
<td>Not available</td>
</tr>
<tr>
<td>Freezing Point</td>
<td>Not applicable</td>
</tr>
</tbody>
</table>
10. Stability and Reactivity

Reactivity: Will not react or polymerise. As with all dusty organic chemicals, the possibility of a dust explosion should be considered.

Chemical Stability: Stable under normal ambient and anticipated storage and handling conditions of temperature and pressure.

Conditions to Avoid: Avoid temperatures above 100°C.

Incompatible Materials: Strong alkalis, oxidising agents and reducing agents destroy the product.

Hazardous

Decomposition Products: At temperatures above 150°C, may liberate toxic gases consisting of oxides of sulphur and nitrogen, and carbon monoxide.

11. Toxicological Information

Toxicity Data (PRODUCT = Chemical identified in Section 1)

- **ACUTE TOXICITY** - Product: ORAL LD50 > 5,000 mg/kg (rat)
  - Ingredients: ORAL LD50 > 2,000 mg/kg (rat) (*)

- **SKIN CORROSION / IRRITATION** - Product: non-irritant (rabbit)
  - Ingredients: non-irritant (rabbit)

- **SERIOUS EYE DAMAGE / IRRITATION** - Product: non-irritant (rabbit eye)
  - Ingredients: non-irritant (rabbit eye)

- **RESPIRATORY OR SKIN SENSITISATION** - Product: In the guinea-pig the product has a sensitising effect (OECD 406, GPMT according to MAGNUSSON-KLIGMAN).
  - Ingredients: Possible respiratory sensitiser (*)
    Skin sensitiser (*)

  - Ingredients: In Vitro Ames Test (with and without metabolic activation)
    Result: Negative
    Species: salmonella typhimurium
    Concentration: 4 - 5,000 micrograms (*)
HEALTH EFFECTS - ACUTE
Swallowed: May cause mild irritation of digestive tract if ingested in large quantities.
Eye Contact: Non-Irritant. May cause temporary redness / mild irritation.
Skin Contact: Non-Irritant. May cause temporary redness / mild irritation.
Inhalation: High dust concentration may result in irritation of the mucous membranes (eyes or respiratory tract.).

HEALTH EFFECTS - CHRONIC:
Repeated exposure to high dust concentration of some reactive dyestuffs may very occasionally cause respiratory hypersensitivity.
Repeated exposure to high dust concentration of some reactive dyestuff POWDERS containing this dyestuff has very sporadically caused respiratory hypersensitivity.

12. Ecological Information

The following data is derived from test results of an analogous product.

Environmental Fate: No data available
Ecotoxicity:
Fish toxicity: LC50 >100 mg/l (96 h, Brachydanio rerio)
Method: 92/69/EEC, C.1
Bacteria toxicity: EC50 > 100 mg/l (3 h, activated sludge micro-organism)
Method: OECD 209

Chemical oxygen demand (COD): 690 mg/l
Biochemical oxygen demand (BOD5): < 30 mg/l

Persistence / Degradability:
Biodegradability: < 10 % Method: static test.

If regulations are followed when introducing effluent into biological waste water treatment plants, no adverse effect on the degradation activity of activated sludge is to be expected.

Bioaccumulative Potential: No data available
Mobility: No data available

Other Data:
Product does not add to the AOX-value of the sewage. (DIN EN 1485)
The product does not contain heavy metals in concentrations of concern for waste water.
The product does not release nitrogen which can contribute to eutrophication.
The product does not contain phosphates or organophosphorus compounds.
13. Disposal Considerations

If utilisation or recycling of product is not possible, product should be disposed of in accordance with local regulations, at an authorised incineration plant or special waste disposal site.

Contaminated packaging should be emptied as much as possible and may be re-used after appropriate cleaning. Packaging that cannot be cleaned should be disposed of as for product.

14. Transport Information

UN Number: None allocated
Proper Shipping Name: None allocated
ADG Class: None allocated
Subsidiary Risk 1: None allocated
Packing Group: None allocated
Hazchem Code: None allocated
EPG: None allocated
Segregation Dangerous Goods: None allocated
Marine Transport: None allocated
Air Transport: None allocated

15. Regulatory Information

All the constituents of this chemical are listed on the Australian Inventory of Chemical Substances (AICS).

Water Hazard Class (Ger.): WGK 2 - impairment of water quality
WGK - Classification in accordance with the German Water Resources Act, Annex 2 WWVWS (Germany) dated May, 17th 1999

16. Other Information

Prepared in accordance with:
Draft National Code of Practice for the Preparation of Safety Data Sheets - December 2006
including hazard categories and statements (see Section 2 of this SDS) according to NOHSC:2011(2003).

Date of Preparation:
Date of Revision: 27/08/2007
Reason(s) for Issue: - Change of SDS format
- Update data in Sections 11

Safety Data Sheets are updated frequently. Please ensure that you have a current copy.

Literary References / Data Sources:

- Supplier SDS: Remazol Navy RGB 150% Gran. (Dystar GmbH) - unless otherwise noted.
- (*) European Chemicals Bureau - IUCLID Dataset

Legend to Abbreviations and Acronyms:

< less than
> greater than
° C degrees Celsius
ACGIH American Conference of Governmental Industrial Hygienists
ADN European Agreement concerning the International Transport of Dangerous Goods by Inland Waterways.
ADR European Agreement concerning the International Carriage of Dangerous Goods by Road.
AICS Australian Inventory of Chemical Substances
approx. approximately
AS Australian Standard
ASCC Australian Safety and Compensation Council (succeeded NOHSC 7/02/2005)
BLV Biological Limit Value
BOD Biological Oxygen Demand
This SDS summarizes our best knowledge of the health and safety hazard information of the product and how to safely handle the product in the workplace. Each user should read this SDS and consider the information in the context of how the product will be handled and used in the workplace, including its use in conjunction with other substances. We have reviewed any information contained herein, which was received from sources outside DYECHEM INDUSTRIES Pty Ltd. However, no warranty or recommendation, expressed or implied, is made as to the accuracy or completeness of the data and information contained in this data sheet. Health and safety precautions and environmental advice noted in this data sheet may not be accurate for all individuals and/or situations. It is the user's obligation to evaluate and use this product safely and to comply with all applicable laws and regulations. No statement made in this data sheet shall be construed as a permission, recommendation or authorization, given or implied, to practise any patented invention without a valid licence. DYECHEM INDUSTRIES Pty Ltd shall not be responsible for any damage or injury resulting from: abnormal use of the chemical; any failure to adhere to recommendations; any hazards inherent in the nature of the chemical. DYECHEM INDUSTRIES Pty Ltd expressly disclaims that the SDS is a representation or guarantee of the chemical specifications for the product.
Safety data sheet in accordance with the EU Directives

Levafix Navy CA gran

Use pattern:
Textile dye

Dyechem Industries
60 - 62 Kylta Road, Heidelberg West VIC 3081
Telephone no. 03-9457-5311 Fax no. 03-9457-5164

Emergency telephone number: 03-9457-5311 / 0407-822-236 Transport and Spill emergencies only

1) Identification of the substance/preparation and company

Levafix Navy CA gran

2) Hazards identification

R52/53 Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

3) Composition/information on ingredients

azo reactive dyestuff preparation

Hazardous ingredients
azo reactive dyestuff
Content: 75 - 85 %

EG-Number 431-830-5

R phrases: 52/53

4) First aid measures

General Information: Take off immediately all contaminated clothing.

After inhalation: Upon inhalation of aerosol/vapour/dust: Take the patient into the fresh air; if there is difficulty in breathing, medical advice is required.

After contact with skin: Remove all contaminated clothing immediately. Cleansing with plenty of water, soap or other non-irritating cleansing agents.

After contact with eyes: Contamination of the eyes must be treated by thorough irrigation with water, with the eyelids held open. A doctor (or eye specialist) should be consulted immediately.

After ingestion: If the product is swallowed, the patient must at once drink water repeatedly, if possible with the addition of activated carbon. If the patient feels unwell, seek medical advice.

5) Fire-fighting measures

Suitable extinguishing media: water mist, foam, dry powder

Extinguishing media that must not be used for safety reasons: CO2

Special protective equipment for firefighting: Firemen have to wear self-contained breathing apparatus.
Safety data sheet in accordance with the EU Directives

Levafix Navy CA gran

Further information: Fire residues and contaminated firefighting water must be disposed of in accordance with the local regulations.

6) Accidental release measures

Personal precautions: Avoid formation and deposition of dust.
Environmental precautions: Do not empty into drains or waters.
Methods for cleaning up/taking up: Take up spilled product with dust-binding material or suitable vacuum cleaner. Fill into labelled, sealable containers.
Additional information: For further disposal measures see chapter 13.

7) Handling and storage

Advice on safe handling: Avoid formation and deposition of dust.
Keep container tightly closed and dry.

Advice on protection against fire and explosion: Observe the usual precautionary measures required for chemicals with dust-explosive properties. Observe national regulations.

Requirements for storage rooms and vessels: Store in original container in a cool, dry place. In filling operations take precautionary measures against static discharges.

Storage class: 11 Combustible solids
Storage stability
Storage period: 60 Months

8) Exposure controls/personal protection

General protective measures: Do not breathe dust. Avoid contact with eyes and skin. Take off immediately all contaminated clothing.
NOTICE: GRANULATE DYESTUFFS ARE FREE-FLOWING, SPEICLALLY DEDUSTED REACTIVE DYESTUFF PREPARATIONS. BY CAREFUL HANDLING DUSTING CAN BE SUPPRESSED ALMOST COMPLETELY.
Inhalation of dust and aerosols must be absolutely prevented by either adequate ventilation or by a suitable mask. People with chronic respiratory problems should not work with reactive dyestuff powders. If symptoms such as tightness in the chest or asthma occur while handling reactive dyestuff powders, a physician should be consulted as soon as possible. If hypersensitivity is confirmed, all contact with reactive dyestuff powders must cease immediately.

Hygiene measures: Keep away from food and drink stuffs.
Do not eat, drink or smoke at work.
Wash hands before breaks and at end of work and use skin-protecting ointment.

Respiratory protection: Dust mask with particle filter.
Hand protection: Wear suitable gloves e.g. of PVC or nitrile rubber. In the event of contamination, change protective gloves immediately.
9) Physical and chemical properties

Form: granules
Colour: dark-blue
Odour: odourless
Melting temperature: > 450 °C
Density: 1.57 g/cm³
Solubility in water: soluble

10) Stability and reactivity

Thermal decomposition: No thermal decomposition when stored and handled correctly.
Hazardous reactions: Dust explosion potential: not ignitable (modified Hartmann tube, VDI 2263/3673).

11) Toxicological information

Acute oral toxicity: LD₅₀ > 2,000 mg/kg (rat)
Acute dermal toxicity: LD₅₀ > 2,000 mg/kg (rat)
Irritant effect on skin: non-irritant (rabbit)
Irritant effect on eyes: non-irritant (rabbit eye)
Sensitization: In the guinea-pig the product did not show a sensitising effect (OECD 406; GPMT according to MAGNUSSON-KLIGMAN).
Subacute toxicity: 250 mg/kg (28 d Wistar rats)
Mutagenicity: Micronucleus test: No indication of mutagenic effects.
Mutagenicity: Salmonella/microsome test (Ames test): No indication of mutagenic effects.
Mutagenicity: In vitro Mammalian Cytogenetic Test: Mutagenic effects possible.

Remarks: Test results for a higher concentrated product
High dust concentration may result in irritation of the mucous membranes (eyes or respiratory tract).
Repeated exposure to high dust concentration of some reactive dyestuffs may very occasionally cause respiratory hypersensitivity. A sensitisation by this dyestuff has not yet been observed.
12) Ecological information

Biodegradability: The product is not easily biodegradable.

Fish toxicity: LC50 > 100 mg/l (96 h, Brachydanio rerio)

Daphnia toxicity: EC50 > 77 mg/l (48 h, Daphnia magna)

Algae toxicity: EC50 20.3 mg/l (Scenedesmus subspicatus)

Bacteria toxicity: EC50 10,000 mg/l

Test procedure: Respiratory inhibition of activated sludge organisms according to D. Brown et al., Chemosphere, 10(3), 245-261 (1981), and conforming to OECD Guideline 209

Chemical oxygen demand (COD): 730 mg/g

Biochemical oxygen demand (BOD5): 30 mg/g

Remarks: Test results for a higher concentrated product

Product does not add to the AOX-value of the sewage. (DIN EN 1485)
The product does not contain heavy metals in concentrations of concern for waste water.
The product does not release nitrogen which can contribute to eutrophication.
The product contains 0.4 % phosphorus as phosphate.

13) Disposal considerations

Product: If utilisation or recycling of the product is not possible, it should be disposed of according to the local regulations and laws, e.g. by incineration in a suitable plant.

European Waste Catalogue (EWC) code: 040217 Dye stuffs and pigments other than those mentioned in 040216

Uncleaned packaging: Sealed, empty containers are to be treated in the same way as the contents.

14) Transport information

<table>
<thead>
<tr>
<th>ADR</th>
<th>Non-hazardous goods</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADNR</td>
<td>Non-hazardous goods</td>
</tr>
<tr>
<td>RID</td>
<td>Non-hazardous goods</td>
</tr>
<tr>
<td>IMDG</td>
<td>Non-hazardous goods</td>
</tr>
<tr>
<td>IATA_C</td>
<td>Non-hazardous goods</td>
</tr>
<tr>
<td>IATA_P</td>
<td>Non-hazardous goods</td>
</tr>
</tbody>
</table>

Other information: Keep dry., Keep separated from foodstuffs.

15) Regulatory information
Labelling in accordance with the EEC directives:

R52/63: Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

S22: Do not breathe dust.

Water Hazard Class (Ger.): WGK 2 - impairment of water quality WGK = Classification in accordance with the German Water Resources Act Annex 2 VwVwS (Germany) dated Mai, 17th 1999

16) Other information

Text of all R phrases referred to in sections 2 and 3:

52/63 Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

This information is based on our present state of knowledge. It should not therefore be construed as guaranteeing specific properties of the products described or their suitability for a particular application.
Material Safety Data Sheet

INTRACRON DARK BLUE CDX-RF

Supplier's Code: IDBCDXRF
Issued: 15/05/2008

1. Identification of the Substance/Mixture and the supplier

Product Name: Intracron Dark Blue CDX-RF
Recommended Use: Textile Dyeing
Supplier: YORKCHEM AUSTRALIA Pty. Ltd
CAN: 108 453 569
Street Address: 50 Old Geelong Road
Brooklyn VIC 3012 Australia
Telephone: +61 3 9315-2466
Facsimile: +61 3 9315-4033
Emergency Number: 9315 2466 during office hours

2. Hazards Identification


Hazard Category:
Risk Phrases:
Safety Phrases: S22 Do not breathe dust
Class:
Subsidiary Risk 1:
Packing Group:
Poisons Schedule:

3. Composition/Information on ingredients

Synonyms: Azo reactive dye

<table>
<thead>
<tr>
<th>Chemical entity</th>
<th>CAS No.</th>
<th>Proportion</th>
</tr>
</thead>
</table>

Proportion (% weight per weight): VHIGH >60, HIGH 30–60, MED 10–29, LOW 1–9, VLOW <1
All the constituents of this material are listed on the Australian Inventory of Chemical Substances (AICS) or are National Registration Authority (NRA) approved active constituents.

4. First Aid Measures

Poison Information Centres in each State capital city can provide additional assistance for scheduled poisons. Phone Australia 13 12 26

Ingestion: If swallowed, rinse mouth with plenty of water and give water to drink. Do not induce vomiting.
Eye Contact: In case of contact with eyes rinse immediately with plenty of water for at least 15 minutes. If irritation persists, or there is any sign of tissue damage, seek medical advice.
Skin Contact: After contact with skin, wash immediately with plenty of water or soap and water. Remove contaminated clothing and wash before re-use.
Inhalation: If symptoms due to inhalation are observed, remove person to fresh air and seek medical advice.
Notes to Physician:

5. Fire-fighting Measures
Suitable Extinguishing Media: Water spray, foam, dry chemical, CO2.

Hazchem Code:

Specific Hazards: This product is not considered a fire hazard. However, in common with many other organic chemicals the product may in certain circumstances form flammable dust clouds in air.

Fire-fighting advice:

6. Accidental Release Measures

Spills and Disposal: Prevent entry into sewers and water course. If such entry has occurred or soil or vegetation has been contaminated, advise the police.

Disposal: Damp down or mix with moist sand and then vacuum or sweep up and place in containers for safe disposal. Containers should be sealed and labelled. Flush away any traces which cannot be recovered by other means with copious amounts of water and detergent if available. Remove container of waste material to disposal site.

7. Handling and Storage

Handling Advice: Follow proper standards of industrial hygiene. Avoid contact with skin and eyes. Do not breathe dust.

Storage Advice: Container should be kept sealed and stored in cool, dry conditions.

8. Exposure Controls / Personal Protection

National Occupational Exposure Limits:

Value assigned for this specific material by the NOHSC:

<table>
<thead>
<tr>
<th>Material</th>
<th>TWA ppm</th>
<th>TWA mg/m³</th>
<th>STEL ppm</th>
<th>STEL mg/m³</th>
<th>Notices</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Data Available</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

TWA – the Time Weighted Average airborne concentration over an eight-hour working day, for a five-day working week over an entire working life.

STEL (Short Term Exposure Limit) – the average airborne concentration over a 15 minute period which should not be exceeded at any time during a normal, eight-hour, working day. According to current knowledge, these concentrations should neither impair the health of, nor cause undue discomfort to nearly all workers.

NOTICES:

These exposure standards are guides to be used in the control of occupational health hazards. All atmospheric contamination should be kept to as low a level as is workable. Exposure standards should not be used as fine dividing lines between safe and dangerous concentrations of chemicals. They are not a measure of relative toxicity.

If the directions for use on the product label are followed, exposure of individuals using the product should not exceed the above standard. The standard was created for workers who are routinely, potentially exposed during product manufacture.

Engineering Measures: Ensure adequate ventilation of work areas, with extractio nif necessary.

Personal Protection:

Respiratory Protection: Dust mask recommended.

Eye Protection: Safety glasses of chemical grade goggles.

Gloves: Impervious gloves, for example PVC.

Clothing: Work overalls. Impervious apron and footwear if handling large quantities.

Industrial Hygiene:

Flammability: NA

Fire/Explosion Hazard: There is the possibility of dust explosion. Precautionary measures should be taken.
9. Physical and Chemical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour / Form / Odour</td>
<td>Dark Blue powder with slight odour</td>
</tr>
<tr>
<td>pH</td>
<td>6.5 – 7.5</td>
</tr>
<tr>
<td>Vapour Pressure</td>
<td>NA</td>
</tr>
<tr>
<td>Vapour Density</td>
<td>Not known</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>NA</td>
</tr>
<tr>
<td>Melting Point</td>
<td>Not known</td>
</tr>
<tr>
<td>Solubility</td>
<td>150g/l @ 60°C</td>
</tr>
<tr>
<td>Specific Gravity/Density</td>
<td>Not known</td>
</tr>
<tr>
<td>Flash Point</td>
<td>NA</td>
</tr>
<tr>
<td>Flammability Limits</td>
<td>NA</td>
</tr>
<tr>
<td>Ignition Temperature</td>
<td>None known</td>
</tr>
</tbody>
</table>

10. Stability and Reactivity

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stability</td>
<td>Stable under normal storage conditions</td>
</tr>
<tr>
<td>Incompatible Materials</td>
<td>Strong reducing agents</td>
</tr>
<tr>
<td></td>
<td>Oxidising agents</td>
</tr>
<tr>
<td>Hazardous</td>
<td></td>
</tr>
<tr>
<td>Polymerisation</td>
<td></td>
</tr>
<tr>
<td>Hazardous</td>
<td></td>
</tr>
<tr>
<td>Decomposition Products</td>
<td>The substances arising from the thermal decomposition of this product cannot</td>
</tr>
<tr>
<td></td>
<td>be accurately predicted. Any fumes are potentially irritant/toxic and suitable</td>
</tr>
<tr>
<td></td>
<td>protected equipment should be worn.</td>
</tr>
</tbody>
</table>

11. Toxicological Information

No adverse health effects expected if product is handled in accordance with this Safety Data Sheet and the product label. Symptoms or effects that may arise if the product is mishandled and overexposure occurs are:

**ACUTE EFFECTS**
- **Ingestion:** Acute oral toxicity (LD50) tested in rats: >2000mg/kg (Predicted value)
- **Eye Contact:** May cause irritation
- **Skin Contact:** Non-irritant
- **Inhalation:** Reactive dyes, of which this is one, have been associated with respiratory sensitization.

**LONG TERM EFFECTS:**

Toxicological Data:

12. Ecological Information

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Environmental Fate</td>
<td>The contamination of rivers and soil should be avoided.</td>
</tr>
<tr>
<td>Aquatic Toxicity</td>
<td>Consideration of the data for similar products suggests that this is unlikely to be harmful to fish.</td>
</tr>
<tr>
<td>Terrestrial Toxicity</td>
<td>The product is not readily biodegradable. BOD5/COD: &lt; 10% (Predicted value)</td>
</tr>
</tbody>
</table>

13. Disposal Considerations

Recovered material and/or unwanted product should be disposed of by land fill or incineration at an authorised site in accordance with local regulations.
14. Transport Information

NOT Classified as Dangerous Goods by the criteria of the Australian Dangerous Goods Code (ADG Code) for transport by Road and Rail.

UN Number:
Proper Shipping Name:
Class:
Subsidiary Risk 1:
Packing Group:
Hazchem Code:
EPG:
Segregation Dangerous Goods:

Air Transport: NOT Classified as Dangerous Goods by the criteria of the International Air Transport Association (IATA) Dangerous Goods Regulations for transport by Air.

15. Regulatory Information

16. Other Information

Date of Preparation: 09/06
Date of Revision: 15/05/2008 (1st Revision Date: 15/05/2008)
Reason(s) for Issue: Update address details

Safety Data Sheets are updated frequently. Please ensure that you have a current copy.

Literary Reference

Acronyms/Abbreviations: NOHSC - National Occupational Health and Safety Commission (Australia)
NIOSH - National Institute of Occupational Safety and Health (USA)
EINECS - European Inventory of Existing Commercial Substances.
ESIS - European chemical Substance Information System.
CAS - Chemical Abstract Service

This MSDS summarises, to the best of our knowledge at the date of issue, the chemical health and safety hazards of the material and general guidance on how to safely handle the material in the workplace. However, no representation, warranty or guarantee is made as to its accuracy, reliability or completeness. Since YorkChem Australia Pty. Ltd. Cannot anticipate or control the conditions under which the product may be used, each user must, prior to usage, review this MSDS in the context of how the user intends to handle and use the product in the workplace (including its use in conjunction with other materials). No statement made in this MSDS shall be construed as a permission, recommendation or authorization, given or implied, to practise any patented invention without a valid licence.

If clarification or further information is needed to ensure that an appropriate assessment can be made, the user should contact this company. Our responsibility for the material as sold is subject to the terms and conditions of sale, a copy of which is available upon request.

End of MSDS