

TECHNICAL FEASIBILITY OF  
DYEING NYLON CARPETS IN  
A RECONSTITUTED DYEBATH

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A RECONSTITUTED DYEBATH

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## SUMMARY

Pollution of natural water resources is one of the major problems facing the textile industry today. A large quantity of wastewater is generated in the dyeing process. For example, the wastewater produced in the dyeing of nylon carpets alone is approximately 39 million gallons per day in the United States. Water pollution control expenditures by the textile industry in 1973 amounted to \$43.5 million. Since the sources of clean natural water are limited, alternative methods must be found to reduce the amount of wastewater generated.

Various alternatives have been investigated for solving this problem, namely, (i) clean-up and discharge of the spent dye liquor, (ii) clean-up and reuse of the spent dye liquor, and (iii) reconstitution and reuse of the spent dye liquor. The objective of this work was to investigate the possibility of obtaining a series of dyeings in a number of different colors, by reconstituting and reusing the spent dyebath after each dyeing. The system chosen for investigation was the beck dyeing of tufted nylon carpets. Batch processes are generally inefficient in their utilization of water, chemicals, and energy, and generate large quantities of wastewater which must be treated subsequently.

Dyeings were carried out on a Nylon 6 tufted carpet, using first a combination of three disperse dyes and then a combination of three acid dyes. The spent dyebath was analyzed to determine the concentrations of the residual dyes. The loss in auxilliary chemicals was estimated from the final volume of dye liquor, by assuming that all the chemicals are completely soluble and hence lost only in the water absorbed by the unloaded carpet. The dye liquor was reconstituted with the required amounts of dyes and chemicals for the next dyeing. A retarder was used to control the dye strike rate when entering the carpet into the hot dyebath.

The results indicate that it is possible to carry out dyeings in a reconstituted dyebath which are comparable in uniformity to those carried out in fresh dyebaths. The reproducibility of these dyeings compares well with the standards accepted in the carpet industry. Considerable savings can be realized in water and chemical costs and the quantity of wastewater generated is drastically reduced. The use of an effective retarder and an accurate analytical technique are of great importance in improving the accuracy and increasing the versatility of this technique.

The constantly changing processes and resulting wastewaters in the textile industry make environmental

protection through adequate wastewater treatment a continuous requirement for acceptable textile manufacturing.

## CHAPTER I

### INTRODUCTION

#### Historical Notes

The carpet industry has played a prominent role in the state of Georgia since the early forties. In 1972, the Georgia mills produced 60% of all the carpets and rugs produced in the United States. About 83% of the total Georgia production came from eight northwest Georgia counties (1). They are Whitfield, Gordon, Bartow, Murray, Catoosa, Chattooga, Floyd and Walker. The 1972 industry shipments of tufted carpets and rugs in Georgia alone, amounted to \$1,704 million compared to the total U.S. shipments of \$2,783 million (2).

In 1974, 90% of the carpets produced in the United States were manufactured by the tufting process, while nylon accounted for 70% of the fibers used for face yarn in the carpet industry (1). Hence a substantial quantity of nylon fibers are used in the production of tufted carpets and rugs. In 1975, shipments of tufted carpets and rugs alone amounted to 787 million square yards having a dollar value of \$2,861 million. This represents 92.4% of the total dollar value of all carpets and rugs shipped in the United States (3). The amount of nylon used for the manufacture of carpets in the United States in 1975, was 805 million pounds (3).

The carpet industry in Georgia is a major water user. About 20 gallons of water are required for each pound of carpet (not including the latex and secondary backing) that is processed, 90% of the total water usage occurring in the dye house (1, 4). Assuming that about 1.2% on weight of fiber (owf) of dye was used on the average and about 5% of that amount was discharged with the wastewater, the amount of dye waste would be 483,000 pounds for the dyeing of nylon carpets alone. The wastewater produced in the dyeing of nylon carpets would be about 39 million gallons per day ( $805 \text{ million pounds/year} \times 20 \text{ gallons per pound} \times 0.90 \div 365 \text{ days/year}$ ), in the United States. Although most of this wastewater is now treated to some extent before being discharged into natural rivers or lakes, it still presents an environmental problem in many regions of the country.

According to the Department of Commerce, in 1974, \$1.9 billion in capital expenditures was spent for water pollution abatement. Water pollution control expenditures by the textile industry alone amounted to \$43.5 million. The Council on Environmental Quality, estimates that cumulative incremental pollution control expenditures for the period 1973 to 1982 will amount to \$194.8 billion in constant 1973 dollars. Of this total, 80% will be spent by private industry (5). Table I compares the total new capital

Table 1. Textile Mill Expenditures in 1973.  
(Costs in Millions of Dollars,  
Quantity in Thousands of Short Tons.)  
(Operational Costs Include Payment  
to Government Units.)

| Area | Industry                    | Total New<br>Capital<br>Expenditure | Pollution Abatement Expenditures |       |     | Operational Costs |                | Quantity<br>of solid<br>waste<br>removed |
|------|-----------------------------|-------------------------------------|----------------------------------|-------|-----|-------------------|----------------|--|
|      |                             |                                     | Capital<br>Expen-<br>ditures     | Total | Air | Water             | Solid<br>Waste |  |
| U.S. | All Text.<br>Mills          | 1,089.8                             | 29.2                             | 38.8  | 6.3 | 23.5              | 9.0            | 565.4                                    |
| GA   | All Text.<br>Mills          | 154.1                               | 2.8                              | 3.7   | 0.3 | 2.5               | 0.9            | 64.9                                     |
| U.S. | Floor<br>Covering<br>Mills  | 90.6                                | 1.5                              | 3.1   | 0.2 | 1.8               | 1.0            | 84.7                                     |
| U.S. | Woven<br>Carpets &<br>Rugs  | 5.9                                 | D                                | D     | D   | D                 | D              | D  |
| U.S. | Tufted<br>Carpets &<br>Rugs | 81.8                                | 1.2                              | 2.8   | 0.2 | 1.8               | 0.8            | 70.2                                     |
| U.S. | Other<br>Carpeting          | 3.6                                 | D                                | D     | D   | D                 | D              | D  |

D = Data withheld to avoid disclosures for individual companies.

expenditures to those allocated for pollution abatement by textile mills in 1973 (6).

Since the sources of clean natural water are limited, alternative methods must be found to reduce the amount of wastewater generated. The Environmental Protection Agency has established limits on permissible effluent discharge with criminal penalties for violators (7, 8, 9, 10). The 1972 amendment to the Federal Water Pollution Control Act (PC 92-500) is the most comprehensive measure taken so far by Congress to restore the nation's waters (11). It requires that industrial plants which are points of discharge to navigable streams;

- 1) Meet the national goal of zero-discharge by 1985.
- 2) Provide Level I treatment designated as Best Practical Control Technology Currently Available, by 1977.
- 3) Provide Level II treatment designated as Best Available Technology Economically Achievable, by 1983.
- 4) Operate under National Pollutant Discharge Elimination System Permits with designated monitoring and reporting procedures.

For textile plants discharging to municipal sewers the Act requires;

- A) Pretreatment of noncompatible waste discharges, flow equilization and neutralization.

B) Repayment of Federal Funds on basis of waste load including the volume discharged.

The real impact will be felt by the industry in pretreatment and Level II rules and regulations, as the true economics of technology are yet to be evaluated. Current processes must be restudied along with new technology in an effort to reduce water usage.

According to E. Fowler of Burlington Industries, the energy required to upgrade all wastewaters to 94% pollutant removal is equivalent to the total output of the TVA system. To raise this to 96% would require two TVA's. To reach 1985's 'no-discharge' standard would require at least five TVA's (12, 13).

#### Definition of the Problem

Having recognized the need to reverse the trend toward further environmental degradation, recent and proposed legislation is focusing on cleaning up the water environment. Textile processing plants, in general, use a wide variety of dyes and auxiliary chemicals such as acids, bases, salts, wetting agents, retarders, detergents, stripping agents and finishes. Most of these are not retained in the final product but are discarded with the process wastewater after they have served their purpose. As many textile wet processes are handled on a batch basis, the concentrations of the



waste materials in the liquid effluent vary widely. The textile industry is composed of over 7,000 plants of which approximately 680 use wet processes or discharge wastewater (14). This wastewater may be treated on site or by municipal treatment plants, or discharged untreated. Some of the major factors in the consideration of pollution from textile wastewater are solids, biochemical oxygen demand (BOD), chemical oxygen demand (COD), temperature, toxic chemicals, pH, and color.

Solids are present in the wastewater generated from the treatment of fibrous substrates. They affect the natural environment by hindering oxygen transfer and reducing light penetration. Solids settling on the bottom can cover the flora and fauna and result in an anaerobic sludge layer. The BOD, resulting from organic process chemicals, varies considerably. Chemicals such as starch are completely biodegradable, while some dyes are essentially nonbiodegradable. Effluents with high BOD could deplete the dissolved oxygen in the receiving waters resulting in the death of fish and objectionable water quality. Biological wastewater treatment systems are sensitive to temperature changes beyond certain rather narrow limits. Wastewater pH can vary greatly over a period of time since some processes require highly acidic conditions and others, highly alkaline. Thus some form of neutralization or equalization is necessary. Most of the dyes used by the textile industry are not readily

degradable by ordinary treatment processes and the treated effluent is often highly colored. The pollutants present make the water visually undesirable for domestic use.

Various approaches have been taken to reduce the environmental problem caused by the pollutants in textile wastewater. The most widely used methods are treatment systems which employ various processes singly or in combination to remove pollutants from the effluent wastewater before it is discharged from the plant site. Basically these methods are the same as those used in municipal and other industrial waste treatment plants. They include sedimentation, stabilization ponds, biological treatment (e.g. activated sludge and trickling filters), chemical treatment (e.g. flocculation, reaction with peat, ion-exchange, and chlorination) and carbon adsorption. Some other processes that have been suggested but are not as yet in commercial use include hyperfiltration or reverse-osmosis, ozone oxidation and the use of ionizing radiation.

Pilot scale attempts have also been made to reutilize the water discharged from the processing plant after it has been treated to remove pollutants and color. This would involve a series of steps such as filtration and ion-exchange or biological and chemical treatment followed by carbon adsorption. Essentially the same treatment methods as those listed above would be used to treat the discharged water before reusing it in the plant.

In spite of the numerous methods available, problems still persist. Many of the auxiliary chemicals used in addition to the dyes are resistant to chemical and biological treatment. The wastes discharged from the various processing operations are different in each case, due to differences in the types of fibers processed and the different end uses. The large volume of effluent water to be processed and the necessity for multiple stages would require a large capital investment in land, construction and equipment and possibly a high treatment cost per unit of water processed.

In addition to simply treating the wastewater, suggestions have been made to treat and reuse the wastewater for subsequent processing. This would be more effective and economical. Dyeing can be done successfully in used water as long as the impurities do not prevent the attainment of the desired color. The residual dye bath needs simply to be reconstituted to the desired dye and reagent concentration before being reused. This process obviously reduces chemical costs and in addition, considerable savings in energy costs can be realized. Since the dyebath is reutilized, the heat contained in the water is also reused. Finally, the volume of wastewater produced per unit weight of goods dyed is drastically reduced in comparison to presently used procedures. This reduces the load on waste treatment facilities, their operating costs, and the capital required for this construction.

Preliminary work done at the Georgia Institute of Technology, School of Textile Engineering indicates good prospects for the application of this method to commercial beck dyeing (15). In the initial research work dyeing tests were conducted on Nylon 6 carpet using a constant temperature dyeing technique, with a combination of acid dyes. In the first series of dyeings, five carpet sections were dyed to the same shade, with the last four dyeings being carried out in recycled dyebaths. The results showed that these dyeings were acceptable when compared to 'standard' dyeings done in fresh dyebaths. Attempts were then made to control the dye strike rate by varying the pH, but this approach was abandoned as it produced excessive turbidity in the dyebath, which hindered analysis of the residual dyebath. In the next series of dyeings one of the acid dyes was replaced with a disperse dye to make the test more representative of commercial dyeings which frequently use a mixture of acid and disperse dyes. This series produced uneven dyeings. Attempts were made to remedy this by adding the dye solution after entering the carpet into the beck and by using a non-ionic retarder to reduce the strike rate of the dyes. But problems still persisted, hence further investigation was left to subsequent workers. In these experiments the carpet was dyed to the same shade in each dyeing series. This did not give any indication of the possibility of dyeing different colors before the spent dyebath is finally

discharged.

### Purpose of Research

The objective of this work was to carry out three sets of dyeings; the first set using a combination of three disperse dyes; the second, using a combination of three acid dyes; and the third, using a mixture of acid and disperse dyes. In each part, a series of dyeing in a number of different colors, would be carried out by reconstituting the dyebath after each dyeing. These series would be repeated and individual shades would be dyed by current industrial methods, to obtain a basis for comparison of the reproducibility and uniformity that could be achieved by this technique. Samples would be examined both visually and instrumentally, to evaluate their acceptability in comparison with current industrial standards.

## CHAPTER II

### LITERATURE REVIEW

The EPA guidelines on wastewater discharge have led to the development of a number of innovative techniques to reduce the pollution of natural water resources. Many of these concentrate on the treatment of wastewater by various methods, both chemical and biological.

In spite of the numerous claims regarding the low cost and high efficiencies of these methods, it must be remembered that these processes require a substantial outlay of capital which does not in any way reduce production costs or increase profits. On the contrary, construction of waste treatment facilities will increase operating costs and the price of textile products. Treatment and reuse of wastewater in the plant has also been given some consideration, but this too requires the construction of waste treatment facilities. Other alternatives such as solvent dyeing have obvious limitations in their use with respect to availability, toxicity, flammability and economy. In contrast, the concept of a recycled dyebath has none of the drawbacks inherent in the above techniques. Reuse of a spent dyebath reduces waste, cuts chemical and dye costs and increases the overall profitability of the operation.

It can be adapted to suit existing equipment and does not require extensive additional capital outlay.

A large amount of work has been done within the textile industry to develop techniques for treating wastewater. Studies are being made at North Carolina State University and at the University of North Carolina on treatment methods for twenty typical dyebaths after exhaustion (12). Techniques being studied include biological oxidation, carbon adsorption, chemical coagulation and ozone treatment. At Clemson University, studies are being carried out on the use of hyperfiltration for renovation of composite wastewater from dyeing and finishing plants (12, 16).

Hyperfiltration or reverse osmosis is a separation process involving the filtration of aqueous solutions by membranes capable of removing not only suspended particles but also substantial fractions of dissolved impurities, both organic and inorganic (4). Application of high pressure to the feed solution causes purified product water to pass through the membrane, leaving the remaining feed as a concentrated solution. Hyperfiltration reduces the amount of wastewater requiring biological treatment.

Flocculation and ion-exchange processes are currently in common use. Inorganic coagulants have been found to be effective in removing dye color from textile wastewater. The chief disadvantage of this type of coagulant is the

poor dewatering characteristics of the resulting solids. At a pH below 7, common aluminium or iron coagulants begin to form a voluminous metal hydroxide floc. Many colloidal particles adsorb onto this floc, forming large fast-settling particles. The metal hydroxide floc thus aids in color removal (17). Polyelectrolytes are used in many different types of wastewater treatment systems to agglomerate particles or to increase the filterability of coagulated solids.

Another chemical method for decolorising dye wastes is a combined polymeric adsorption - ion exchange process (18, 19). This process involves adsorption on a synthetic polymer and claims several operating and performance advantages. The polymeric adsorbent can be regenerated in situ by a common solvent like methanol. There are no losses on regeneration and the solvent can be reclaimed. Adsorption on activated carbon has been extensively evaluated for treatment of textile wastes. Activated carbon adsorption has several limitations. The carbon must be periodically regenerated and regeneration losses frequently average 3% to 4% per cycle. Metallic residues can coat the carbon surface, when treating premetallized dye wastes, thus reducing the adsorption capacity.

An integrated ozone oxidation - carbon adsorption process has also been used. Here the two phenomena are combined to produce a synergistic effect in addition to



their own individual effects (20, 21). It is claimed that this process is effective in decoloration and removal of organic substances and is simple and economical to operate.

The majority of treatment facilities employ biological systems for treating wastewater (22, 14). Biological treatment of industrial wastewater involves contact between the wastewater and a mixed culture of micro-organisms under a favourable environment. The micro-organisms metabolize the wastewater components for energy and synthesis of cells. They use dissolved oxygen, produce carbon dioxide and synthesis new cells. These reactions are continually occurring in nature but the rate is limited owing to one or more controlling parameters such as dissolved oxygen, available nutrients and microbial concentrations. In biological wastewater treatment, the rate is greatly accelerated by providing high concentrations of micro-organisms to feed on nutrients in the wastewater, by substantial mixing or other arrangements to give adequate dissolved oxygen and by good agitation for frequent contact between the 'food' and the micro-organisms. There are two major methods of biological waste treatment, aerobic and anaerobic. In aerobic processes, degradation of organic matter takes place in the presence of and through combination with dissolved oxygen. The release of carbon dioxide serves to reduce alkalinity in textile wastes. Oxidation of organic matter

supplies energy to the microbial population for synthesis of new cells. Aerobic processes require temperatures below 100°F and are characterized by nearly complete metabolism and high growth rates. Anaerobic micro-organisms exist where there is little or no oxygen. Since they require molecules other than hydrogen and oxygen acceptors, anaerobic processes are reductive in nature and can tolerate higher temperatures (125°F). Anaerobic processes exhibit lower growth rates and incomplete metabolism with resulting higher energy of the products. The products formed include hydrogen sulfide and methane.

Biological treatment is usually preceded by sedimentation, but other forms of pretreatment such as screening, equilization, neutralization or coagulation may also be used. Following the biological treatment, sedimentation is required to remove the suspended micro-organisms that settle as sludge. The amount of sludge produced depends on the type of biological treatment, the organic loading, the temperature, and the efficiency of sedimentation. The biological treatment methods applicable to textile wastewater are, trickling filters, activated sludge, rotating biological disks, extended aeration and lagoons.

The use of peat as a medium for treating dyehouse effluents has also been suggested (23). In this process, raw effluent is subjected to the scrubbing action of a

moving mat of common garden peat. The process does not involve filtration, but chemical adsorption and complexing. An insoluble complex salt is formed by the ionic and coordinate bonding peculiar to the molecular structure of the peat. The process requires carefully controlled conditions, but claims virtual elimination of color, phosphates, suspended solids, and heavy-metal pollutants. The pollutants are actually removed, not merely changed into less offensive form or replaced by nonpolluting compounds.

Some work has also been done on the use of a combined radiation-oxidation process for decolorizing textile wastewater (24). Many organic molecules are strongly affected by ionizing radiation such as high energy gamma rays. These effects may be intensified in aqueous solution where the products of radiolysis of water, e.g. free radicals and peroxides, may also react with the organic molecule. Other organic species or dissolved oxygen, may alter the nature and rate of the reaction involved. Decolorization is inhibited by some materials such as thiourea and carbon dioxide. Organic molecules may also be degraded by chemical oxidation through the use of chlorine, hydrogen peroxide, and ozone. In the above mentioned study, aqueous solutions of several commercial dyestuffs and a textile dye waste of unknown composition were subjected to radiation from a cesium 137 gamma ray source in both the presence and absence

of chlorine. The results indicated that the synergistic effect of gamma radiation and chemical oxidation can be successfully used in decolorizing solutions of commercial textile dyestuffs. Chlorine acts as an effective and economical oxidant in this process. However, the decolorizing effects are not uniform enough to enable prediction of the results for the treatment of specific types of dyes. There is a slight reduction in chemical and biological oxygen demand and the amount of chlorine and radiation required depends on the particular effluent to be treated. The dyes investigated included anthraquinone, azo, metallized azo, sulfur, and triphenylmethane dyes. The estimated cost for a 240,00 gallons per day facility is \$0.31 per 1000 gallons for a design treatment of 60 k rads and 75 ppm. chlorine.

In some cases, shortage of water supply and variability in the chemical makeup and quality of municipal water supply have led some mills to reuse their wastewater after preliminary treatment at the plant (25, 14). Hollytex Carpet Mills has two plants where 80% to 85% of the wastewater is treated and stored for later use. At their manufacturing plant in Southampton, Pa. shortage of water supply and a lack of sufficient sewer facilities, forced the management to consider the possibility of reusing wastewater. The management decided to use a granular carbon system and constructed a plant which began operating in 1969. The

company reclaimed and treated 80% of its wastewater. This was primarily rinse water and dye solutions from dyeing of light shades. The remaining 20% was discharged to the sewer. The treatment plant operates as follows. Wastewater from the dye becks flow into sumps through vibrating screens used to remove lint. From the sumps, the water is forced against gravity, through a moving bed carbon column containing 50,000 pounds of Calgon Filtrasorb 400 (12 x 40 sieve size). The plant operates at a carbon-exhaustion rate of 0.55 pound per 1,000 gallons of waste water treated. The treated water, free of color and organic materials is then pumped through a cooling tower and stored for reuse. The exhausted carbon is withdrawn from the bottom of the column and transferred to a multiple-hearth, gas-fired reactivation furnace, where the organic materials are oxidized and the carbon is restored to near original activity. This plant, now owned by Stephen-Leedom Carpet Co., has been operating successfully since 1969.

The other plant still owned by Hollytex Carpet Mills, is located in City of Industry, California. Their dye water reclamation process used, has been so successful that it is being marketed to other carpet mills throughout the country. However the company is reluctant to give information on how the system actually works. One and a half million gallons of water are recycled daily. This has

resulted in savings in water costs, and reduction in phosphate costs by \$25,000 a month. In addition, fuel costs are reduced since the water reenters the mill already heated to 140°F.

The techniques mentioned above emphasize treatment and discharge or treatment and reuse of wastewater. The use of organic solvents in the place of water in textile processing has also been considered (26). This has not been an acceptable solution to the pollution problem because organic solvents are not as readily available as water. They are much more expensive and in some cases, hazardous due to their inherent toxicity and/or flammability.

Another alternative to the waste treatment processes, is the concept of reusing the spent dyebath. This technique makes no attempt to remove the remaining dyes and chemicals in the spent bath. On the contrary, it uses the water without treatment for subsequent dyeings. Not only does this method drastically reduce the volume of wastewater that would eventually require treatment, but it also makes effective use of residual dyes and chemicals instead of discarding them to become pollutants.

The dyebath recycle technique has two important requirements which must be met if the technique is to be used successfully. (i) It must be possible to enter the carpet into the spent dyebath at a relatively high temperature (about 70°C), without most of the residual dye

exhausting onto the leading end of the carpet. Cooling the bath would eliminate the savings to be gained from shorter dyeing cycles and the thermal energy stored in the water. (ii) It must be possible to control the dye strike rate as the temperature is being raised to the dyeing temperature, so that dye exhaustion is uniform and a level dyeing is obtained.

The two following examples illustrate the effective use of a retarding system to control the dye strike rate at high temperatures. This is a major problem that must be solved if the recycled dyebath technique is to be used effectively, and it becomes especially important when each successive dyeing is different in color from the proceeding one.

Constant temperature dyeings at over 90°C have been carried out using cationic dyes on acrylic knit goods (27, 28), and acid dyes on nylon (29, 30). In both cases a retarding agent was used to control the dye strike rate at the high temperature involved and thus obtain a level dyeing. The major advantage of the constant temperature dyeing method is the time saved by the elimination of the slow temperature rise step.

The FAL Constant Temperature Process for acrylic goods uses acetic acid and a salt, either sodium chloride or anhydrous sodium sulfate, as a retarding and leveling

system. By pretreating and dyeing in the same bath with sufficient acetic acid to obtain an initial pH of 3.0 to 3.5 and a quantity of salt related to the depth of shade, an efficient retarding and leveling system is obtained which does not affect the saturation capabilities of the fiber. The bath is set at 60°C (140°F) with salt and acetic acid and the temperature raised quickly to the pre-selected dyeing temperature and held for about ten minutes. The dye solution is then added and the dyeing continued until 90 - 95% exhaustion is obtained. The temperature is then quickly raised to 99°C (210°F) for 15 minutes to fully develop the shade. The bath is then cooled slowly to 60°C and the goods rinsed and finished as usual. The addition of the acetic acid (80%) reduces the ionization of the dye as well as the dissociation of the acidic groups in the fiber. Consequently, the affinity of the dye for the fiber is lowered considerably and the dyeing is more readily controlled.

The constant temperature process as applied to nylon is basically as follows. The nylon is pretreated under acidic conditions with an anionic levelling agent. The dyebath is then raised to the boil as rapidly as the equipment will allow. After about 30 minutes, the acid dye mixed with cationic leveling agent is added. The dye exhausts rapidly but evenly across the fabric. Shading is



also possible at the boil. Simple theory suggests that the anionic agent, being substantive on nylon, retards dye uptake by competing for the dye sites on the fiber. The cationic agent complexes with the anionic dyes and the rate of release of free dye from this complex controls the rate of dyeing. Hughes et. al. (29) carried out a number of tests to determine these mechanisms more precisely. Lissapol D was used as the anionic agent, Dispersol CWL as the cationic agent and a number of different acid dyes were used in their investigation. The dyeings indicate that Lissapol D has a greater retarding effect on low affinity dyes. Hence high affinity dyes will show higher levels of exhaustion. The retarding effect of Dispersol CWL alone, reduces the final exhaustion by a considerable amount. This action is greater with dyes forming a more stable complex. The retardation obtained in the early stages of the dyeing, using a mixture of agents, is greater than that obtained using either of the components alone. This investigation shows that retarding action is dependant on two factors: (i) the ability of the dye to be absorbed by nylon in the presence of Lissapol D, which in turn depends on the relative affinities of the dye and the agent; (ii) the stability of the complex formed between the dye and Dispersol CWL compared with that of the complex formed between Dispersol CWL and Lissapol D.

Blackburn and Dawson (30) conducted further studies, using this technique to investigate the utility of these agents in retardation, migration and coverage of barre. Their studies confirmed the results of Hughes et. al. and in addition indicated that, (i) the reduction in final exhaustion was less with the mixture than with Dispersol CWL alone, and (ii) the mixture of agents has little effect on the compatability of dyes applied in the combination. Conventional migration tests showed that both Lissapol D and Dispersol CWL greatly improved migration. However, Dispersol CWL was slightly more advantageous on a weight for weight basis. For certain dyes, the levelling was less dependent on pH in the presence of Dispersol CWL than in the presence of Lissapol D. At higher pH values (pH 6), the mixture of agents was as effective as the individual agents. In testing for coverage of physical irregularities, Lissapol D showed better results than Dispersol CWL.

These results show the applicability of constant temperature techniques to conventional dyeing methods. In addition, savings in processing time and energy can be realized. This technique has an advantage over the two-stage process entailing application of an anionic agent at 95°C and then dropping and recharging the bath for dyeing.

In applying the technique used by Hughes, Dawson and their co-workers to recycled dyebaths, it should be

noted that subsequent dyeings in the series will contain both anionic and cationic agents, at the beginning of the dyeing. In this case the retarding action of the anionic agent will be reduced due to the presence of the cationic agent with which it will form a complex. The build up in concentration of the two agents in the dyebath will lead to their presence in excessive amounts which may be detrimental to the dyeing system in terms of the final level of exhaustion. In such a case, the critical factor will probably be the relative stability of the complex formed between the dye and Dispersol CWL compared to the Dispersol CWL - Lissapol D complex.

The present work involved the use of disperse dyes on nylon. As disperse dyes are insensitive to chemical irregularities, they can not be effectively controlled by the use of anionic and cationic agents. However, a similar retarding action can be obtained by pretreating the nylon with a non-ionic surfactant. The dye must displace the surfactant before being adsorbed by the fiber. The greater the energy required to displace the surfactant, the higher is the temperature at which the dye can be added to the recycled dyebath. Another approach to retarding initial dye exhaustion would be to use a retarder which formed a temperature dependent complex with the dyes. At lower temperatures, the retarder should complex the dyes and keep them from being adsorbed by the fibers. At higher

temperatures the dye would be released from the complex as the temperature was raised. This would facilitate the entry and removal of the goods at temperatures slightly below the dyeing temperature. This effect could probably be achieved by a two phase system where the dye was soluble in water at higher temperatures and in the other liquid phase at lower temperatures.

The preliminary work, using the recycled-bath constant temperature dyeing technique, was carried out on nylon carpet using first a mixture of acid dyes and then a combination of acid and disperse dyes. In this study, all the dyeings in a particular series were made to the same shade. In the first series of dyeings, using acid dyes only, the recycled bath dyeings were not uniform, probably due to the rapid dye strike rate at the high entrance temperature. Hence in the next series, an attempt was made to use pH control to reduce the initial diffusion rate of the dyes and thus improve the overall levelness of the dyeings. The change in pH seemed to aggravate the problem further rather than solve it. In addition, the residual dyebath was turbid and could not be used to give satisfactory values for the residual dye concentration. Therefore this series was discontinued after only two dyeings. At this point the dyeings with acid dyes were discontinued in favour of a combination of acid and disperse dyes, to

determine if this combination could improve the levelness of the dyeings. The next three series of dyeings used a combination of two acid dyes and one disperse dye. This improved the levelness slightly but not to a satisfactory extent. In the following series, the dye solution was added after entering the carpet into the bath. This was expected to improve the levelness since the procedure reduced the amount of dye that would be present initially before entering the carpet. However, this change did not improve the levelness significantly. In the final series of dyeings, a nonionic retarding agent was used to control the strike rate of the dyes. This produced the best results but in the last two dyeings in the series, some non-uniformity was apparant.

The results of the foregoing work indicate two areas that need further study. (i) The possibility of having a series in which each carpet would be dyed a different color. (ii) Investigation of a retardation system for disperse dyes and acid dyes individually before combining them in the dyebath.

At present, the textile mills that treat their waste generally use biological or chemical treatments, chlorination (31), reverse osmosis (32); combinations of filtration, adsorption and ion-exchange techniques have also been used (33). These systems either alone or in combination, will continue to be used in the future (34-38). On the other

hand, constant temperature dyeing methods, even though they increase the complexity of the dye-fiber system, should prove to be far more economical than waste treatment methods because they could not only reduce pollution but also produce savings in water, thermal energy and chemicals and reduce the dyeing time required. With technology tending towards the more resistant dyes, all alternatives should be considered in order to optimize treatment and attain the most economical and efficient solution possible.

## CHAPTER III

### EXPERIMENTAL PROCEDURES

#### Selection of Carpet and Dyes

Initial development of the dyebath recycle process was aimed primarily at the open beck dyeing of nylon carpets. Batch processes are generally inefficient in the utilization of water, chemicals and energy and generate large quantities of waste which must be treated later on. However, their versatility, ease of control and short run capability make them an attractive method of coloration for many textile products. Beck dyeing is a major method of carpet coloration. In 1974, 35% by weight of all the nylon carpet colored and 90% by weight of all the polyester carpet colored were dyed in becks (1). The shade matching requirements for dyed carpet are less stringent than those for other types of textile products. Hence, process changes in carpet dyeing could be accommodated that would not be tolerated in other dyeing operations. Finally, the range of dyes used in carpet coloration is narrow, so the residual dyebath analysis would not be complicated by the presence of a large number of dyes.

There were a number of requirements to be considered in the selection of the sample carpet. A synthetic primary backing rather than a jute primary backing was chosen

since this is reflective of the current trend. A plain level loop carpet was preferred as this would facilitate color measurements with the colorimeter and eliminate the variability due to sample presentation encountered in the previous work. The tufting yarn should contain monofilaments with a uniform number of end groups. This would eliminate color variations due to the inherent variation in the fibers' chemical properties. This special requirement could not be met because many industrial carpets are made from cotexturized yarn consisting of deep and regular dyeing filaments. These filaments differ in the number of amino end groups incorporated into the polymer. The difference in the number of end groups is insignificant when dyeing with disperse dyes, but it is an important factor when trying to obtain level dyeings with acid dyes. Regular and deep dye yarns dye to the same shade with disperse dyes but to different shades with acid dyes. Hence experiments involving acid dyes would probably require the yarns to be removed from the carpet for color measurement.

The sample finally obtained was a level loop tufted nylon carpet with polypropylene backing. The nylon 6 yarns were cotexturized and consisted of regular and deep dyeing filaments. The sample had 20 ounces of face yarn per square yard.



The dyes were selected from a list of commonly used dyes in the carpet industry. The ones used in largest volume were preferentially selected. The next criterion was the location of the absorption peak in the visible spectrum. To obtain an accurate analysis of the residual dye concentration it was important that the overlap between the absorption peaks be kept at a minimum. It would also be advantageous if the absorbance of each dye in the peak wavelength regions of the other dyes was as small as possible. The list of acid and disperse dyes finally selected and the manufacturers from whom they were obtained is given in Appendix A. Their absorbance spectra in the visible region of the spectrum are given in Appendix E.

### Disperse Dyes

#### Praxitest Experiments.

Having selected the dyes and the carpet, it was now necessary to choose a suitable retarder for the disperse dyes. For the recycled dyebath technique to be effective it is necessary to enter the carpet into the dyebath at a relatively high temperature. As indicated by the previous work, at these temperatures, the dye strike rate is high. A retarder is necessary to control the strike rate on entering the goods and during the rest of the dyeing. The effects of the retarders on the selected dyes could be observed from the curves on the Praxitest strip chart

recorder. These would indicate which retarder had the greatest effect on the exhaustion rate and the final level of exhaustion. A retarder producing a low exhaustion rate but a relatively high final exhaustion would be preferred.

The Praxitest (HCR) System Ellner - Original Hanau, manufactured by Quartzlampen Gesellschaft M.B.H., Hanau, is marketed by Brinkmann Instruments, Westbury, New York. This instrument makes it possible to observe wet processing procedures under conditions which are very close to actual practice. It is possible to dye loose fiber, top, yarn, and piece goods at liquor ratios varying from 7 to 1, to 80 to 1 and at temperatures from 10°C to 135°C. The heating rate can be regulated by a built in thermostat. The instrument is fitted with a colorimeter and a recorder and the degree of exhaustion and temperature of the liquor can be recorded simultaneously. The clearing of the dye solution is determined by the colorimeter and the degree of exhaustion recorded directly as a percentage. A detailed description and operating instructions can be found in the technical manual (39).

GAF Corporation produces a number of non-ionic surfactants that can be used as retarders in the dyeing of nylon with disperse dyes. They vary in their hydrophobic components (octyl phenol and nonyl phenol) and in the average number of ethylene oxide units in the hydrophilic portion of the molecule.

A study of their technical bulletins indicated that the samples chosen would probably have the same effect on the dyes. A 50 lb. bag of Igepal DM 970 was ordered together with small samples of Igepals CA 620, CO 610, CO 630, CO 990, CO 710, DM 730, CO 880, DM 430, CA 897, and CO 210. The retardation action of each of these was observed in small scale dyeings done in the Praxitest.

Samples of carpet weighing about 15 gms were used for the Praxitest dyeing. The dyebath consisted of 2% owf trisodium phosphate to serve as a buffer, 0.5% owf Plexene D which acts as a sequestering agent to complex metal impurities present in the water, 1% owf disperse yellow 3, and 1% owf of the retarder. The liquor ratio used was 45 to 1. Before the dyeing, the recorder was adjusted to show 100% exhaustion with a blank dyebath (no dye present) in circulation and 0% exhaustion with the initial dye concentration present in the dye liquor. Each carpet sample was initially scoured in a solution containing 2% owf Igepal DM 970. In carrying out the test, the scoured sample was first placed in the sample tube and the blank dyebath circulated for about 10 mins. at room temperature. The dye solution was then added into the expansion tank and the temperature was raised at 1.5°C per min. to 98°C. When the recorder showed that there was no further change in dye exhaustion, the heater was turned off, the dye liquor drained, and the sample removed. A test dyeing was made with no

Igepal in the dye liquor and this was used as a basis for comparison. The maximum exhaustion could be read off the chart directly and the rate of exhaustion calculated from the slope of the exhaustion curve.

The first dyeing on the Praxitest was made without any retarding agent so that it could be used as a basis for comparison. (Exhaustion values for the Praxitest indicate % of total dye added.) The dye was added at room temperature and the heater switched on. The immediate exhaustion was approximately 10%. From 22°C to 40°C (18 mins.) the exhaustion rate was 1% per minute. From 42°C to 48°C (4.5 mins.) the exhaustion rate increased to 2.5% per minute. From 48°C to 61°C (10.5 mins.) the exhaustion rate was 5% per minute. The exhaustion curve then leveled out to 94% at 74°C. It increased slightly during cooling to give a maximum exhaustion of 95%. The average heating rate from 22°C to 74°C was 1.1°C per minute.

In the dyeing with Igepal DM 970 present, the dyes were added at 45°C. The immediate exhaustion was about 18%. The temperature was held between 42°C and 46°C for 15 minutes to determine if the exhaustion rate would remain steady. It did not. The average exhaustion rate in this range was 2% per minute. From 46°C to 60°C (9.5 mins.) the exhaustion rate was 4% per minute. The exhaustion had leveled out to 90% at 75°C and on cooling increased to 91%.

This shows that Igepal DM 970 did have a slight retarding effect as exhibited by the decrease in exhaustion rates between 40°C and 60°C. The retardant did not have a significant effect above 60°C, hence this fact limited the temperature at which the carpet sections could be entered into the hot dyebath.

These tests indicated that there was some difference between the retarding action of the various Igepals, the variation being in the dye strike rate or the final exhaustion level. However none of them had the optimum combination of the characteristics required. Hence, since a large quantity of DM 970 was readily available, this was used in the subsequent dyeings.

#### Dye Shade Selection

After selecting the dyes and the retarder, the next step was to select the shades to which the samples would be dyed. This was done by surveying samples of carpets displayed in department stores, to obtain an idea of the colors in which carpets are currently dyed. Having obtained a general idea of the required colors, it was necessary to arrange them in a sequence that would be theoretically feasible for dyeing consecutively. The colors initially selected were light blue, yellow, pink, brown, olive, and black. Approximate recipes were written for these colors using the three dyes, Disperse Yellow 3, Disperse Red 55,

and Disperse Blue 7. Samples were then dyed in an Atlas Launder-Ometer to determine if the approximate recipes produced the expected shades. This instrument was an AATCC Standard Launder-Ometer, Model B5, Type LHD-EF, manufactured by Atlas Electric Devices Co., of Chicago, Ill. It has a rotating rod equipped with shelves to hold stainless steel containers with the samples inside. The Launder-Ometer can be filled with water and electrically heated. The dyeing procedure used was similar to that suggested by Du Pont for dyeing nylon carpet with disperse dyes, in "Dyes and Chemicals Technical Bulletin" (40).

The dyebath consisted of 2% owf Igepal DM 970, 2% owf trisodium Phosphate, 0.5% owf Plexene D, disperse dyes according to the recipe and water. The liquor ratio was 30 to 1 and the weight of each sample was 15 gms. Containers with the samples were placed in the Launder-Ometer and the system was heated from room temperature to 190°F over a period of 60 mins. The containers were rotated to facilitate mixing and uniform dyeing. The temperature was held at 190°F for 60 mins. and then the heater was turned off and the system cooled by flushing with cold water. The dyed samples were removed from the container, rinsed and dried. After numerous adjustments through trial and error, a series of eight shades was selected. Colors in the series were light blue, yellow, orange, pink, brown, black, olive and dark blue. The first and last shades were selected so that

it would be possible to recycle through the series without draining off the bath, after dyeing the eight shades.

#### Measurement of Absorbancy Constants of Dyes

Absorbancy constants are required to calculate the concentrations of the dyes in the residual dyebath.

The spectrophotometer used in these and subsequent measurements was a Bausch & Lomb Spectronic 70, (Catalog No. 33-30-74). This instrument was selected because of its low cost, and ease of operation, which would make it suitable for use in a carpet dyehouse. The instrument was equipped with a tungsten lamp for measurements in the visible region of the spectrum. All measurements were made in the range of 300 nm to 700 nm. For each measurement, the instrument was calibrated to zero absorbance with the reference solution and then the absorbance reading of the sample solution was obtained.

For each of the three disperse dyes a plot of absorbance versus wavelength was made over the range of 350 nm to 700 nm. to find the wavelength at which maximum absorbance occurs (See Appendix E). Next, at this wavelength of maximum absorbance, a plot of absorbance versus dye concentration was made with the dye being dispersed as well as possible in water. The reference solution in each case was tap water. Theoretically, the reference solution ought to contain all the chemicals present in the sample solution,

except the dye. However, the actual quantities of these chemicals would not be known when using a recycled dyebath since their concentrations were not being measured. Hence tap water was used as a reference. Having obtained the above data, the Beer-Lambert law can be used to determine the concentrations of the residual dyes. The Beer-Lambert law can be expressed as, Absorbance = Absorbance index x Concentration x Cell Thickness. Since the concentration of the solution and the cell thickness are known and the absorbance is read from the instrument, the absorbance index of the dye can be calculated for the particular wavelength at which the absorbance was determined. The absorbance index of a dye is a constant at a particular wavelength and the cell thickness is constant since the same cells are used for all the measurements. Hence these two values can be grouped together as a single constant K, called the absorbancy constant to give the modified equation,

$$A = K \times c \text{ at } \lambda \text{ max.}$$

The absorbancy constant can therefore be calculated for each dye from the slope of the absorbance versus dye concentration plot.

For a system containing a mixture of dyes, the total absorbance is the sum of the individual absorbances of each dye in the mixture. Hence at a particular wavelength, for



a mixture of three dyes, the relation is,

$$A_{\lambda_1} = K_1' C_1 + K_2' C_2 + K_3' C_3 \text{ at } \lambda_1$$

Since there are three unknown values in this equation, two more measurements must be made at two other wavelengths so as to obtain a system of three equations in three unknowns.

$$A_{\lambda_2} = K_1'' C_1 + K_2'' C_2 + K_3'' C_3 \text{ at } \lambda_2$$

$$\text{and } A_{\lambda_3} = K_1''' C_1 + K_2''' C_2 + K_3''' C_3 \text{ at } \lambda_3$$

Here  $K_1$ ,  $K_2$  and  $K_3$  are the absorbancy constants of the three dyes at the wavelengths  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  respectively. Values of the absorbancy constants for the disperse dyes and acid dyes at the maximum wavelengths are given in Table 2.  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  are chosen to be the maximum absorbance wavelengths of each of the three dyes in the mixture, so as to obtain maximum sensitivity of the instrument while making the measurements. The Beer-Lambert law as expressed above is a linear relationship. Quite often, plots of absorbance versus concentration show nonlinearity at higher concentrations due to a decreasing activity coefficient of the solute with increasing concentration. Hence for measurements of the absorbancy index, the linear region of the plot should always be used. The three equations can then be solved to obtain the values of  $C_1$ ,  $C_2$  and  $C_3$ , which will be the concentrations of the three dyes in the mixture.

Table 2. Values of Absorbancy Constants  
(lit./gm.)

| <u>Disperse Dyes</u>             |                 |               |               |
|----------------------------------|-----------------|---------------|---------------|
| <u><math>\lambda</math> n.m.</u> | <u>Yellow 3</u> | <u>Red 55</u> | <u>Blue 7</u> |
| 355                              | 180.0           | 5.97          | 0.5           |
| 515                              | 10.0            | 46.45         | 3.5           |
| 585                              | 6.0             | 4.19          | 14.0          |

| <u>Acid Dyes</u>                 |                   |                |                |
|----------------------------------|-------------------|----------------|----------------|
| <u><math>\lambda</math> n.m.</u> | <u>Yellow 135</u> | <u>Red 337</u> | <u>Blue 25</u> |
| 350                              | 23.47             | 5.10           | 10.12          |
| 495                              | 1.80              | 14.70          | 5.13           |
| 605                              | 0.88              | 0.68           | 27.78          |

| <u>Disperse Dyes</u> |        | <u>Acid Dyes</u> |       |
|----------------------|--------|------------------|-------|
| Yellow 3             | -13.9% | Yellow 135       | -5.0% |
| Red 55               | +15.4% | Red 337          | +2.0% |
| Blue 7               | -11.0% | Blue 25          | +6.0% |

Figure (1) shows the absorbance versus concentration plots, for the three disperse dyes used, from which the absorbancy constants were calculated.

#### Dyebath Analysis and Reconstitution.

Analysis of the residual dyebath was one of the most crucial steps in the implementation of the recycled dyebath technique. In order to be able to dye the next shade correctly, it was necessary to know the residual amounts of each dye in the spent dyebath. Several different techniques for dyebath reconstitution were used during the course of this investigation. These different techniques are described below for each series of dyeings.

Series I. In this set of dyeings a sample of the residual dyebath was taken, 10 ml. of methanol were added, and the absorbance of the solution measured in the spectrophotometer. The concentrations of the dyes were calculated as explained in the previous section. A graduated glass tube was used to estimate the volume of dye liquor in the beck. The required amounts of dyes for the next shade were calculated. The full complement of chemicals required for the next dyeing was added to the residual dye liquor. The next carpet was then entered, the calculated amount of dyes added and the dyeing carried out.

Results of the spectrophotometric analysis often gave negative concentrations for the residual amount of

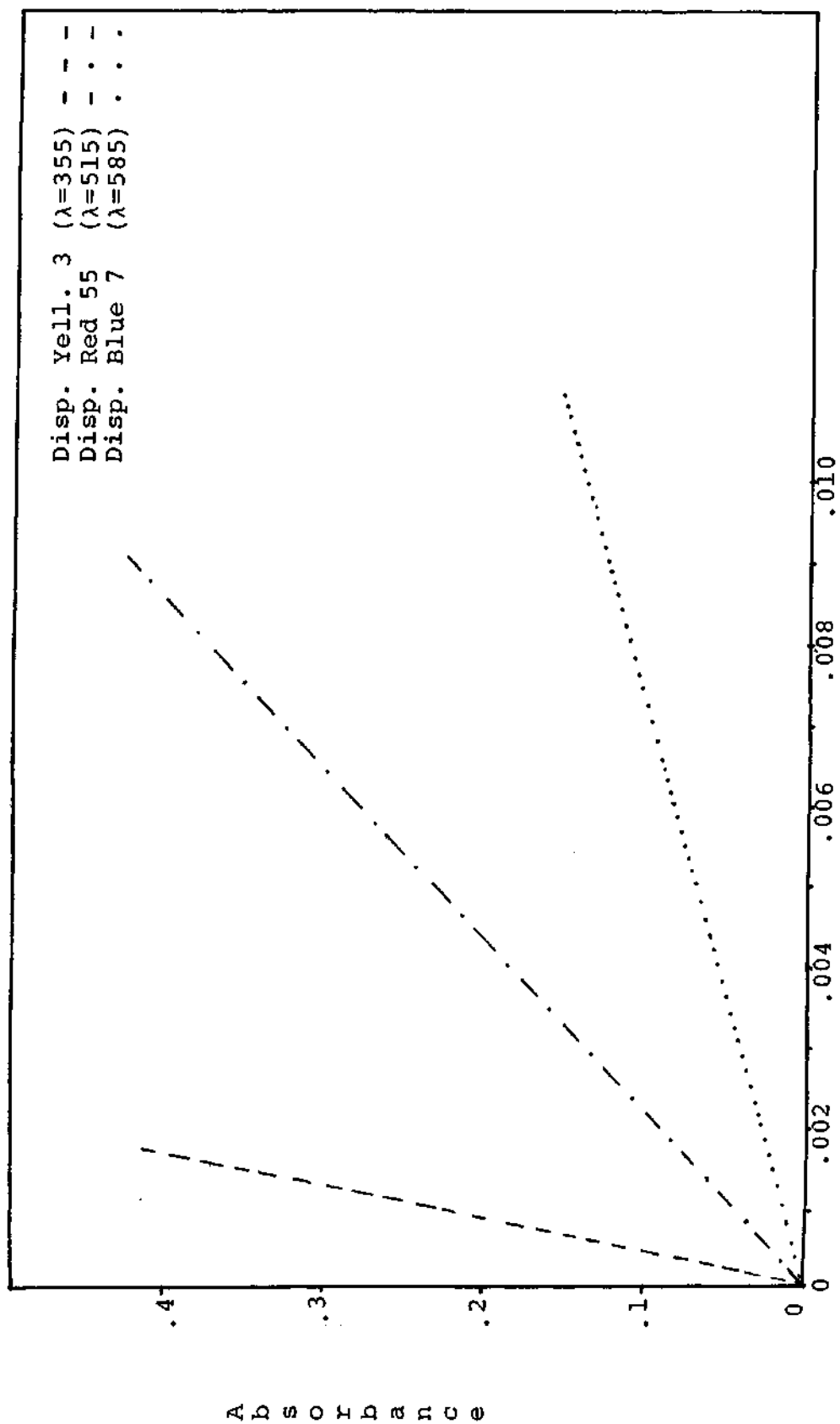


Figure 1. Absorbance as a Function of Concentration - Disperse Dyes

dye. It was assumed that this may be due to interference from the dispensing agent and diluents which are always present in commercial samples of disperse dyes. These materials make up about 80% by weight of the commercial dye samples. It is absorbed by the carpet in small amounts, hence its concentration builds up in the residual dye liquor and makes the analysis difficult. It is more soluble in water than the dye itself. Hence it was decided to extract the dyes from the dye liquor and thus prevent interference from the dispersing agent. This was rather simple since disperse dyes are relatively insoluble in water compared to the other constituents of the dyebath. Perchloroethylene was found to be a suitable solvent for this purpose since it is a good solvent for disperse dyes and has a high boiling point.

The following procedure was involved to extract and analyze the dyes in the residual dyebath. Initially, for calibration purposes known amounts of each dye were used in making the absorbance versus wavelength and absorbance versus concentration plots. One liter of dye solution, consisting of a known amount of dye dispersed in water, was diluted with one liter of 2% Igepal DM 970. To this was added 70 ml. of perchloroethylene. The mixture was then heated to 190°F in a three liter metal can with occasional stirring. The can was fitted with an air condenser to

prevent excessive loss of perchloroethylene. The heated mixture was then poured into another container and allowed to cool to approximately 130°F. At this point it was poured into a large bottle and shaken 150 times to extract as much dye as possible into the perchloroethylene layer. The mixture was allowed to stand for about five minutes to allow the perchloroethylene layer to separate. Forty mls. of saturated salt solution were added to hasten the separation. Most of the supernatant water layer was then decanted and the remaining mixture poured into a separatory funnel to facilitate removal of the perchloroethylene layer from below. The perchloroethylene layer was emulsified with the surfactant solution and had to be heated with about 60 ml. of saturated salt solution to break the emulsion. This was done in a 300 ml round bottom flask fitted with an air condenser. When the perchloroethylene layer became transparent, part of the supernatant water layer was carefully decanted and the remaining solution was poured into a clean, dry separatory funnel. After cooling to room temperature fifty ml. of the perchloroethylene layer was drained off from the bottom, filtered through filter paper (wetted with perchloroethylene) and collected in a measuring cylinder. This 50 ml. was then poured into a 100 ml. volumetric flask and the solution brought up to volume with methanol. The mixture was shaken and methanol was added to compensate the volume reduction. This solution was then used for

spectrophotometric measurement. A solution of pure perchloroethylene and pure methanol, in a 1 to 1 volume ratio was used as the reference solution. After measuring the absorbance and solving three simultaneous equations, the values obtained for  $C_1$ ,  $C_2$  and  $C_3$  are the number of grams of dye in the volume of dyebath taken for analysis. Knowing the total volume of dyebath, the total amount of residual dye was easily calculated.

The values of the absorbancy indices for the three disperse dyes at three wavelengths were obtained using this procedure. They are shown in Table 4. This procedure was tested by taking a mixture of known composition and analysing it. The values obtained for the dye concentrations  $C_1$ ,  $C_2$  and  $C_3$  did not exactly match the actual amounts of dye known to be present in the mixture. The percentage differences from the actual values are shown in Table 4. At this time it was felt that these errors would not be significant, hence they were not taken into account in the experimental calculations, for determining residual dye concentrations.

The values of the absorbancy indices, for the three disperse dyes, at three wavelengths were obtained using this procedure. They are shown in Table 2. This procedure was tested by taking a mixture of known composition and analysing it. The differences between the calculated and actual values are also shown in Table 2. At this time it was

felt that these errors would not be significant, hence no corrections were made. The results obtained from the analysis of the extracted dye mixture seemed to be more reasonable.

Series II. In this set of dyeings, the full complement of required chemicals and the calculated amount of dyes as determined after analysis by the above procedure were added.

After this series of dyeings, some thought was given to the manner in which the auxiliary chemicals were to be replenished in the spent dyebath. There did not seem to be any necessity to add the full complement of chemicals for each dyeing. At the same time, analysis of the dyebath to determine the residual amounts of each chemical would be extremely time consuming.

Series III. In this series of dyeings, the full complement of chemicals was added after every three dyeings. No chemicals were added inbetween. The dyebath was analyzed as in series II, and the required amount of dyes added.

Series IV. In this series of dyeings, 40% of the required amount of chemicals for each dyeing was added. The dyebath was analyzed as in Series II, and the required amount of dyes added.

At this point it was felt that since all the chemicals added are completely soluble in water, only the chemicals



in the water that was lost should be replaced.

Series V & VI. In both these series, only the chemicals in the water that was lost were replaced. The dyebath was analysed as in series II, and the required amount of dyes added.

#### Pilot Scale Dyeings.

Having decided on the sequence of dyeings and the analytical procedure, pilot scale dyeings were attempted. It was first necessary to prepare carpet samples for dyeing by cutting out sections from the large carpet roll. To make the process representative of industrial dyeings, it was decided to make the samples as large as possible. The restrictions on the size of the sample were placed by the dimensions of the dyeing and scouring equipment. The scouring unit could not take samples wider than 12 inches. Hence the sample width was kept between 10 and 11 1/2 inches. The maximum practicable liquor volume for the dye beck was determined to be 80 liters. This would leave sufficient volume for liquor expansion and foaming, thus eliminating the possibility of the dye liquor overflowing during the dyeing. Since the liquor ratio was fixed at 30 to 1 the sample weight required was about 2.67 kg. (5 lbs. 14 ozs). The original carpet roll was 15 ft. wide and 450 ft. long. Eight sections of carpet varying in length from 35 to 40 ft. were cut out and labeled A through H. Each section was

then cut into strips about 10 to 11 1/2 inches wide, 35 to 40 ft. long and weighing between 5 1/2 and 6 1/8 lbs. The strips from each section were numbered 1, 2, 3, etc. from the left side of the carpet roll to indicate their position in the section. The numbered strips were selected randomly for dyeing. Two tufted yarns along the edges of each strip were removed to expose a small section of the backing on each edge. This was singed with a butane torch so that the individual filaments fused together, and thus prevented the face yarn along the edges from unravelling while the carpet was being dyed. The selected carpet strip was then scoured on a Williams Unit. Scouring was necessary to remove the finish that is put on the nylon yarns when they are manufactured. If the finish is not removed, the dye exhaustion is reduced and is non-uniform. The Williams unit, manufactured by Morrison Machine Co., of Paterson, N. J., was also used to rinse the carpet after dyeing. The unit is approximately 50 inches long, 36 inches wide, and 45 inches high. It consists of four wells 24 inches deep with removable baffles and suitable for 50 lbs steam pressure. It has 3 1/4 inch nip rolls suitable for 700 lbs. microset pressure and a three roll padder. Between the padder and the wells is a rack and pinion type compensator for maintaining uniform fabric tension. The carpet was scoured in a hot solution of 2% owf Igepal DM 970. The wet carpet

was squeezed between the nip rolls before it entered the dye beck.

The dye beck used was manufactured by the Hunter Machine Co. The beck dimensions are 17 by 25 inches in the horizontal plane and it has a depth of 40 inches. The maximum volume of the beck is 125 liters. The drive wheel which rotates the carpet in the beck has a diameter of 7 inches and a length of 14 inches. A smaller guide reel provides support for the carpet as it moves over the driving reel. The heating source is a closed steam coil, separated from the carpet by a perforated steel partition. The speed of the drive wheel was adjusted to turn over approximately 55 ft. of carpet per minute. The dye beck has an inlet for a thermocouple. As the thermocouple was inoperative, it was replaced by a tap to facilitate withdrawal of samples of the spent dye liquor. The temperature of the dyebath was measured by means of a mercury thermometer fixed into the side of the beck. The volume of the dye liquor was measured by means of a graduated glass tube. The beck was filled using a one liter measuring cylinder. Every ten liters the glass tube was inserted and the level marked off. To measure the volume of water in the beck, the glass tube was inserted, the top end was sealed by placing the thumb over it and the tube was withdrawn with a column of water in it. The volume was then estimated from the water level in the graduated

tube. (After completing the experiments with the disperse dyes, this system was modified. A simple measuring guage consisting of a narrow bore glass tube and a graduated scale was fixed into the side of the beck. The scale was calibrated by filling the beck with a one liter measuring cylinder. The scale was marked off at two liter intervals. The volume of the dye liquor could be read from the scale by noting the corresponding level of the liquid in the glass tube. This procedure was more precise than the previous one.) A detailed description of the beck is given in references (15) and (41).

Series I. The object of this series of dyeing was to verify if different shades could be dyed in succession without discarding the dyebath. It was necessary to determine if the selected series of shades was appropriate for this purpose. The second objective of this series was to determine a suitable temperature at which the carpet could be entered into the beck without producing an unlevel dyeing.

The dyebath was made up with 2% owf Igepal DM 970, 2% owf trisodium Phosphate, and 0.5% owf Plexene D. The liquor ratio was 30 to 1. The scoured carpet section from the Williams unit was directly entered into the beck, and rotated in the solution for about 10 mins. The dyes, dispersed in water, were then added over a period of five

minutes, and the temperature raised to 95°C at approximately 1.5°C per minute. The liquor temperature was held at 95°C  $\pm$  1°C for one hour. The steam was then turned off and the system allowed to cool. All carpets were unloaded at 60°C from the beck, rinsed in the Williams Unit in a cold water solution of 1% owf Tanapal XNC and hung up to dry. A sample of the dyebath was then taken for spectrophotometric analysis to determine the concentration of the residual dyes. The volume of the dyebath was estimated by means of the glass tube. From the dye analysis the required amounts of dyes for the next shade were calculated. Five dyeings were made in this series.

In Series I the dye analysis was carried out before starting the next dyeing. To reduce the total time taken by the dyeing and analysis procedure, this sequence was slightly modified for subsequent series. The dye analysis results of this set of dyeings had indicated that the exhaustion for the dye forming the major component of the mixture was of the order of 90% or greater. Instead of waiting to carry out the dye analysis, an assumption could be made about the dye exhaustion in the dyeing of the preceding sample. A major portion of the dyes from the next formula could be added and the dyeing begun. Then, while the dyeing was in progress, the sample taken from the previous dyebath could be analysed. Thus, knowing the amounts of the residual dyes and the amounts added at

the beginning of the dyeing now in progress, a correction add could be made before the end of the dye cycle to bring the carpet to the proper shade.

The results of this series of dyeings indicated that for light shades the carpet should be entered into the dyebath at 40°C and for dark shades at 60°C.

Series II. Using the modified dyeing and analytical procedures another series of dyeings was attempted. In this series, for the light shades, the carpet section was entered into the beck at 40°C and for the dark shades at 60°C. The dyeings were carried out as a series I. At the end of this series an attempt was made to dye the light blue shade again. This was not successful as the carpet section turned out to be greenish.

At this point it was felt that a review of the dye recipes and the dyeing sequence was necessary. The total quantity of dye being used was reduced by making the dark shades 'lighter'. Their order of dyeing was also rearranged and intermediate shades were added where necessary so that it would be possible to dye the light blue shade again at the end of the series. The modified list of shades, recipes and order of dyeing is given in Table 3a.

Series III. Once again an attempt was made in this series, to dye through the various shades and repeat the light blue shade at the end, before discarding the dyebath. Nine dyeings were made in this series. The dyeing and

Table 3a. Modified Dye Recipes After  
Series II - Disperse Dyes.

| <u>Shade</u> | Amount of dye as % on wt. of carpet |                     |                     |
|--------------|-------------------------------------|---------------------|---------------------|
|              | <u>Dis. Yell. 3.</u>                | <u>Dis. Red 55.</u> | <u>Dis. Blue 7.</u> |
| Light Blue   | .005                                | .006                | .12                 |
| Light Green  | .16                                 | .001                | .05                 |
| Yellow       | .5                                  | .0005               | .005                |
| Orange       | .13                                 | .1                  | .005                |
| Pink         | .02                                 | .19                 | .0005               |
| Black        | .9                                  | 1.8                 | 1.26                |
| Brown        | 1.0                                 | .6                  | .16                 |
| Olive        | .52                                 | .26                 | .26                 |
| Dark Blue    | .03                                 | .05                 | .85                 |

Table 3b. Modification After Series III

| <u>Shade</u> | <u>Dis. Yell. 3.</u> | <u>Dis. Red 55</u> | <u>Dis. Blue 7.</u> |
|--------------|----------------------|--------------------|---------------------|
| Olive        | .52                  | .26                | .26                 |
| Turquoise    | .037                 | .05                | .85                 |
| Dark Blue    | .01                  | .02                | 1.5                 |

analysis procedure was the same as that in series II.

A problem was encountered with the dark blue dyeing which required a slight modification of the list of shades as shown in Table 3b.

Series IV. With the modified list of shades another attempt was made to dye all the shades and repeat the light blue at the end. The dyeing and analysis procedure followed were as in series II. A total of eleven carpet sections were dyed and the light blue was successfully repeated at the end of the series.

Series V. The dyeings in this series were carried out the same way as those in series IV. Eleven carpet sections were dyed with the light blue being repeated at the end of the series.

Series VI. In the previous two series, the light blue shades dyed at the end looked 'dirty' and did not match the light blue sections dyed at the beginning of the series very closely. The object of this series was to determine whether this problem was due to a light shade being dyed after a dark shade or simply due to the large number of dyeing previously carried out in the same bath. Hence this series of dyeings consisted of only four shades: olive, turquoise, dark blue and light blue.

Series VII. This was the 'standard' series in which each shade was dyed in a fresh bath as is done in conventional dyeing operations. For light shades the



carpet section was entered into the beck at 40°C and for dark shades at 60°C. The dyeing procedure followed was the same as described previously. This series consisted of eight dyeings since samples of light blue and olive, that had been dyed in a fresh bath, were available from the other series. This series was used as a basis for evaluating the reproducibility and uniformity of the experimental dyeings.

#### Entering Carpet at High Temperature.

After the dyeings with disperse dyes had been completed, another retarder was received which was expected to be a good retarder for disperse dyes on nylon. This retarder was Tanapal CAL manufactured by Tanatex. As determined from the previous series of dyeings, for the light shades, the carpet section could not be entered into the beck at a temperature higher than 40°C. This is a great disadvantage in a recycled dyebath procedure since it requires cooling of the bath and thus reduces the savings in energy which could have been achieved. Cooling the bath also increases the time lag between successive dyeings, and increases the time required to reheat the bath to the dyeing temperature. By having an effective retarder which could reduce the dye strike rate at higher temperatures, a uniform dyeing could still be obtained and the loss of time and energy eliminated.

Trial dyeings were made, using Tanapal CAL, to determine if the carpet could be entered at a higher temperature into the beck when dyeing light shades. The first sample dyed was Pink. It was dyed in a fresh bath containing Tanapal Cal (1.2% owf) instead of Igepal DM 970. The dyeing procedure followed was the same as before, except that after the prescour with Igepal DM 970, the carpet was entered into the beck with the dye liquor at 60°C. The dyed sample was evaluated visually and judged to be of good uniformity. Since this dyeing was successful another dyeing was attempted. This time the sample was dyed orange and the carpet section was entered into the beck with the dye liquor at 70°C. The uniformity of the orange sample was judged to be almost as good as that of the pink sample (See Table 16, 17).

Having established a higher entrance temperature for dyeing the light shades, a slight modification was made. In the next dyeing, both Tanapal CAL (1.2% owf) and Igepal DM 970 (0.2% owf) were added to the dye liquor to determine if the retarding action could be enhanced by the use of both agents simultaneously. The carpet entry temperature was 70°C and the shade chosen to be dyed was light blue. The dyeing was unacceptable because the sample showed pronounced streaks.

This concluded the test dyeings with the disperse dyes.

### Acid Dyes

Having completed the experiments with disperse dyes, an attempt was made to adapt this technique for dyeings using a mixture of acid dyes only. The dyeing procedure was kept as similar as possible to that used with disperse dyes. The reason for this was that if the series with acid dyes were successful, a third set of dyeings using a mixture of acid and disperse dyes would be attempted. The general approach for this set of dyeings was to be the same as with the disperse dyes. A suitable retarder would have to be selected. This would be followed by formulation of dye recipes and determination of dyeing sequence. No problems were anticipated in the dyebath analysis since acid dyes are readily soluble in water. Also, no other colored material is present in the commercial dye samples which would interfere with the spectrophotometric analysis. However, acid dyes exhaust more readily than disperse dyes. Hence the crucial step was expected to be the control of the initial strike rate when the carpet first entered the hot dye liquor.

### Selection of Dyes and Retarder.

For the selection of the acid dyes, the same criteria were applied as in the case of the disperse dyes. The dyes selected were Acid Yellow 135, Acid Red 151 and Acid Blue 25. The retarder was selected by experiments on the

Praxitest. Samples of carpet weighing 15 gms. each were prescoured in 2% owf Igepal DM 970, before dyeing in the Praxitest. The dye liquor contained 0.25% owf Plexene D, 0.5% owf trisodium Phosphate, 2% owf Igepal DM 970, 2% owf monosodium Phosphate, 1% owf Acid Yellow 135, and acetic acid to adjust the pH to  $6.1 \pm 0.2$ . The liquor ratio used was 30 to 1. The same dyeing procedure was followed as with the disperse dyes on the Praxitest. For the trial with Igepal DM 970 the dyebath turned turbid about halfway through the dyeing. The final exhaustion was almost as high as in the dyeing without the Igepal. The next trial was made with Gaftex PFB, manufactured by G.A.F., being substituted in the dye liquor for Igepal DM 970. In this case too there was some turbidity but the final exhaustion of the dye was lower than with Igepal DM 970. Because of the turbidity during the dyeings no conclusion could be drawn regarding the retarding action on the initial strike rate. Hence Gaftex PFB was chosen because it gave a lower final exhaustion.

#### Dye Recipes and Dyeing Sequence.

Sample dyeings were done in the Launder-Ometer to compare the actual shades with the dye recipes initially formulated. The same dyeing procedure was used as with the disperse dyes. The samples were prescoured in 1% owf Igepal DM 970. The dye liquor contained 0.25% owf Plexene

D, 0.5% owf trisodium Phosphate, 2.0% owf monosodium Phosphate, 2.0% owf Gaftex PFB and acetic acid to adjust the pH to  $6.1 \pm 0.2$  units. The liquor ratio was 30 to 1. The carpet samples weighed 15 gms. Through trial and error a list of dye recipes and a dyeing sequence were obtained for the initial series of dyeings. This list is shown in Table 4.

#### Analysis of the Residual Dyebath.

For each of the three acid dyes a plot of absorbance versus wavelength was made over the range of 350 to 700 nm. to determine the wavelength at which maximum absorbance occurred (Appendix E). At the maximum absorbance wavelength, a plot of absorbance versus concentration was prepared (Figure 2). The analysis and calculations were then carried out as with the disperse dyes. No extraction of the dyes from the dyebath was required as the acid dyes did not contain the dispersing agent present in the disperse dyes. The residual dyebath was simply filtered and used for absorbance readings in the spectrophotometer. The reference cell contained clear tap water. The absorbancy constants used to calculate the residual dye concentrations are given in Table 2. As the analysis took less than 15 minutes the correct amount of dye required for the next dyeing could be calculated and added at the beginning of the dyeing.

Table 4. List of Dye Recipes and Dyeing Sequence for Acid Dyes.

| <u>Shade</u> | Amount of dye as % on wt. of carpet |                     |                     |
|--------------|-------------------------------------|---------------------|---------------------|
|              | <u>Acid Yell. 135</u>               | <u>Acid Red 151</u> | <u>Acid Blue 25</u> |
| Light Blue   | .008                                | .005                | .08                 |
| Light Green  | .16                                 | .001                | .05                 |
| Yellow       | .8                                  | .0005               | .005                |
| Orange       | .5                                  | .085                | .005                |
| Pink         | .02                                 | .19                 | .0005               |
| Brown        | 1.65                                | .23                 | .19                 |
| Olive        | 1.76                                | .055                | .154                |
| Turquoise    | .3                                  | .07                 | .7                  |
| Black        | 1.25                                | 1.55                | 1.1                 |
| Dark Blue    | .1                                  | .1                  | .85                 |

N.B. Though the names used for the dye shades are the same as those used with the disperse dyes, the actual shades were obviously slightly different.

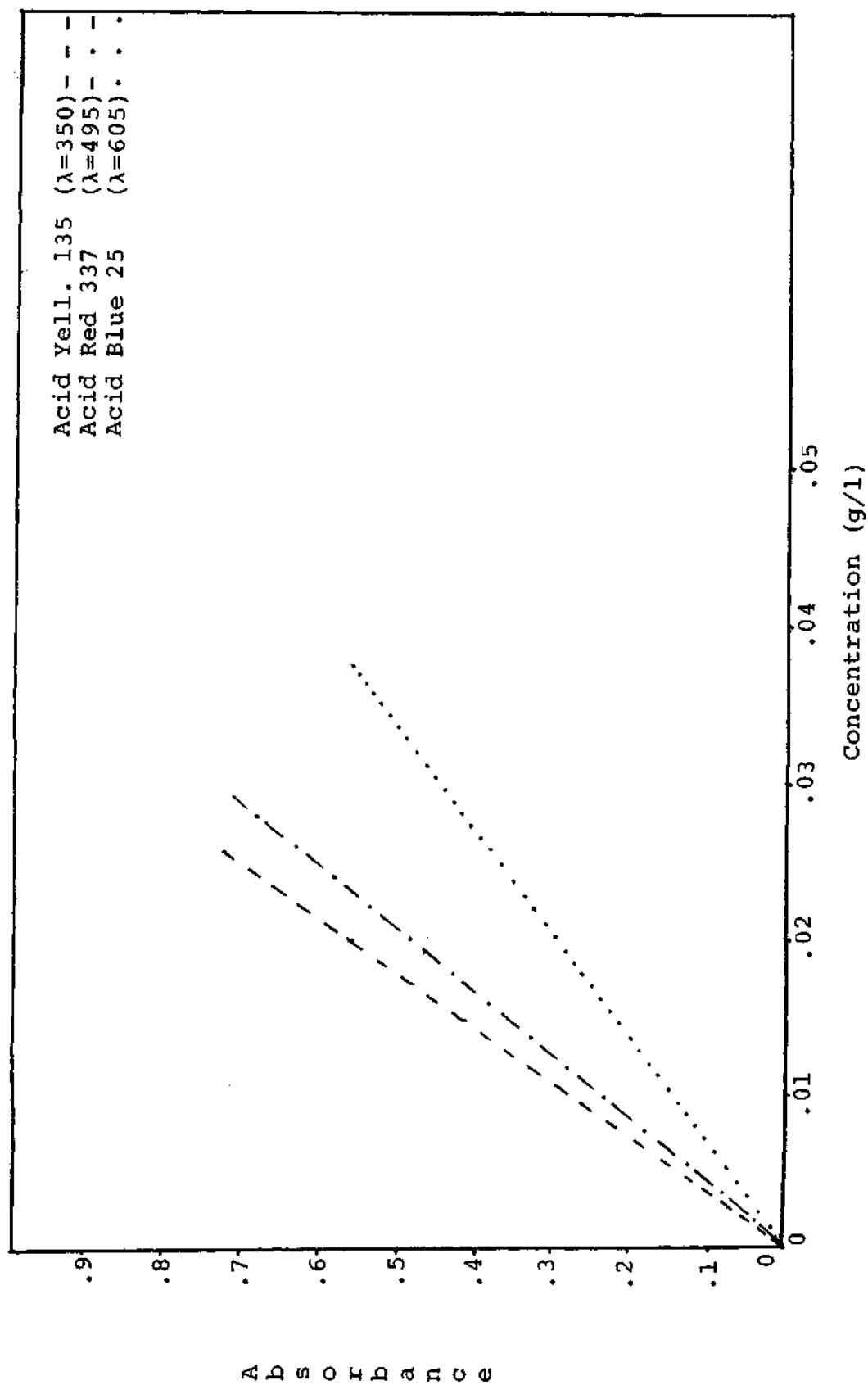


Figure 2. Absorbance as a Function of Concentration - Acid Dyes

### Pilot Scale Dyeings.

Series I. As with the disperse dyes, the object of this series was to determine if the various shades could be dyed in succession and the light blue repeated at the end before discarding the dyebath. The dyeing procedure was similar to the one used for disperse dyes. The carpet section was prescoured in the Williams unit using a hot solution of 1% owf Igepal DM 970. The scoured samples were entered into the beck at 40°C. The dyebath contained 0.25% owf Plexene D, 0.5% owf trisodium Phosphate, 2.0% owf monosodium Phosphate and 2.0% owf Gaftex PFB. The pH was 6.25. After entering the carpet the temperature was slowly raised and the dyes were added at 45°C. Acetic acid was then added to adjust the pH at about 6.0 units. The dyeing was then continued as previously described. Samples in this series were unlevel. It was felt that this might be due to the addition of the dyes into an acidic dyebath, thus increasing the initial strike rate. In the next dyeing Ammonium Hydroxide was added to raise the pH to 8.4 units, before entering the carpet. The dyes were added at 50°C and after 30 minutes the pH was dropped to 5.3 units with acetic acid. Once again the dyeings were unlevel. This series was aborted and an attempt was made to find a leveling agent to reduce the non-uniformity of the dyeings.



Trial dyeings were made in the Launder-Ometer. Five samples were dyed using a different leveling agent for each sample. The samples were dyed light green. The leveling agents tried were Alkanol ND (Du Pont), Migrassist NYL (Tanatex) and Gaftex PFB (G.A.F.), all at a concentration of 2.0% owf. The results showed that Alkanol ND was by far the best leveling agent. Hence it was used as a substitute for Gaftex PFB in all subsequent dyeings. The next problem was to estimate the maximum amount of Alkanol ND that would be exhausted in each dyeing. This was found to be approximately 40% of the amount present at the beginning of the dyeing. The procedure and calculations are shown in Appendix B.

Series II. Another set of dyeings was attempted using Alkanol ND as the leveling agent. The same dyeing procedure was used as in series I. The chemicals were replenished according to the quantity of water lost, as was done with the disperse dyes. No problems were encountered until the dyeing of the pink shade. This sample was extremely non-uniform. It was also observed that much of the red dye added did not dissolve and settled to the bottom of the dye beck. Therefore it was decided to substitute Acid Red 337 for the red dye. A trial dyeing was made using Acid Red 337 instead of Acid Red 151, but this did not improve the uniformity substantially. Hence the attempt to dye a series of different shades was abandoned.

It was then decided to dye a series of five carpets to the same shade using the recycled dyebath technique. The shade chosen was light blue and the dye recipe was:

| <u>Shade</u> | Amount of dye as % on wt. of carpet |                     |                     |
|--------------|-------------------------------------|---------------------|---------------------|
|              | <u>Acid Yell. 135</u>               | <u>Acid Red 337</u> | <u>Acid Blue 25</u> |
| Light Blue   | .008                                | .005                | .08                 |

Series III. The object of this series was to dye five carpet sections to the same shade. The carpet was prescoured in the Williams Unit using a hot solution of 1% owf Igepal DM 970. Excess solution was squeezed out as the carpet entered the beck. The chemicals in the beck were, Plexene D 0.4% owf, trisodium Phosphate 0.5% owf, monosodium Phosphate 2% owf and Alkanol ND 3% owf. The liquor ratio used was 30 to 1. The pH of the dyebath on entering the carpet was slightly acidic to neutral and the temperature was 70°C. The dye solution was then added at 70°C, and the carpet rotated for about 10 to 15 minutes to allow the dyes to level out on the carpet. Acetic acid was then added to lower the pH to  $6.2 \pm 0.2$ , and at the same time the steam was turned up to heat the dyebath from 40°C to 95°C at a rate of 1.5°C per minute. The temperature was held at  $95^\circ\text{C} \pm 1^\circ\text{C}$  for an hour and then the steam was turned off and the dyebath allowed to cool to 80°C. All carpets were unloaded from the beck at 80°C, rinsed in the Williams Unit in a cold water solution of 1% owf Tanapal

XNC and hung up to dry. A sample of the dyebath was taken for spectrophotometric analysis to determine the concentrations of the residual dyes. The next carpet sample was then prepared for dyeing. The required amount of auxiliary chemicals were calculated from the amount of water lost and added into the spent dye liquor before entering the next carpet. The first dyeing was done in fresh water with the carpet being entered into the cold dyebath and was considered a 'standard' dyeing.

The dyed samples were evaluated for end-to-end and between sample color variations by the same procedure as used for the disperse dyes.

#### Color Measurement

On completing the dyeings, the dyed samples were evaluated for levelness and reproducibility. The samples had to be examined for end-to-end color variations to determine whether the dyeing technique produced uniformly dyed samples. Each dyeing in the experimental series was compared to the respective dyeing of that shade in the standard series, to determine whether the recycled bath dyeing technique could accurately reproduce colors dyed according to current industrial techniques. In addition, the samples were visually examined to detect streaks, spots, bands or barre problems.

It was expected that the experimental samples would not exactly match the 'standard' dyed samples. Therefore,

it was necessary to know what is considered an acceptable color match in the carpet industry, so that the same criteria could be applied in this case. However, color differences are not usually determined for commercially dyed carpet samples. Some work had previously been done at the Georgia Tech, School of Textile Engineering, in which arrangements were made with a quality carpet manufacturer to collect samples of carpet dyed over a one week period that the shift dyers had considered acceptable matches to the color standard. Color measurements were made to determine the color difference between the industrial samples and standards. The samples taken were from carpets that had already been shipped. Hence the color differences determined can be taken as industrially acceptable values. These values are shown in Table 22. The color difference values obtained for carpets dyed by the recycled bath technique are shown in Table 18. The data from industrial samples indicates that color differences as large as 10 MacAdam units are considered acceptable in commercial carpet dyeing.

A Diano/LSCE automated system, manufactured by Diano Corporation of Mansfield, Mass. (42) was used for the color measurements. The usual procedure is to cut out small pieces from the carpet and use these for measurements. In this case, the samples were left intact and the whole section was placed against the instrument window when the measurements were made. They were made at random points

approximately three feet apart along the length of the sample. In this way, the complete sample was always available for visual evaluation. The light source used in the instrument was CIE Illuminant C. The instrument was used to measure the  $X$ ,  $X'$ ,  $Y$  and  $Z$  tristimulus values which were subsequently converted to the C.I.E.  $X$ ,  $Y$  and  $Z$  values, and these were used to calculate color differences in MacAdam Units (43). About ten to fifteen measurements were made along each carpet section. In evaluating the dyeing uniformity, the color difference was taken as the value at any point along the sample minus the mean value for that sample. This gave some indication of the end-to-end color variation along each sample. The color difference for reproducibility was taken as the mean value of the sample dyeing minus the mean value of the standard dyeing. The color difference calculations were done by use of the FMC II Color Difference Program (44), which gave the color differences in MacAdam Units. A MacAdam unit is defined as the least perceptable color difference seen by a trained observer. It is the most commonly used unit of color difference in the textile industry. The program was recorded on magnetic cards for use with a Hewlett Packard Model 9100 B programable calculator. The input data required for the calculations were the  $X$ ,  $X'$ ,  $Y$  and  $Z$  tristimulus values recorded from the color eye measurements. The peripheral equipment required with the calculator were

a teletype for printing the results, a Hewlett Packard Model 9101 A extended memory to store the program and a coupler/controller for interconnecting the various components.

To determine the effect of instrument repeatability, repeated readings were made at a single spot on a carpet. The variance in these readings would provide some measure of the instrument variability during the color measurements. This variance in tristimulus values is shown in Table 21.

## CHAPTER IV

### RESULTS

In the evaluation of dyed carpets, color difference measurements are of great importance in assessing the uniformity and reproducibility of the sample. End-to-end and side-to-side color variations give a good indication of the dyeing uniformity, while between sample color differences indicate the reproducibility of the process, from sample to sample. These criteria are used in the carpet industry in assessing the quality of the dyed carpet and hence color difference measurements have been made on the dyed samples to evaluate their uniformity and reproducibility.

The following set of tables (5-16) give the color difference values measured along the length of each carpet. These values, in MacAdam units, were calculated by the use of the equations in Appendix C. They were calculated according to the formula:

$$\text{Color Difference} = [\text{CIE XYZ value at a point along the sample}] - [\text{Mean CIE XYZ value for that sample}].$$

Tables 5-14 show the values for the Disperse dyes series. For the light blue shade in series IV and V, (a)

indicates the light blue dyeing at the beginning of the series, and (b) indicates the light blue dyeing at the end of the series.

Table 15 shows the color difference values for the acid dyes in the light blue shade.

Table 16 shows the color difference values for the trial dyeings with disperse dyes, in which the carpets were entered into the bath at a higher temperature than that used in the other dyeings.

Visual examination of the dyed samples confirmed the results obtained from the color difference measurements.



Table 5. Color Difference Along Carpet Sample  
Disperse Dyes - Light Blue

Color Difference Values in MacAdam Units

| Std. Carpet<br>Ser. IV (a) | Sample Carpets |          |         |            |            |         |
|----------------------------|----------------|----------|---------|------------|------------|---------|
|                            | Ser. II        | Ser. III | Ser. IV | Ser. V (a) | Ser. V (b) | Ser. VI |
| 1.39                       | 1.54           | 2.67     | 2.74    | 1.11       | 3.36       | 2.43    |
| 1.03                       | 1.05           | 0.37     | 1.20    | 1.56       | 0.62       | 2.20    |
| 1.65                       | 1.56           | 0.54     | 0.66    | 0.49       | 1.51       | 0.17    |
| 0.50                       | 0.91           | 0.71     | 0.88    | 1.32       | 3.61       | 0.58    |
| 0.63                       | 0.73           | 1.09     | 0.77    | 2.25       | 1.62       | 0.66    |
| 0.58                       | 1.25           | 1.13     | 0.97    | 0.94       | 2.68       | 1.59    |
| 0.79                       | 0.33           | 0.66     | 1.29    | 0.63       | 1.06       | 1.34    |
| 0.23                       | 1.36           | 0.76     | 1.46    | 0.42       | 2.95       | 1.64    |
| 0.89                       | 0.82           | 1.48     | 0.76    | 0.44       | 1.10       | 0.70    |
| 0.87                       | 0.27           | 0.78     | 0.98    | 0.59       | 1.52       | 0.58    |
| 0.99                       | 1.82           | 0.83     | 0.82    | 1.51       | 1.58       | 0.98    |
| 0.65                       | 1.38           | 0.93     |         | 1.60       | 1.63       | 1.07    |
| 1.28                       | 1.16           | 0.98     |         | 1.42       |            | 2.18    |
| 1.57                       | 0.87           | 2.29     |         | 0.82       |            | 1.56    |
| 2.35                       | 0.74           | 1.23     |         | 3.50       |            | 1.07    |
|                            | 0.89           | 1.88     |         |            |            | 2.03    |

Table 6. Color Difference Along Carpet Sample  
Disperse Dyes - Light Green

Color Difference Values in MacAdam Units

| Std. Carpet<br>Ser. VII | Sample Carpets |          |         |        |
|-------------------------|----------------|----------|---------|--------|
|                         | Ser. II        | Ser. III | Ser. IV | Ser. V |
| 2.00                    | 2.93           | 3.36     | 1.94    | 3.20   |
| 1.59                    | 1.36           | 0.62     | 0.55    | 0.56   |
| 1.72                    | 1.05           | 0.52     | 1.27    | 1.46   |
| 1.52                    | 0.43           | 0.97     | 1.29    | 0.68   |
| 2.00                    | 0.42           | 0.36     | 0.43    | 0.46   |
| 0.62                    | 2.06           | 1.96     | 0.65    | 1.77   |
| 0.89                    | 0.52           | 1.20     | 1.02    | 1.12   |
| 0.81                    | 1.23           | 0.75     | 0.90    | 1.19   |
| 0.29                    | 0.88           | 1.02     | 1.46    | 0.55   |
| 0.49                    | 0.70           | 1.22     | 0.67    | 0.59   |
| 1.09                    | 1.36           | 0.82     | 1.06    | 0.95   |
| 1.86                    | 0.35           | 1.68     | 1.83    | 0.80   |
| 1.10                    | 1.63           | 2.01     | 0.42    | 1.07   |
| 2.00                    | 1.48           |          | 1.26    | 0.88   |
| 3.41                    | 0.85           |          |         |        |
|                         | 1.04           |          |         |        |

Table 7. Color Difference Along Carpet Sample  
Disperse Dyes - Yellow

Color Difference Values in MacAdam Units

| Std. Carpet<br>Ser. VII | Sample Carpets |          |         |        |  |
|-------------------------|----------------|----------|---------|--------|--|
|                         | Ser. II        | Ser. III | Ser. IV | Ser. V |  |
| 1.02                    | 1.86           | 2.85     | 2.77    | 1.95   |  |
| 0.43                    | 1.06           | 1.36     | 1.45    | 0.62   |  |
| 0.90                    | 1.42           | 1.56     | 0.61    | 0.85   |  |
| 0.44                    | 1.74           | 0.30     | 1.52    | 0.70   |  |
| 2.05                    | 0.69           | 0.81     | 2.14    | 0.69   |  |
| 1.16                    | 1.10           | 1.36     | 1.45    | 1.36   |  |
| 0.70                    | 1.11           | 1.56     | 0.70    | 1.18   |  |
| 1.33                    | 1.68           | 0.64     | 1.51    | 0.24   |  |
| 0.43                    | 1.37           | 1.29     | 0.97    | 1.29   |  |
| 0.62                    | 0.76           | 2.31     | 1.19    | 1.83   |  |
| 0.63                    | 1.04           | 0.60     | 1.47    | 1.04   |  |
| 1.71                    | 1.03           | 0.97     | 1.74    | 0.98   |  |
| 1.04                    | 1.51           | 0.58     | 1.36    | 0.62   |  |
| 0.30                    | 0.89           | 1.17     |         | 0.82   |  |
| 0.19                    | 0.82           | 1.06     |         | 2.64   |  |
| 2.07                    | 1.27           |          |         |        |  |
|                         | 0.93           |          |         |        |  |

Table 8. Color Difference Along Carpet Sample  
Disperse Dyes - Orange

Color Difference Values in MacAdam Units

| Std. Carpet<br>Ser. III | Ser. II |          | Sample Carpets |        | Ser. V |
|-------------------------|---------|----------|----------------|--------|--------|
|                         | Ser. II | Ser. III | Ser. IV        | Ser. V |        |
| 0.98                    | 2.34    | 3.44     | 2.74           | 2.61   |        |
| 0.81                    | 0.45    | 0.60     | 0.43           | 1.16   |        |
| 0.40                    | 0.83    | 0.39     | 0.79           | 1.62   |        |
| 1.45                    | 1.32    | 0.56     | 1.41           | 0.22   |        |
| 1.70                    | 1.37    | 0.23     | 0.34           | 0.46   |        |
| 0.09                    | 1.94    | 0.51     | 1.07           | 0.61   |        |
| 0.58                    | 1.71    | 1.44     | 0.35           | 1.03   |        |
| 0.67                    | 1.96    | 0.51     | 0.81           | 0.57   |        |
| 0.85                    | 0.69    | 1.75     | 1.33           | 0.68   |        |
| 0.72                    | 1.09    | 1.01     | 2.33           | 1.68   |        |
| 1.10                    | 1.12    | 0.94     | 1.06           | 1.94   |        |
| 0.52                    | 1.18    | 0.20     | 1.08           | 0.66   |        |
| 1.10                    | 0.83    | 1.60     | 0.34           | 0.33   |        |
| 0.79                    | 3.38    | 0.43     |                | 0.86   |        |
| 2.56                    |         | 0.42     |                | 2.73   |        |
|                         |         | 0.49     |                |        |        |

Table 9. Color Difference Along Carpet Sample  
Disperse Dyes - Pink

Color Difference Values in MacAdam Units

| Std. Carpet<br>Ser. VII | Sample Carpets |          |         |        |  |
|-------------------------|----------------|----------|---------|--------|--|
|                         | Ser. II        | Ser. III | Ser. IV | Ser. V |  |
| 1.88                    | 1.01           | 1.13     | 2.56    | 1.88   |  |
| 0.46                    | 2.46           | 1.15     | 1.02    | 2.01   |  |
| 1.42                    | 0.77           | 1.44     | 0.78    | 1.23   |  |
| 0.24                    | 0.46           | 1.11     | 0.44    | 1.26   |  |
| 0.72                    | 2.13           | 0.66     | 0.83    | 0.98   |  |
| 0.51                    | 1.57           | 0.50     | 1.19    | 0.93   |  |
| 0.25                    | 2.10           | 0.54     | 0.95    | 0.55   |  |
| 1.80                    | 0.66           | 1.32     | 0.73    | 0.92   |  |
| 1.25                    | 0.66           | 1.44     | 0.54    | 1.34   |  |
| 1.23                    | 1.48           | 0.86     | 0.80    | 0.48   |  |
| 1.77                    | 1.70           | 0.87     | 0.27    | 0.37   |  |
| 0.56                    | 2.49           | 0.67     | 0.65    | 0.32   |  |
| 0.53                    | 0.94           | 1.54     | 0.67    | 0.57   |  |
| 1.82                    | 2.41           | 0.44     | 1.39    | 2.31   |  |
| 3.20                    |                | 2.18     | 1.25    |        |  |

Table 10. Color Difference Along Carpet Sample  
Disperse Dyes - Black

Color Difference Values in MacAdam Units

| Std. Carpet<br>Ser. VII | Sample Carpets |          |         |        |  |
|-------------------------|----------------|----------|---------|--------|--|
|                         | Ser. II        | Ser. III | Ser. IV | Ser. V |  |
| 1.25                    | 1.76           | 2.65     | 2.35    | 4.93   |  |
| 0.98                    | 1.05           | 0.84     | 0.84    | 1.77   |  |
| 3.87                    | 1.61           | 1.61     | 0.25    | 1.67   |  |
| 2.33                    | 1.02           | 0.39     | 1.99    | 0.91   |  |
| 2.28                    | 0.45           | 1.07     | 3.16    | 0.00   |  |
| 0.97                    | 1.35           | 1.18     | 3.49    | 1.25   |  |
| 2.63                    | 4.98           | 3.19     | 2.11    | 1.06   |  |
| 0.68                    | 1.27           | 0.66     | 0.59    | 3.10   |  |
| 1.00                    | 0.58           | 0.72     | 1.67    | 0.41   |  |
| 2.25                    | 1.55           | 0.88     | 0.35    | 1.32   |  |
| 0.38                    | 3.09           | 0.66     | 1.14    | 2.23   |  |
| 3.84                    | 1.65           | 1.27     | 0.95    | 1.83   |  |
|                         | 0.44           | 1.54     | 1.47    | 2.20   |  |
|                         | 1.31           | 1.76     | 2.18    | 2.11   |  |
|                         | 1.79           | 3.33     |         |        |  |

Table 11. Color Difference Along Carpet Sample  
Disperse Dyes - Brown

Color Difference Values in MacAdam Units

| Std. Carpet<br>Sec. VII | Sample Carpets |          |         |        |
|-------------------------|----------------|----------|---------|--------|
|                         | Ser. II        | Ser. III | Ser. IV | Ser. V |
| 1.51                    | 0.73           | 3.54     | 3.35    | 0.61   |
| 1.53                    | 2.50           | 2.34     | 1.97    | 0.41   |
| 0.84                    | 2.97           | 0.85     | 1.18    | 0.54   |
| 1.07                    | 1.39           | 0.85     | 1.23    | 1.03   |
| 0.33                    | 1.42           | 0.66     | 1.07    | 0.94   |
| 0.71                    | 1.18           | 2.44     | 0.75    | 0.68   |
| 0.62                    | 0.47           | 1.95     | 1.73    | 0.32   |
| 2.99                    | 0.69           | 0.71     | 1.47    | 0.81   |
| 0.46                    | 1.06           | 0.94     | 0.55    | 1.41   |
| 1.28                    | 0.72           | 1.48     | 1.41    | 1.16   |
| 0.52                    | 1.12           | 1.24     | 2.30    | 0.70   |
| 0.61                    | 0.42           | 0.71     | 0.43    | 0.81   |
| 0.77                    | 2.28           | 1.21     | 0.67    | 1.09   |
| 2.17                    | 1.59           | 1.18     |         |        |
|                         | 2.28           | 2.16     |         |        |

Table 12. Color Difference Along Carpet Sample

## Color Difference Values in MacAdam Units

| Std. Carpet<br>Ser. VI | Sample Carpets |          |         |        |
|------------------------|----------------|----------|---------|--------|
|                        | Ser. II        | Ser. III | Ser. IV | Ser. V |
| 1.54                   | 2.63           | 1.75     | 1.92    | 1.46   |
| 2.73                   | 1.26           | 2.12     | 1.07    | 1.07   |
| 0.16                   | 2.40           | 0.73     | 0.28    | 0.87   |
| 0.67                   | 2.54           | 0.66     | 0.63    | 0.51   |
| 1.17                   | 0.48           | 1.80     | 0.81    | 1.01   |
| 0.56                   | 0.43           | 0.55     | 0.41    | 1.19   |
| 0.99                   | 1.04           | 1.63     | 1.15    | 1.53   |
| 1.22                   | 0.91           | 0.61     | 1.52    | 0.74   |
| 1.32                   | 0.81           | 1.26     | 1.19    | 1.25   |
| 1.12                   | 1.35           | 0.94     | 0.70    | 2.17   |
| 1.26                   | 0.63           | 0.81     | 1.34    | 1.70   |
| 1.39                   | 1.58           | 0.64     | 1.72    | 2.17   |
| 1.05                   | 1.23           | 0.40     | 1.15    |        |
| 0.96                   | 0.94           | 1.01     | 1.45    |        |
| 3.29                   | 1.28           | 1.58     |         |        |
|                        | 2.00           |          |         |        |



Table 13. Color Difference Along Sample  
Disperse Dyes - Turquoise.

Color Difference Values in MacAdam Units

| Std. Carpet<br>Ser. VIII | Ser. IV | Ser. V | Ser. VI |
|--------------------------|---------|--------|---------|
| 1.79                     | 3.06    | 2.61   | 1.99    |
| 0.76                     | 0.49    | 1.96   | 0.98    |
| 3.67                     | 1.29    | 1.24   | 0.19    |
| 0.66                     | 0.89    | 0.78   | 0.82    |
| 0.94                     | 0.85    | 0.63   | 1.51    |
| 1.75                     | 0.78    | 0.61   | 0.43    |
| 0.82                     | 0.26    | 0.65   | 0.66    |
| 0.72                     | 0.47    | 0.71   | 0.23    |
| 1.15                     | 1.00    | 0.81   | 0.24    |
| 1.54                     | 1.27    | 1.17   | 0.53    |
| 1.86                     | 0.77    | 0.76   | 0.91    |
| 0.52                     | 1.06    | 0.45   | 0.37    |
| 1.39                     | 0.67    | 0.62   | 0.50    |
| 1.74                     | 0.82    | 0.70   | 0.73    |
|                          | 1.38    | 1.76   |         |
|                          |         | 0.90   |         |

Table 14. Color Difference Along Sample  
Disperse Dyes - Dark Blue

Color Difference Values in MacAdam Units

| Std. Carpet<br>Ser. VII | Ser. II | Ser. IV | Ser. V | Ser. VI |
|-------------------------|---------|---------|--------|---------|
| 1.23                    | 1.85    | 2.67    | 2.67   | 1.73    |
| 0.70                    | 0.95    | 1.31    | 0.89   | 0.47    |
| 1.52                    | 2.50    | 2.14    | 0.46   | 0.66    |
| 0.93                    | 1.31    | 0.74    | 0.59   | 1.23    |
| 0.81                    | 1.07    | 1.12    | 0.32   | 1.13    |
| 0.59                    | 0.35    | 1.33    | 1.07   | 1.46    |
| 1.54                    | 2.16    | 0.38    | 0.96   | 1.58    |
| 0.90                    | 0.62    | 0.55    | 0.53   | 0.75    |
| 0.52                    | 0.56    | 1.50    | 0.69   | 0.58    |
| 1.07                    | 0.84    | 0.57    | 1.18   | 0.43    |
| 0.26                    | 4.72    | 0.75    | 0.34   | 2.53    |
| 0.46                    | 2.18    | 1.24    | 0.45   | 0.51    |
| 1.86                    | 2.90    | 1.24    | 0.77   | 1.78    |
|                         | 0.85    | 1.00    |        |         |
|                         | 0.70    | 0.84    |        |         |

Table 15. Color Difference Along Sample  
Acid Dyes - Light Blue

| Color Difference Values in MacAdam Units |      |      |      |      |  |
|--|------|------|------|------|--|
| Std. Carpet                              | 2    | 3    | 4    | 5    |  |
| 1.86                                     | 2.15 | 1.64 | 1.05 | 0.98 |  |
| 1.47                                     | 0.70 | 0.13 | 1.18 | 0.66 |  |
| 0.65                                     | 1.52 | 3.65 | 0.73 | 2.05 |  |
| 0.68                                     | 0.60 | 1.11 | 0.72 | 1.76 |  |
| 0.41                                     | 3.28 | 0.58 | 1.16 | 1.70 |  |
| 1.48                                     | 1.80 | 1.25 | 0.65 | 2.03 |  |
| 0.83                                     | 1.18 | 2.19 | 1.26 | 1.20 |  |
| 1.17                                     | 2.00 | 2.26 | 0.69 | 0.79 |  |
| 0.71                                     | 1.31 | 0.56 | 1.93 | 0.96 |  |
| 0.35                                     | 0.41 | 4.12 | 2.07 | 0.44 |  |
| 0.60                                     | 0.88 | 0.58 | 0.29 | 0.91 |  |
| 1.07                                     | 0.91 | 0.76 | 1.47 | 1.68 |  |
| 0.41                                     | 1.34 | 1.38 | 1.46 | 1.18 |  |
| 1.07                                     | 2.10 | 5.56 | 1.21 | 0.92 |  |
| 1.41                                     |      | 1.44 | 0.97 | 0.31 |  |

Table 16. Color Difference Along Sample: High  
Temperature Trials, Disperse Dyes

| Color Difference Values in MacAdam Units |      |        |
|--|------|--------|
| Pink                                     | Blue | Orange |
| 2.71                                     | 1.60 | 2.43   |
| 1.53                                     | 5.58 | 0.96   |
| 1.72                                     | 2.71 | 3.01   |
| 1.50                                     | 2.64 | 0.75   |
| 1.64                                     | 0.10 | 0.88   |
| 0.51                                     | 0.74 | 0.54   |
| 2.16                                     | 0.99 | 1.50   |
| 1.11                                     | 0.47 | 2.24   |
| 0.57                                     | 1.42 | 1.20   |
| 1.99                                     | 2.48 | 2.48   |
|  | 1.02 | 0.93   |
|  | 0.18 | 2.82   |
|  | 3.69 |        |
|  | 1.63 |        |

Table 17 shows the variance in the color difference values along each sample for the disperse dyes series and the acid dyes series. A comparison of the variance along the 'standard' carpets and the experimental samples gives some indication of the uniformity (end-to-end color variation) obtained in the standing bath dyeing technique.

The formula used for the calculation of variance is:

$$\text{Variance} = \frac{\sum (x_i)^2 - \frac{(\sum x_i)^2}{n}}{n - 1}$$

where;

$n$  = the number of measurements made along a carpet sample.

$x_i$  = the color difference between each measurement and the mean value for that carpet sample. (i.e. the values shown in Tables 5 - 16).

Table 18 shows the color differences calculated for reproducibility only, between the experimental and the standard carpets, in this work.

Table 17. Variance in Color Difference Values Along Each Sample as a Measure of Dyeing Uniformity.

Disperse Dyes Series.

| Shade       | Standard | II   | III  | IV     | V    | VI     |
|-------------|----------|------|------|--------|------|--------|
| Light Blue  | 0.30     | 0.19 | 0.41 | (Std.) | 0.72 |        |
| Light Green | 0.64     | 0.46 | 0.67 | 0.24   | 0.51 |        |
| Yellow      | 0.35     | 0.12 | 0.45 | 0.32   | 0.35 |        |
| Orange      | 0.36     | 0.60 | 0.69 | 0.56   | 0.64 |        |
| Pink        | 0.68     | 0.75 | 0.23 | 0.29   | 0.40 |        |
| Black       | 1.40     | 1.31 | 0.86 | 1.00   | 1.46 |        |
| Brown       | 0.56     | 0.62 | 0.70 | 0.65   | 0.10 |        |
| Olive       | 0.62     | 0.50 | 0.30 | 0.23   | 0.28 | (Std.) |
| Turquoise   | 0.66     | -    | -    | 0.42   | 0.36 | 0.26   |
| Dark Blue   | 0.23     | 1.38 | -    | 0.37   | 0.38 | 0.42   |
| Light Blue  | -        | -    | -    | 0.34   | 0.93 | 0.46   |

Acid Dyes Series  
(Light Blue Shade)

|            |      |      |      |      |      |
|------------|------|------|------|------|------|
| Dyeing No: | Std. | 2    | 3    | 4    | 5    |
| Variance:  | 0.21 | 0.60 | 2.34 | 0.23 | 0.31 |

Disperse Dyes-High Temperature Trials

|        |          |
|--------|----------|
| Shade  | Variance |
| Pink   | 0.46     |
| Blue   | 2.29     |
| Orange | 0.79     |

Table 18. Color Differences for Reproducibility  
Disperse Dyes

| Shade       | Color Difference from Standard |          |           |   |
|-------------|--------------------------------|----------|-----------|---|
|             | Series IV                      | Series V | Series VI |   |
| Light Blue  | -                              | 2.08     | -         | - |
| Light Green | 5.26                           | 5.64     | -         | - |
| Yellow      | 21.02                          | 5.14     | -         | - |
| Orange      | 1.56                           | 13.20*   | -         | - |
| Pink        | 6.30                           | 5.78     | -         | - |
| Black       | 2.32                           | 2.37     | -         | - |
| Brown       | 11.83                          | 11.78    | -         | - |
| Olive       | 1.38                           | 1.78     | -         | - |
| Turquoise   | 9.09                           | 9.91     | 3.38      |   |
| Dark Blue   | 2.16                           | 4.03     | 1.71      |   |
| Light Blue  | 4.39                           | 11.67    | 0.56      |   |

\*Error in dye bath analysis.

|                    |      |       |       |      |
|--------------------|------|-------|-------|------|
| Acid Dyes          |      |       |       |      |
| (Light Blue Shade) |      |       |       |      |
| Dyeing No.         | 2    | 3     | 4     | 5    |
| Color Diff.        | 9.52 | 13.43 | 11.65 | 8.99 |

Table 19 shows the mean value of the color difference between the experimental carpets and the standard carpet of that color. These are calculated from the values in Table 18. Due to the variations in dyebath reconstitution procedure in the disperse dyes series, all the series cannot be used for the evaluation of reproducibility between standard and experimental carpets. Series IV and V were selected because they were expected to give better results, due to the improved dyebath reconstitution procedure.

The variance between the color difference values of each experimental carpet from the standard of that color is also given in Table 19. The variance was calculated as in Table 17, except that in this case,  $x_i$  was the color difference obtained by the formula,

$$\text{Color Diff.} = [\text{Mean CIE XYZ value of sample}] - [\text{Mean CIE XYZ value of standard}]$$

The variance in color difference values gives an indication of the reproducibility between the experimental series themselves.

Table 20 shows the analysis of variance between series V and the standard series VII.

The results obtained from the calculations following Table 20 indicate that the procedural differences between the two series were almost negligible.



Table 19. Reproducibility of the Experimental Dyeings

| Disperse Dyes Series |   |                                       |  |
|----------------------|---|---------------------------------------|--|
| Shade of Dyed Carpet | Mean Value of Color Diff. Series IV & V | Variance in Color Diff. Series IV & V |  |
| Light Blue           | -                                       | -                                     |  |
| Light Green          | 5.45                                    | 0.07                                  |  |
| Yellow               | 13.08                                   | 126.09                                |  |
| Orange               | 7.38                                    | 67.74                                 |  |
| Pink                 | 6.04                                    | 0.14                                  |  |
| Black                | 2.35                                    | 0.00                                  |  |
| Brown                | 11.81                                   | 0.00                                  |  |
| Olive                | 1.58                                    | 0.08                                  |  |
| Turquoise            | 9.50                                    | 0.34                                  |  |
| Dark Blue            | 3.10                                    | 1.75                                  |  |
| Light Blue           | 8.03                                    | 26.50                                 |  |

| Acid Dyes Series     |                                |                                    |
|----------------------|--------------------------------|------------------------------------|
| Shade of Dyed Carpet | Mean Value of Color Difference | Variance in Color Different Values |
| Light Blue           | 10.90                          | 4.17                               |

Table 20. Analysis of Variance (Disperse Dyes)

| Carpet<br>Shade | Std.     |       | Expt.<br>Ser. V |
|-----------------|----------|-------|-----------------|
|                 | Ser. VII |       |                 |
| Light Blue      | 1.03     | 1.26  |                 |
| Light Green     | 1.43     | 1.09  |                 |
| Yellow          | 0.94     | 1.11  |                 |
| Orange          | 0.95     | 1.14  |                 |
| Pink            | 1.18     | 1.08  |                 |
| Black           | 1.87     | 1.78  |                 |
| Brown           | 1.10     | 0.81  |                 |
| Olive           | 1.30     | 1.31  |                 |
| Turquoise       | 1.38     | 1.02  |                 |
| Dark Blue       | 0.95     | 0.84  |                 |
| Light Blue      | 1.03     | 1.94  |                 |
| Total           | 13.16    | 13.38 |                 |
| Mean            | 1.196    | 1.216 |                 |
| Grand Total     |          | 26.54 |                 |
| Grand Mean      |          | 1.206 |                 |

Calculations for Analysis of Variance, based on Table 20.

$$\text{Total Variance } S_T^2 = \frac{\sum (x_{ij} - \bar{x})^2}{N-1}$$

$x_{ij}$  = each  $i$  value of  $x$  in column  $j$

$\bar{x}$  = grand mean

$N$  = total number of  $x$  observations

$$\therefore S_T^2 = \frac{2.056}{21} = 0.098$$

$$\text{Column Variance } S_C^2 = \frac{\sum_{j=1}^c \sum_{i=1}^h (x_j - \bar{x})^2}{c-1}$$

$\bar{x}_j$  = mean of each column

$c$  = number of columns

$n$  = number of observations in each column

$$\therefore S_C^2 = \frac{0.0022}{1} = 0.002$$

$$\text{Residual Variance } S_R^2 = \frac{\sum (x_{ij} - \bar{x}_j)^2}{N-c}$$

$$\therefore S_R^2 = \frac{2.118}{9} = 0.235$$

$$F_{1,9} \text{ ratio (calc.)} = \frac{S_C^2}{S_R^2} = 0.009$$

$$F_{1,9} \text{ (99\% confidence) = 10.56 (from tables)}$$

Since the  $F$  ratio calculated is much smaller than that obtained from the tables, the two series are similar.

Table 21 shows the repeatability of the color eye used for the measurement of the tristimulus values. The numbers shown are the variance between fifteen readings taken at the same point on a carpet sample.

One of the major factors leading to variability in color difference values is the variability in the instrument used for the measurements. When this variability is large, it can cause errors in the assessment of the uniformity and reproducibility of the dyed sample. In this case the variability in the instrument was negligible.

Table 22 shows typical color difference values for five nylon and polyester carpets shipped from a commercial dyehouse as first quality merchandise. These values include the effect of uniformity and reproducibility on the color difference measurements.

Table 21. Instrument Repeatability  
(Variance in Tristimulus Values)

|    |   |       |
|----|---|-------|
| x  | = | 0.014 |
| x' | = | 0.001 |
| y  | = | 0.003 |
| z  | = | 0.001 |

Table 22. Commercially Acceptable Carpet Dyeings  
Color Differences in MacAdam Units

| Nylon Shag<br>#1 | Nylon Shag<br>#2 | Nylon Shag<br>#3 | Polyester<br>High Low<br>Loop | Polyester<br>level loop |
|------------------|------------------|------------------|-------------------------------|-------------------------|
| 4.28             | 6.35             | 3.96             | 2.72                          | 4.47                    |
| 1.06             | 1.11             | 3.06             | 3.61                          | 3.58                    |
| 2.18             | 1.57             | 3.31             | 2.82                          | 4.08                    |
| 3.81             | 5.12             | 2.65             | 2.74                          | 4.94                    |
| 4.39             |                  | 5.49             | 4.00                          | 5.26                    |
| 1.24             |                  | 2.15             | 10.67                         | 3.46                    |
| 0.83             |                  | 3.87             | 6.14                          | 5.66                    |
| 3.06             |                  | 1.26             | 8.50                          | 6.77                    |
| 5.62             |                  | 1.60             | 1.05                          | 2.21                    |
| 3.65             |                  | 1.25             | 4.26                          | 2.25                    |
| 3.31             |                  | 1.57             | 2.87                          | 5.00                    |
| 2.40             |                  |                  | 6.07                          | 3.47                    |
|                  |                  |                  | 3.52                          | 3.37                    |
|                  |                  |                  | 1.97                          | 5.76                    |
|                  |                  |                  | 0.66                          | 2.76                    |
|                  |                  |                  | 3.83                          | 3.23                    |
|                  |                  |                  | 1.19                          | 3.45                    |
|                  |                  |                  |                               | 5.16                    |
|                  |                  |                  |                               | 5.04                    |
|                  |                  |                  |                               | 3.53                    |

## CHAPTER V

### DISCUSSION

#### Pilot Scale Dyeings

##### Disperse Dyes:

Series I. Various problems were encountered in this series. When the carpet sections were entered at 60°C for dyeing light shades, the dyeings turned out to be unlevel. The levelness of the dark shades was acceptable. Therefore it was decided to reduce the entrance temperature to 40°C for the light shades. Another problem encountered was in the dye analysis. In this series the dyebath samples were analysed spectrophotometrically after the addition of 10 ml. of methanol to dissolve the dyes. The results of this analysis often gave negative concentrations for the dyes. Hence the dye analysis procedure was modified. (See Dyebath Analysis and Reconstitution section.) The new analysis procedure required a much longer period of time hence the "shading" procedure, as described in Chapter III was instituted.

Series II. The dyeings in this series incorporated the modifications in entrance temperature, analytical and dyeing procedures. However, after dyeing the dark blue shade at the end of the series, an attempt was

made to dye the light blue shade again before discarding the dyebath. This was unsuccessful as the sample was greenish in color. This indicated that the exhaustion of the yellow dye was not as high as expected. Therefore, the total quantity of dye being used was decreased so that the residual amounts of dye would be smaller. The dark shades were also rearranged so that they used decreasing amounts of Yellow 3 dye. The modified series of shades is given in Table 3 a.

Series III. In this set of dyeings all the shades except the last one turned out as expected. The dark blue shade was slightly greenish. Instead of changing the recipes this greenish-blude shade was added to the series and called turquoise. An additional shade, dark blue, was added to the series. (Table 3 b).

Series IV & V. In both these series, eleven dyeings were made and the light blue was successfully repeated at the end of the series. The modified chemical reconstitution procedure helped to reduce foaming by reducing the total amount of chemicals in the bath. With the modified procedure, a smaller amount of steam was required to heat the dyebath to the dyeing temperature. The dyeings were visually judged to be of good uniformity. The eleventh dyeing in each series, light blue, was observed to have a "dirty" appearance. This may be due to the fact that the residual material in the dyebath at this point, far



exceeded the quantity of dye in the dyebath, and may have been partially adsorbed onto the surface of the carpet, thus competing with the dye and leading to an off-shade dyeing.

Series VI. This series contained only four dyeings, olive, turquoise, dark blue and light blue and showed that a light shade could be successfully dyed after three dark shades. This light blue shade was judged to be of good uniformity and almost indistinguishable in color from the standard fresh bath dyeing. It did not have the dirty appearance encountered in the two previous series.

#### High Temperature Trials

Three dyeings were carried out with the light shades, where the carpet section was entered into the beck with the dyebath at 60°C and 70°C. The first dyeing with the carpet being entered at 60°C, was judged to be of good uniformity. The second dyeing, with the carpet being entered at 70°C was almost as good. To determine whether the uniformity could be improved before going to a higher entrance temperature, Igepal DM 970 was included in the dyebath in addition to Tanapal CAL. However this produced an extremely streaky (See Tables 16 & 17) dyeing so it was assumed that this may be due to an incompatibility between the Tanapal CAL and the Igepal DM 970. No further dyeings were made with the disperse dyes. The

carpet samples dyed with disperse dyes using Tanapal CAL as the retarder, can not truly be compared with the dyeings using Igepal DM 970. But, it should be noted that the use of Tanapal CAL makes it possible to enter carpets into the dyebath at 70°C, even when dyeing light shades.

#### General Observations Regarding the Disperse Dye Series

The disperse dyes chosen were the ones most commonly used for dyeing in the carpet industry. Blue 7 was readily soluble in water while Red 55 was sparingly soluble. Yellow 3 was of intermediate solubility. The affinity of these dyes for nylon was observed to be roughly in the same order as their solubilities. The solubility of the dyes affected the results of the dyebath analysis, since Red 55 was most easily extracted by perchloroethylene, but Blue 7 was difficult to extract. The partitioning effect was found to be temperature dependant, hence a fixed procedure was followed every time for the analysis. At higher temperatures the dyes were more readily soluble in perchloroethylene than in water, but the perchloroethylene - dyebath mixture had to be cooled to 130°F to avoid cracking the bottle in which the hot liquid mixture was shaken. Consequently, when Blue 7 was present in very small amounts, it could not be detected in the perchloroethylene layer, and the exhaustion had to be assumed as 100%.

Errors in the analysis were also present due to the fact that the solution of the three linear simultaneous equations did not give the exact amounts of the dyes present. (See Table 4). The volume of the residual dyebath in the beck was not known exactly, but only estimated, since the volume expansion of the dye beck and the dye liquor at higher temperatures were not taken into account. This volume error was later observed to be of the order of five liters.

The surfactant and leveling agent chosen, Igepal DM 970, was known to have a significant effect on the exhaustion of Yellow 3, but did not seem to effect the exhaustion of the other two dyes. Red 55 was controlled by the presence of the other two dyes and by its lower affinity for the nylon fiber. Blue 7 showed the highest exhaustion levels. This may be one of the reasons for the large variance and color difference values obtained for shades which contain substantial amounts of Yellow 3 and relatively small amounts of Blue 7, for example, Yellow, Orange and Brown. (Table 19).

The variation in the chemicals replenishment procedure among the series, probably had some effect on the reproducibility of the dyeings. Disperse dyes generally contain about 30% to 80% dispersing agent (by weight). The dispersing agent acts as a surfactant. But as its concentration in the dyebath increased, it competed with

the dyes for exhaustion onto the nylon. This may have led to the poor reproducibility of the light blue shade dyed at the end of Series IV and V. The procedure finally selected for replenishing the chemicals assumed that they were completely soluble in water, and the required amounts were calculated by determining the difference in the volume of water present in the beck at the beginning and end of each dyeing. This is not entirely correct since all the water lost is not due to absorption onto the unloaded carpet. Part of the water is lost by evaporation and no chemicals are removed in this process. The results of Table 20 reflect the procedural differences between the standard and experimental series.

The uniformity of the experimental dyeings was in most cases as good as or better than that of the standard dyeings. (See Table 17). This may be due to the leveling action of increasing amounts of dispersing agent left over after each dyeing. In the case of the black shade, where the end-to-end color variation is relatively large compared to other dyeings, (Table 17), the reason for non-uniformity may be that the dyes were not thoroughly mixed when they were added into the beck. The black shade requires about 3% owf of total dye stuff and this large amount of dye is quite difficult to disperse thoroughly with water in the three liter container which was being used for that purpose.

## Acid Dyes

Series I. No effective retarder had been obtained for the acid dyes system. Owing to the turbidity in the Praxitest dyeings with Igepal DM 970 and Gaftex PFB no information was available on the retardation capabilities of these chemicals, with regard to acid dyes. Since Gaftex PFB caused a decrease in exhaustion of the yellow dye, it was assumed that it may decrease the strike rate also. A limited amount of pH control was also used to control the strike rate. The main problem encountered in these dyeings was the composition of the nylon yarns in the carpet. The yarn was made up of deep and regular dyeing fibers, which differ in their amine end group content. Hence it was impossible to get a "solid shade" using acid dyes only, when dyeing light shades like light blue. This set of dyeings was very streaky, so after further tests in the Launder-Ometer, Alkanol ND was selected since it was a better levelling agent.

Series II. In this series, problems were encountered with the red dye chosen. It was not readily soluble in water and settled to the bottom of the dye beck. The pink dyeing was noticeably non-uniform. Therefore Red 151 was substituted by Red 337 which was more soluble in water. But this did not improve the uniformity. It may be possible that Alkanol ND did not have the same leveling action on the red dyes as it did on the yellow and blue

dyes. (The Launder-Ometer trials with Alkanol ND had been done for a light green shade using yellow and blue dyes only). At this point, attempts to dye ten different shades were abandoned and it was decided to dye the same shade five times.

Series III. This series contained five dyeings, all light blue in color. Variation in pH was used to control the strike rate. A major problem in this set of dyeings was the fact that when the dye solution was added into the beck, it did not diffuse quickly throughout the dye liquor. The dye solution had a tendency to remain in one section of the dye liquor and thus become adsorbed in large quantities on that part of the carpet which happened to be nearest to the dyes. This resulted in some non-uniformity (Table 17).

The large color difference between the experimental and standard dyeings (Table 18) was due to an inherent error in the spectrophotometric analysis. Consecutive analysis of the residual dyebaths during the series showed increasing residual amounts of Yellow 135, even beyond the amounts actually added. Measurements of the dyed carpet on the color-eye showed that the experimental samples were much bluer than the standard sample, indicating an addition of excess amounts of Blue 25 during the dyeings. No reasonable explanation could be found for this strange phenomenon. Hughes et.al. (29) have mentioned the possi-

bility of complex formation between acid dyes and non-ionic or cationic agents, which changed the  $\lambda_{\max}$  and absorption spectra. However, in their case the shift in the maximum absorbance peak was of the order of 50 nm. only.

The color difference values shown in Tables 5 - 16 and the variance in these values, shown in Table 17, indicate that in most of the dyeings with disperse dyes, the uniformity of the sample dyeing was as good as or better than that of the standard dyeing. Though the dyeings with acid dyes were generally non uniform, at least one dyeing was comparable in uniformity to that of the standard. There were no standards for numerical comparison in the case of the high temperature dyeing with disperse dyes. These were evaluated visually and the Pink and Orange shades were found to be of good uniformity.

The reproducibility of the dyeings (Table 18) was comparable to that accepted in commercial carpet dyeing. However, the reproducibility between the two experimental series IV and V was much better than between the experimental and standard series. The large color differences observed for the Brown and Turquoise shades, may have resulted from an incorrect choice of dye shade sequence.

The poor uniformity and reproducibility of the acid dyes series could be due to the difficulties encountered in controlling the dye strike rate.

### Economics of Dyebath Recycle

Tables 23 and 24 show the comparative chemical costs between currently used industrial beck dyeing techqniques and the recycled dyebath technique. The acid dyes series of five dyeings shows an overall savings for the series of about 40% in chemicals, dyes and water expenses combined. The deisperse dyes series of ten dyes has a comparative savings of 19% in expenses. The chemical and dye prices used in evaluating dyeing costs are shown in Appendix A, and were obtained directly from the manufacturers quoted. The figures in Table 23 show that the savings in dye costs alone are negligible but substantial savings can be realized in chemical and water costs. Table 25 shows comparative costs for dyeing industrial sized loads by the conventional and recycled bath techniques. Table 28 shows the relative cost savings for each individual dyeing and the overall savings for the dyeings taken as a series. Tables 26 and 27 shows individual and cummulative costs respectively for experimental and standard series. The figures in Table 28 were obtained from Tables 26 and 27. Table 26 shows the change in costs as each additional dyeing is carried out in the series. Table 28 was formulated as an attempt to determine the optimum number of dyeings in a series to obtain maximum savings. Table 28 shows that the savings increase to about 44% for the first five dyeings in the series, then drop and remain constant at



about 19% for the next five dyeings. The first five dyeings are light shades and the next five are dark shades. Hence it may be deduced that if a series consists of light shades only, the savings will be maximum for a series of five dyeings. The increase in savings between the fourth and fifth dyeing is only 2%, so any savings obtained by dyeing a sixth light shade will probably be insignificant. The drop in savings when the series goes from light to dark shades is due to the increase in dye costs. However, as the series continues, increased dye costs are offset by decreasing chemical costs, which together average out to give an overall cost savings of 19%.

It can be seen from Table 27 that although the reduction in dye usage is not very great, the reduction in water and auxiliary chemicals used is almost 70%.

Due to the sequence followed for the dyeings in this set of experiments, the results seem to indicate that greater savings can be attained for light shades than for dark shades. Simple theory suggests that the reverse case should be true. Dye costs make up a major portion of the dyeing expenses. In dyeing dark shades, a greater quantity of dyes should be left over in the residual liquor for reuse. Hence savings should be greater.

The fact is that the major portion of the savings in dye costs would be realized in the second dyeing. Further increases in savings get smaller for subsequent

dyeings. For dark shades chemical costs are a small fraction of the dyeing expenses. Since a major portion of the savings come from reduced water and chemical usage the percentage savings seem to be greater for light shades than for dark shades.

In the current industrial methods, fresh water has to be heated up from room temperature to the dyeing temperature for each batch of goods. This requires a considerable amount of heat energy. In the recycled bath technique, the next batch of goods can be loaded into the beck when the spent dye liquor has cooled to 70°C. Thus the energy required to heat the water from room temperature to 70°C is saved, and so is the time that would be spent in heating the water. Hence the potential overall savings can be far greater than those realized from reduced chemical costs alone.

Table 23. Cost Analysis for Disperse Dye Series  
Calculated from a series of ten dyeings  
(Figures for Expt. Series are for Series V)

| Constituent<br>in dye bath                    | Total Amount Used |              | Unit<br>Price                | Cost       |            |
|---|-------------------|--------------|------------------------------|------------|------------|
|   | Std.              | Expt.        |                              | Std.       | Expt.      |
| Disp. Yellow 3                                | .198480 lb.       | .186608 lb.  | \$2.29/lb.                   | \$ .454519 | \$ .427332 |
| Disp. Red 55                                  | .168899 lb.       | .159736 lb.  | \$7.25/lb.                   | 1.22452    | 1.15809    |
| Disp. Blue 7                                  | .229317 lb.       | .239780 lb.  | \$7.50/lb.                   | 1.71988    | 1.79835    |
| Plexene D                                     | .288656 lb.       | .072467 lb.  | \$0.455/lb.                  | .131338    | .032972    |
| Igepal DM 970                                 | 1.13280 lb.       | .292952 lb.  | \$0.70/lb.                   | .792960    | .205066    |
| TriSodium Phosphate                           | 1.13280 lb.       | .286344 lb.  | \$0.188/lb.                  | .212966    | .053833    |
| Water   | 208.190 gal.      | 53.1044 gal. | \$0.4414/10 <sup>3</sup> gal | .091895    | .023440    |
| Wt. of Carpet Dyed                            | 57.8524 lb.       | 57.5220 lb.  | -                            | -          | -          |
| Total   |                   |              | 4.6181                       | 3.6990     |            |
| Total Cost of Materials per lb of carpet dyed |                   |              |                              |            |            |
| Total Cost of Materials per sq. yd. of carpet |                   |              | \$0.0798                     | \$0.0643   |            |
|   |                   |              | \$0.0997                     | \$0.0804   |            |

Reduction in water usage per lb. of carpet dyed is 2.68 gals.

$$\frac{\text{Cost of Materials for Expt. Series}}{\text{Cost of Materials for Std. Series}} = \frac{0.81}{1.00}$$

Savings in dye costs \$ .07/1000 lbs. carpet  
Savings in chemicals cost \$14.58/1000 lbs. carpet  
Savings in water costs \$1.18/1000 lbs. carpet  
These savings are calculated for the whole series.

Table 24. Cost Analysis for Acid Dyes Series  
Calculated from a series of ten dyeings

| Constituent<br>in dye bath   | Total Amount Used |             | Unit<br>Price                | Cost       |            |
|--|-------------------|-------------|------------------------------|------------|------------|
|  | Std.              | Expt.       |                              | Std.       | Expt.      |
| Acid Yellow 135  | .002313 lb.       | .000793 lb  | \$ 4.25/lb                   | \$0.009830 | \$0.003370 |
| Acid Red 337   | .001432 lb        | .000419 lb  | \$ 5.70/lb                   | .008162    | .002388    |
| Acid Blue 25   | .023568 lb        | .022313 lb  | \$10.00/lb                   | .235680    | .223130    |
| MonoSodium Phosphate   | .882159 lb.       | .352863 lb. | \$0.179/lb.                  | .157906    | .063162    |
| TriSodium Phosphate  | .029405 lb.       | .015793 lb  | \$0.188/lb                   | .005528    | .002969    |
| Plexene D  | .117841 lb.       | .048238 lb. | \$0.455/lb                   | .053618    | .021984    |
| Alkanol ND   | 1.02976 lb.       | .539668 lb  | \$0.585/lb                   | .602398    | .315694    |
| Acetic Acid  | -                 | .160793 lb  | \$0.07/lb                    | -          | .011256    |
| Water  | 105.680 gal.      | 43.3239 gal | \$0.4414/10 <sup>3</sup> gal | .046647    | .019125    |
| Wt. of Carpet dyed   | 29.4053 lb        | 28.9648 lb  | -                            | -          | -          |
| Total  |                   |             |                              | \$1.1198   | \$0.6631   |
| Total Cost of Materials per lb. of carpet dyed   |                   |             |                              | \$0.0381   | \$0.0229   |
| Total Cost of Materials per sq. yd. of carpet  |                   |             |                              | \$0.0476   | \$0.0286   |
| Reduction in water usage per lb of carpet dyed is 2.10 gals.   |                   |             |                              |            |            |
| $\frac{\text{Cost of Materials for Expt. Series}}{\text{Cost of Materials for Std. Series}} = \frac{0.60}{1.00}$ |                   |             |                              |            |            |

Table 25. Comparative Savings for Industrial Sized Loads Disperse Dyes - Experimental and Standard Series

| Shade       | Position in Dyeing Sequence | Cost for 800 lbs carpet Conventional | Recycled bath | Savings |
|-------------|-----------------------------|--------------------------------------|---------------|---------|
| Light Blue  | 1                           | \$ 24.96                             | \$ 24.96      | -       |
| Light Green | 2                           | 23.28                                | 8.24          | \$15.04 |
| Yellow      | 3                           | 24.40                                | 12.48         | 11.92   |
| Orange      | 4                           | 31.12                                | 13.52         | 17.60   |
| Pink        | 5                           | 28.72                                | 14.40         | 14.32   |
| Black       | 6                           | 213.68                               | 198.56        | 15.12   |
| Brown       | 7                           | 80.00                                | 54.80         | 25.20   |
| Olive       | 8                           | 57.52                                | 39.76         | 17.76   |
| Turquoise   | 9                           | 71.84                                | 57.36         | 14.48   |
| Dark Blue   | 10                          | 127.76                               | 88.56         | 39.20   |
| Light Blue  | 11                          | 24.96                                | 4.08          | 20.88   |

Cost figures are taken from Table 27.

Table 26. Comparative Costs for Experimental  
and Standard Series - Disperse Dyes

Disperse Dyes Series V (Expt.)

| Dyeing<br>No. | Weights of Chemicals & Water |            |           |               |              |           |               | Total<br>Cost<br>\$ | Cost per<br>lb. of<br>\$ carpet |
|---------------|------------------------------|------------|-----------|---------------|--------------|-----------|---------------|---------------------|---------------------------------|
|               | Y-3<br>gm                    | R-55<br>gm | B-7<br>gm | Plexene<br>gm | DM 970<br>gm | TSP<br>gm | Water<br>lit. |                     |                                 |
| 1             | .16                          | .16        | 3.24      | 13.5          | 54.0         | 54.0      | 81.0          | 0.185333            | 0.031164                        |
| 2             | 3.88                         | 0          | 1.08      | 2.0           | 8.0          | 8.0       | 5.0           | 0.055644            | .010332                         |
| 3             | 13.19                        | 0          | 0.08      | 2.0           | 10.0         | 10.0      | 20.0          | 0.091736            | .015598                         |
| 4             | 7.25                         | 2.64       | 0.06      | 2.0           | 8.0          | 8.0       | 10.0          | 0.098531            | .016945                         |
| 5             | 0.3                          | 4.9        | 0         | 2.4           | 10.0         | 10.0      | 13.0          | 0.103234            | .017957                         |
| 6             | 23.4                         | 46.74      | 32.89     | 2.0           | 8.0          | 8.0       | 14.0          | 1.427039            | .248228                         |
| 7             | 23.89                        | 11.44      | 3.31      | 2.0           | 8.0          | 8.0       | 7.0           | 0.376332            | .068479                         |
| 8             | 12.17                        | 5.51       | 6.5       | 2.0           | 8.0          | 8.0       | 18.0          | 0.276495            | .049711                         |
| 9             | 0.5                          | 0.92       | 23.24     | 3.0           | 15.0         | 12.0      | 23.0          | 0.434910            | .071673                         |
| 10            | 0                            | 0.21       | 38.46     | 2.0           | 4.0          | 4.0       | 10.0          | 0.649701            | .110682                         |
| 11            | 0                            | 0          | 1.05      | 1.0           | 4.0          | 4.0       | 10.0          | 0.027372            | .005082                         |

Table 26. Comparative Costs for Experimental  
and Standard Series - Disperse Dyes  
(Continued)

Disperse Dyes Series VII (Std.)

Weights of Chemical & Water

| Dyeing<br>No. | Y-3<br>gm | R-55<br>gm | B-7<br>gm | Plexene<br>gm | DM 970<br>gm | TSP<br>gm | Water<br>lit. | Carpet<br>lb. | Total<br>Cost<br>\$ | Cost per<br>lb. of<br>\$ carpet |
|---------------|-----------|------------|-----------|---------------|--------------|-----------|---------------|---------------|---------------------|---------------------------------|
| 1             | .14       | .17        | 3.34      | 13.90         | 55.70        | 55.70     | 84.0          | 6.1344        | .191219             | .031172                         |
| 2             | 4.31      | .03        | 1.35      | 13.45         | 53.78        | 53.78     | 81.0          | 5.9361        | .172587             | .029074                         |
| 3             | 13.35     | .01        | 0.13      | 13.35         | 53.40        | 53.4      | 80.0          | 5.8810        | .179593             | .030538                         |
| 4             | 8.01      | 2.67       | 0.13      | 13.28         | 53.12        | 53.12     | 80.0          | 5.8811        | .228835             | .038910                         |
| 5             | 0.54      | 5.12       | 0.01      | 13.48         | 53.90        | 53.9      | 81.0          | 5.9361        | .212982             | .035879                         |
| 6             | 21.96     | 43.92      | 30.74     | 12.12         | 48.47        | 48.47     | 73.0          | 5.3745        | 1.435369            | .267070                         |
| 7             | 26.7      | 16.02      | 4.27      | 13.35         | 53.4         | 53.4      | 80.0          | 5.8810        | .588146             | .100008                         |
| 8             | 13.88     | 6.94       | 6.94      | 13.35         | 53.4         | 53.4      | 80.0          | 5.8811        | .422591             | .071856                         |
| 9             | 0.99      | 1.34       | 22.7      | 13.28         | 53.12        | 53.12     | 80.0          | 5.8810        | .528201             | .089815                         |
| 10            | 0.23      | 0.46       | 34.5      | 11.5          | 46.0         | 46.0      | 69.0          | 5.0661        | .808808             | .159651                         |

In the Std. series each dyeing was done in a fresh dye-bath.

In the Expt. series, after the first one, each subsequent dyeing was done in a reconstituted bath.







Table 28. Relative and Overall Savings - Disperse Dyes Series

| Dyeing No. | Shade       | *Relative Savings | Overall Savings † |
|------------|-------------|-------------------|-------------------|
| 1          | Light Blue  | -                 | -                 |
| 2          | Light Green | 64%               | 29%               |
| 3          | Yellow      | 49%               | 36%               |
| 4          | Orange      | 56%               | 42%               |
| 5          | Pink        | 50%               | 44%               |
| 6          | Black       | 7%                | 18%               |
| 7          | Brown       | 31%               | 20%               |
| 8          | Olive       | 31%               | 22%               |
| 9          | Turquoise   | 20%               | 19%               |
| 10         | Dark Blue   | 30%               | 20%               |
| 11         | Light Blue  | 83%               | 21%               |

\* Relative Savings =  $\frac{\text{Cost of Std.} - \text{Cost of Expt.}}{\text{Dyeing Cost of Std. Dyeing}} \times 100$   
for each dyeing

These figures are calculated from the cost analysis shown in Table 26.

† Overall Savings =  $\frac{\text{Cost of n Std.} - \text{Cost of n Expt.}}{\frac{\text{Dyeings Cost of n Std. Dyeings}}{\text{Dyeings}}} \times 100$   
for n dyeing  
taken collectively  
Where n = 1,2,3,...11.

These figures are calculated from the cost analysis shown in Table 27.

Hence, the overall results indicate that beck dyeing in a reconstituted dyebath is technically and economically feasible. Though improvement of the reproducibility is desireable, this can be achieved by better analytical and dyebath reconstitution techniques. The savings possible in time, energy and chemical costs would improve the profitability of most beck dyeing operations and the limited wastewater discharged would reduce the necessity of requiring on-site waste treatment facilities.

## CHAPTER VI

### CONCLUSIONS

Based on the foregoing results, the following conclusions can be drawn regarding the recycled bath dyeing technique.

Dyeings carried out in a reconstituted dyebath are comparable in uniformity to those carried out in fresh dyebaths. (Tables 5-17).

The variance in color difference values, between dyeings in Series IV and V (of the disperse dyes) is small for most shades. (Table 19). Thus, in accordance with industrially acceptable standards (Table 22) the reconstituted bath dyeings show good reproducibility compared to the standard dyeings.

The recycled dyebath technique is more economical in its use of water and chemicals than the current industrial techniques. (Tables 23, 24, 26, 27). It must be noted here that the figures obtained in these tables relate to this particular set of dyeings only. In general they will be dependent on the dye recipes and dyeing sequence actually used. When the additional savings in time and energy for heating the dyebath are taken into account, the total savings will be far greater.

The results of Series VI indicate that it is possible

to dye a light shade after a small number of dark shades, without discarding the dye liquor.

The use of Tanapal CAL shows promise in facilitating the entry of carpets into the hot dyebath at temperatures around 60°C.

This technique can be used on currently installed becks with a few minor modifications to the equipment. One of them would be a device to measure the volume of the residual dye liquor accurately. All the chemicals used are readily available to the textile industry. In addition to the economic advantages offered by this technique, this process is desirable from the environmental point of view. The chemicals that are reused, would otherwise have been discarded to pollute the environment. The reduction in water usage reduces the burden on natural sources of supply. The quantities of chemicals discarded in this process are small enough to be easily handled by existing waste treatment plants.

## CHAPTER VII

### RECOMMENDATIONS

Significant improvements or modifications in the analytical techniques used would be required to reduce errors and improve the reproducibility of the dyeings.

The possibility of entering the carpet into the spent bath at temperatures above 60°C would increase the savings in energy costs. The trials in this work showed good promise and further work in this area is recommended.

Further study with larger samples is recommended since the samples used were not of sufficient width to give a good indication of side-to-side color variation.

Further work in developing dye-retarder systems is also important. A two phase system with the dye carrying phase becoming soluble in water only at higher temperatures would be desirable. A retarder whose action on the dyes is temperature dependent would probably be ideal.

## APPENDICES

## APPENDIX A

Price List Used in Computing Dyeing Costs.  
 Price Obtained From the Manufacturers Listed.  
 Prices as of June 1976

| <u>Item</u>   | <u>Supplied<br/>By</u>    | <u>Unit Price</u>  |
|---|---------------------------|--|
| Acetamine Yellow CG (Disp. Yell. 3)   | Du Pont                   | \$2.29 / lb.   |
| Celanthrene Fast Blue 2G (Disp. Blue 7)   | Du Pont                   | \$7.50 / lb.   |
| Latyl Cerise YLN (Disp. Red 55)   | Du Pont                   | \$7.25 / lb.   |
| Merpacyl Red G (Acid Red 337)   | Du Pont                   | \$5.70 / lb.   |
| Nylomine Yellow A-G (Acid Yell. 135)  | I.C.I.                    | \$4.25 / lb.   |
| Nylomine Blue A-G (Acid Blue 25)  | I.C.I.                    | \$10.00 / lb.  |
| Alkanol ND  | Du Pont                   | \$0.585 / lb.  |
| Mono Sodium Phosphate   | Farm<br>Ind.              | \$0.179 / lb.  |
| Trisodium Phosphate   | Farm<br>Ind.              | \$0.188 / lb.  |
| Plexene D   | Tanatex                   | \$0.455 / lb.  |
| Tanapal XNC   | Tanatex                   | \$0.445 / lb.  |
| Nofoam J  | Tanatex                   | \$0.485 / lb.  |
| Igepal DM 970   | G.A.F.                    | \$0.70 / lb.   |
| Acetic Acid.  | Farm<br>Ind.              | \$0.07 / lb.   |
| Water   | Ga. Bureau<br>Water Supp. | \$0.44 /10 <sup>3</sup> gal.<br>or<br>\$0.12 /10 <sup>3</sup> lit. |
| Antisil Blue Green (Disp. Blue 7)<br>(Manufacture of Disp. Blue 7 has been discontinued<br>by Du Pont). | Sandoz                    | \$13.40 / lb.  |



## APPENDIX B

### Estimation of Maximum Exhaustion of Alkanol ND

Two blank dyebaths were prepared containing all the auxilliary chemicals, but no dyes. In addition, one of the dyebaths had no Alkanol ND in it. Samples of the two dyebaths were scanned on a Beckman Model DB-G Grating Spectrophotometer to detect a characteristic peak for Alkanol ND that would be suitable for measuring its concentration in the dyebath. The solution containing no Alkanol ND was used as the reference solution in this measurement. Alkanol ND was found to have a characteristic absorbance at 238 nm in the UV region of the spectrum. The absorbance of the solution at 238 nm was noted. Carpet samples were then introduced into each solution and the blank dyebaths were put through a typical dye cycle in the Launder-Ometer. After the dye cycle, the absorbance was once again measured and the difference in absorbance used to calculate the percentage exhaustion of Alkanol ND.

### Determination of the Maximum Exhaustion of Alkanol ND

#### Composition of the blank dyebaths.

Plexene D 0.25% owf.

Trisodium Phosphate 0.5% owf

Mono Sodium Phosphate 2.0% owf.

Acetic Acid to adjust pH at 6.1

Alkanol ND 2.5% owf. - in the sample solution only.

Liquor ratio 30:1. Total Volume 450 ml.

2 ml of dyebath with Alkanol ND was diluted to 100 ml with water for spectrophotometric measurements.

Absorbance at  $\lambda = 238$  nm before dyeing = 0.58

Absorbance at  $\lambda = 238$  nm after dyeing = 0.325

$$\begin{aligned}\therefore \% \text{ Exhaustion} &= \frac{0.58 - 0.325}{0.58} \times 100 \\ &= 43.96\%\end{aligned}$$

An exhaustion of 40% was assumed when reconstituting the dyebath.

## APPENDIX C

The FMC - II Color Difference Formula used for calculating color difference values.

$$\Delta E = [ (\Delta C)^2 + (\Delta L)^2 ]^{1/2}$$

$$\Delta C = K_1 \Delta C_1 \quad \Delta L = K_2 \Delta L_2$$

$$\Delta C_1 = \left[ \left[ \frac{\Delta C_{rg}}{a} \right]^2 + \left[ \frac{\Delta C_{yb}}{b} \right]^2 \right]^{1/2}$$

$$\Delta L_1 = \frac{P\Delta P + Q\Delta Q}{(P^2 + Q^2)^{1/2}}$$

$$\Delta C_{rg} = \frac{Q\Delta P - P\Delta Q}{(P^2 + Q^2)^{1/2}}$$

$$\Delta C_{yg} = \frac{S\Delta L_1}{(P^2 + Q^2)^{1/2}} - \Delta S$$

$$\Delta L_2 = \frac{0.279 \Delta L_1}{a}$$

$$K_1 = 0.55669 + 0.049434Y - 0.82575 \times 10^{-3} Y^2 \\ + 0.79172 \times 10^{-5} Y^3 - 0.30087 \times 10^{-7} Y^4$$

$$K_2 = 0.17548 + 0.027556Y - 0.57262 \times 10^{-3} Y^2 \\ + 0.63893 \times 10^{-5} Y^3 - 0.26731 \times 10^{-7} Y^4$$

$$a^2 = \frac{17.3 \times 10^{-6} (P^2 + Q^2)}{1 + \frac{2.73 P^2 Q^2}{P^4 + Q^4}}$$

$$b^2 = 3.098 \times 10^{-4} (S^2 + 0.2015 Y^2)$$

$$P = 0,724 X + 0.382 Y - 0.098 Z$$

$$Q = -0,48 X + 1,37 Y + 0.1276 Z$$

$$S = 0.686 Z$$

$$\Delta \Rightarrow \text{Sample} - \text{Standard}$$

# APPENDIX D

## Percent Dye Exhaustion Analyzed for Each Shade Disperse Dyes Series

| Shade       | Series III<br>% Dye |     |     | Series IV<br>% Dye |    |     | Series V<br>% Dye |    |     | Series VI<br>% Dye |    |    | Series VII Std.<br>% Dye |     |     |
|-------------|---------------------|-----|-----|--------------------|----|-----|-------------------|----|-----|--------------------|----|----|--------------------------|-----|-----|
|             | Y                   | R   | B   | Y                  | R  | B   | Y                 | R  | B   | Y                  | R  | B  | Y                        | R   | B   |
| Light Blue  | 43                  | 69  | 87  | 64                 | 81 | 95  | 79                | 81 | 96  | -                  | -  | -  | -                        | -   | -   |
| Light Green | 94                  | 100 | 97  | 91                 | *  | 47  | 95                | 66 | 96  | -                  | -  | -  | 97                       | *   | 40  |
| Yellow      | 98                  | 100 | 100 | 92                 | *  | *   | +                 | +  | +   | -                  | -  | -  | 95                       | 100 | 100 |
| Orange      | 94                  | 96  | 100 | 94                 | 93 | *   | 97                | 97 | 98  | -                  | -  | -  | 94                       | 95  | 77  |
| Pink        | 88                  | 91  | 100 | 68                 | 93 | *   | 83                | 95 | *   | -                  | -  | -  | 96                       | 97  | 100 |
| Black       | 97                  | 95  | 98  | 95                 | 92 | 98  | 95                | 92 | 98  | -                  | -  | -  | 96                       | 95  | 95  |
| Brown       | 94                  | 94  | 100 | 95                 | 92 | 100 | 96                | 93 | 100 | -                  | -  | -  | 96                       | 96  | 100 |
| Olive       | 83                  | 86  | 100 | 93                 | 87 | 83  | 96                | 93 | 97  | 96                 | 97 | 99 | -                        | -   | -   |
| Turquoise   | -                   | -   | -   | 71                 | 81 | 94  | 75                | 77 | 94  | 93                 | 90 | 96 | 94                       | 92  | 97  |
| Dark Blue   | -                   | -   | -   | 70                 | 67 | 95  | 58                | 66 | 95  | 80                 | 71 | 96 | 74                       | 85  | 97  |
| Light Blue  | -                   | -   | -   | 15                 | 0  | 82  | 0                 | 22 | 83  | 38                 | 37 | 88 | -                        | -   | -   |

N.B. 100% exhaustion indicates residual amount of dye was too small to detect by this analytical procedure.

\* indicates that analytical results show greater quantity of dye present than was added in the dyeing.

- indicates dyeing not carried out, or not of proper shade.

+ indicates error during analysis.

Light Blue (Series IV) & Olive (Series VI) were used as Standards.

## APPENDIX E

## Absorbance Spectrum of Disperse Yellow 3 (conc. 0.01 g/l)

| <u>Wavelength (nm)</u> | <u>Absorbance</u> | <u>Wavelength (nm)</u> | <u>Absorbance</u> |
|------------------------|-------------------|------------------------|-------------------|
| 320                    | 0.22              | 510                    | 0.02              |
| 340                    | 0.26              | 520                    | 0.02              |
| 350                    | 0.27              | 540                    | 0.02              |
| 360                    | 0.26              | 560                    | 0.02              |
| 380                    | 0.23              | 580                    | 0.01              |
| 400                    | 0.18              | 600                    | 0.01              |
| 420                    | 0.15              | 620                    | 0.01              |
| 440                    | 0.12              | 640                    | 0.01              |
| 460                    | 0.08              | 660                    | 0.01              |
| 480                    | 0.04              | 680                    | 0.01              |
| 500                    | 0.03              | 700                    | 0.01              |

## Absorbance Spectrum of Disperse Red 55 (conc. 0.058 g/l)

| <u>Wavelength (nm)</u> | <u>Absorbance</u> | <u>Wavelength (nm)</u> | <u>Absorbance</u> |
|------------------------|-------------------|------------------------|-------------------|
| 320                    | 0.62              | 540                    | 0.37              |
| 340                    | 0.38              | 545                    | 0.37              |
| 360                    | 0.27              | 550                    | 0.37              |
| 380                    | 0.22              | 560                    | 0.33              |
| 400                    | 0.19              | 580                    | 0.27              |
| 420                    | 0.18              | 600                    | 0.24              |
| 440                    | 0.19              | 620                    | 0.18              |
| 460                    | 0.22              | 640                    | 0.14              |
| 480                    | 0.27              | 660                    | 0.12              |
| 500                    | 0.32              | 680                    | 0.11              |
| 520                    | 0.36              | 700                    | 0.09              |

## Absorbance Spectrum of Disperse Blue 7 (conc. 0.045 g/l)

| <u>Wavelength (nm)</u> | <u>Absorbance</u> | <u>Wavelength (nm)</u> | <u>Absorbance</u> |
|------------------------|-------------------|------------------------|-------------------|
| 320                    | 0.72              | 540                    | 0.28              |
| 340                    | 0.36              | 560                    | 0.37              |
| 360                    | 0.29              | 580                    | 0.43              |
| 380                    | 0.22              | 600                    | 0.45              |
| 400                    | 0.20              | 605                    | 0.46              |
| 420                    | 0.16              | 610                    | 0.45              |
| 440                    | 0.14              | 620                    | 0.44              |
| 460                    | 0.15              | 640                    | 0.40              |
| 480                    | 0.15              | 660                    | 0.36              |
| 500                    | 0.16              | 680                    | 0.30              |
| 520                    | 0.21              | 700                    | 0.23              |



## Absorbance Spectrum of Acid Yellow 135 (conc. 0.03 g/l)

| <u>Wavelength (nm)</u> | <u>Absorbance</u> | <u>Wavelength (nm)</u> | <u>Absorbance</u> |
|------------------------|-------------------|------------------------|-------------------|
| 320                    | 0.41              | 510                    | 0.01              |
| 340                    | 0.62              | 520                    | 0.0               |
| 350                    | 0.67              | 540                    | 0.0               |
| 360                    | 0.62              | 560                    | 0.0               |
| 380                    | 0.46              | 580                    | 0.0               |
| 400                    | 0.38              | 600                    | 0.0               |
| 420                    | 0.32              | 620                    | 0.0               |
| 440                    | 0.26              | 640                    | 0.0               |
| 460                    | 0.16              | 660                    | 0.0               |
| 480                    | 0.07              | 680                    | 0.0               |
| 500                    | 0.03              | 700                    | 0.0               |

## Absorbance Spectrum of Acid Red 337 (conc. 0.029 g/l)

| <u>Wavelength (nm)</u> | <u>Absorbance</u> | <u>Wavelength (nm)</u> | <u>Absorbance</u> |
|------------------------|-------------------|------------------------|-------------------|
| 340                    | 0.16              | 500                    | 0.42              |
| 350                    | 0.11              | 520                    | 0.36              |
| 360                    | 0.10              | 540                    | 0.21              |
| 380                    | 0.10              | 560                    | 0.07              |
| 400                    | 0.11              | 580                    | 0.02              |
| 420                    | 0.14              | 600                    | 0.01              |
| 440                    | 0.19              | 620                    | 0.0               |
| 460                    | 0.28              | 640                    | 0.0               |
| 480                    | 0.39              | 660                    | 0.0               |
| 490                    | 0.41              | 680                    | 0.0               |
| 495                    | 0.43              | 700                    | 0.0               |

## Absorbance Spectrum of Acid Red 151 (conc. 0.03 g/l)

| <u>Wavelength (nm)</u> | <u>Absorbance</u> | <u>Wavelength (nm)</u> | <u>Absorbance</u> |
|------------------------|-------------------|------------------------|-------------------|
| 320                    | 0.25              | 510                    | 0.86              |
| 340                    | 0.34              | 520                    | 0.83              |
| 350                    | 0.38              | 540                    | 0.67              |
| 360                    | 0.37              | 560                    | 0.42              |
| 380                    | 0.32              | 580                    | 0.18              |
| 400                    | 0.32              | 600                    | 0.08              |
| 420                    | 0.32              | 620                    | 0.04              |
| 440                    | 0.32              | 640                    | 0.03              |
| 460                    | 0.40              | 660                    | 0.03              |
| 480                    | 0.60              | 680                    | 0.02              |
| 500                    | 0.81              | 700                    | 0.02              |

## Absorbance Spectrum of Acid Blue 25 (conc. 0.01 g/l)

| <u>Wavelength (nm)</u> | <u>Absorbance</u> | <u>Wavelength (nm)</u> | <u>Absorbance</u> |
|------------------------|-------------------|------------------------|-------------------|
| 320                    | 0.12              | 540                    | 0.16              |
| 340                    | 0.10              | 560                    | 0.21              |
| 360                    | 0.09              | 580                    | 0.26              |
| 380                    | 0.09              | 600                    | 0.29              |
| 400                    | 0.07              | 605                    | 0.295             |
| 420                    | 0.05              | 610                    | 0.29              |
| 440                    | 0.03              | 620                    | 0.28              |
| 460                    | 0.03              | 640                    | 0.27              |
| 480                    | 0.04              | 660                    | 0.18              |
| 500                    | 0.07              | 680                    | 0.09              |
| 520                    | 0.11              | 700                    | 0.04              |

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