

ALKYLATED AND HYDROGENATED NAPHTHALENE AND BENZENE DERIVATIVES AS  
POLYESTER DYE CARRIERS

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Travis Watts Honeycutt

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Approved:

[Redacted signature]

Chairman

[Redacted signature]

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Date approved by Chairman Oct 22, 1968

## DEDICATION

To my wife, Irene, and  
my children, Tom and Leah

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## SUMMARY

Those substances commonly referred to as polyester dye carriers are products which accelerate the rate of disperse dye uptake by polyester fibers, and are primarily used when dyeing at atmospheric pressure.

Compounds of varied chemical types have been employed as dye carriers for polyester fibers. These include: acids, esters, halides, amines, phenols, ketones, ethers, and straight chain hydrocarbons. Systematically only the aromatic derivatives of the aforementioned compounds show significant dye accelerant activity. Weight for weight, the aromatic hydrocarbon substances tend to give the highest rate of dyeing and equilibrium sorption when compared to the other types of carriers.

Two alkyl aryl compounds, methylnaphthalene (a mixture of alpha and beta isomers) and 1,2,3,4-tetrahydronaphthalene were examined as a part of a homologous series and were found to have potential as commercially viable polyester dye carriers based on their dye rate accelerations and equilibrium sorptions. Both methylnaphthalene and 1,2,3,4-tetrahydronaphthalene are liquids at ambient temperatures which offers advantages over solid products, such as biphenyl.

Polyethylene terephthalate and poly(1,4-dimethylol)cyclohexyl terephthalate fibers were employed as experimental substrates. The fibers were dyed with a standard commercial sample of C. I. Disperse Blue 60 under practical conditions.

## CHAPTER I

### INTRODUCTION

#### Polyester Fiber

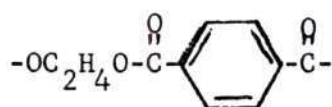
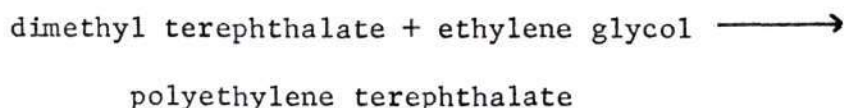
Polyester fibers are fibrous materials produced from crystalline reaction products of dibasic acids and bifunctional alcohols. Currently there are two general types of polyester fibers being marketed. One is a reaction product of ethylene glycol and terephthalic acid; the other is produced from 1,4 dimethylolcyclohexane and terephthalic acid. Typical of the polyethylene terephthalate type is duPont's Dacron 54. Tennessee Eastman Company's Kodel II is the only polyester now being marketed in the United States that is produced from terephthalic acid and 1,4 dimethylolcyclohexane.

The polyester fiber of the polyethylene terephthalate type was first spun as Fiber V in the United States by the E. I. duPont de Nemours and Company, Inc. in 1953 at its plant in Kinston, North Carolina (1). Dr. W. H. Carothers published work on the synthesis of fibrous polyester materials as early as 1939, but the fibers suffered mainly from low melting points (2).

Dickson and Whinfield (3) developed a polyester fiber using aromatic dicarboxylic acids which had a higher melting point than those of Carothers and led to the development of Terylene, Imperial Chemical Industries' registered trademark for polyethylene terephthalate fiber in the United Kingdom.

In 1946 duPont acquired the U.S.A. patent rights to polyethylene terephthalate and began producing Dacron in 1953.

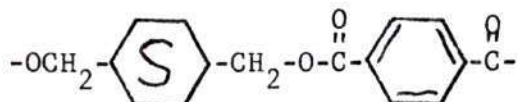
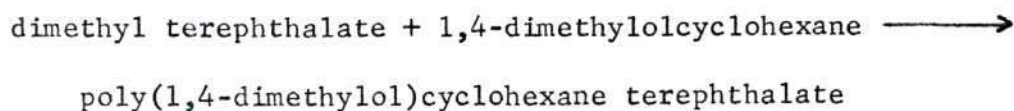
Polyethylene terephthalate fiber is synthesized by reacting dimethyl terephthalate and ethylene glycol via the ester interchange route to produce polyethylene terephthalate as follows:



(repeating unit of polyethylene terephthalate)

Kodel II polyester fiber was first produced by Tennessee Eastman Company in the U.S.A. about 1956 (4). As would be forecasted by examining the molecular constituents of the fiber, this polyester fiber is less dense than the polyethylene terephthalate type. Kodel II has a specific gravity of 1.22 as compared to 1.38 for the Dacron 54 type.

Poly(1,4-dimethylol)cyclohexane terephthalate fibers are synthesized by the following route:



(repeating unit of poly(1,4-dimethylol)cyclohexane terephthalate)

#### Disperse Dyes

Disperse dyes are more aptly called nonionic dyes. Their inability



to ionize renders them only slightly soluble in aqueous media from which most dyeings are made. Although this class of dyes is only very slightly soluble, this solubility is said to be very significant (5). Before these dyes can be applied to any fiber from an aqueous media, they must be ground very finely to give a stable water dispersion. Thus, the evolution of the term "dispersed" dyes. Vickerstaff and Waters (6) when studying dye crystal particle size, observed that the dye rate could be increased considerably by reducing the particle size by grinding.

Following the introduction of secondary cellulose acetate fibers, the dispersed dyes were first introduced in the 1920's for dyeing this material, the first practical hydrophobic man-made fiber. Until the introduction of the cellulose acetate fibers, the dyers and finishers had experience only with hydrophilic natural fibers such as silk, cotton, ramie, and wool. None of the existing dyestuffs could be satisfactorily applied to cellulose acetate using existing equipment. Therefore, it became necessary to develop a series of dyes suitable for coloring cellulose acetate fibers. It was discovered that simple cellulose acetate dyes were applicable to nylon and later polyester fibers. These simple cellulose acetate dyes also served as building blocks for the later synthesis of more complex polyester and nylon dyes. Fourness (7) has thoroughly discussed the history and application of disperse dyes.

#### Disperse Dye Carriers

A disperse dye carrier is a substance which, when added to the aqueous dyebath, increases the rate of dyeing of hydrophobic fibers, notably those of the polyester type.

Suitable dye carriers for polyester fibers can be found among several classes of compounds: acids, alcohols, esters, ethers, hydrocarbons, phenols, amines and halogenated compounds. Waters (8) claims that in each class of compounds, the aromatic derivatives are superior in dye rate acceleration to the aliphatic derivatives.

The mechanism of dye carrier action has been investigated by several researchers and their findings will be discussed in the next section of this thesis. However, it is generally agreed that the name carrier is a misnomer and that the mode of action is not one of carrying the dye into the fiber as the name suggests; rather, the carrier acts by reducing the fiber-to-fiber forces, increasing the pore-size of the fibers thereby making it easier for the bulky dye molecules to enter the fiber. The dye carrier acts on the fiber rather than on the dyes.

### Review of the Literature

Waters (9) was one of the earlier investigators into the choice of dyeing accelerants for polyester fibers. For his work, he used Terylene (polyethylene terephthalate) and examined the mechanism for the action of the carriers and the choice of suitable carriers. One of his most important findings was that polyester fibers have the ability to sorb as much or more disperse dyes than acetate or nylon. Polyester fibers only lacked an ability to allow the dyes to diffuse from the dye-bath into the fiber.

Waters (10) noted that compounds with ionizable or water solubilizing groups were particularly ineffective as dye carriers when compared to insoluble compounds. For instance, he concluded that benzene was a



better carrier than benzoic acid and beta-naphthol is better than beta-naphtholsulfonic acid, etc. However, he did note that water soluble groups on the carrier provided convenient means of removing the carrier when the dyeing was completed. He also established that increasing the molecular weight of the carrier decreased efficiency of the carrier after a certain point and that not all agents that swell polyester increase the dyeing rate of the fiber.

Waters (11) concluded that the most practical agent for dye carrier use at the time was meta-cresol which required a dyebath concentration of two per cent to be effective. He also noted that the carriers were temperature "sensitive" and only worked above a temperature of 70°C. This temperature is near the glass transition point for polyesters.

Research to develop new techniques for dyeing Dacron polyester resulted in the examination of several classes of materials for carrier action (12). It was concluded that, from a performance standpoint, benzoic and salicylic acids were the most satisfactory dye carriers. This is in apparent conflict with earlier findings. It was noted that 20 grams per liter (g/l) of the acids was required and that the cost would be high.

The usefulness of aromatic compounds was reiterated by these workers as they stated: "Early studies on the dyeing of Dacron showed that the incorporation of certain aromatic compounds in the dyebath greatly improved the affinity and exhaustion efficiency of disperse acetate dyes." They examined aromatic derivatives of the following groups and found carrier action: acids, esters, ethers, hydrocarbons, phenols, and halogenated hydrocarbons. Several aliphatic alcohols and substituted ureas

were evaluated but no carrier action was determined. Meta-cresol was found to be an effective and economical agent for dyeing polyester fibers. However, it was learned that the dispersing agent for the dyes and the meta-cresol had to be selected with care. In addition, the meta-cresol gave hard packages when yarn dyeing due to yarn shrinkage and had an obnoxious odor. For these reasons, new carriers replaced meta-cresol. It is also interesting to note that meta-cresol (cresylic acid) is a toxic stream pollutant.

Tetralin (duPont's trademark for 1,2,3,4-tetrahydronaphthalene) was evaluated by the duPont workers and discovered to be effective as a dye carrier. Some problems with unlevelness and carrier removal after dyeing were noted and for these reasons Tetralin was not mentioned further. The Tetralin was effective at 4 g/l (50 per cent active) and certainly appeared to be promising. Tetralin was emulsified 1:1 with Merpen-tine or Alkanol DW which is probably not the best emulsion system since excessive amounts of emulsifier were used. It will be seen later that the choice and amount of emulsifier used will play a large role in the efficiency of the dyebath.

Vickerstaff (13) in his considerations on the use of dyeing assistants or carriers provides us with one of the first insights into the mechanism of their action. Vickerstaff outlined four mechanisms which he stated might account for their mode of action. These are:

1. Increased Solubility of Dyestuff in the Aqueous Phase

Dyeing with an 'insoluble' disperse dyestuff probably takes place from the extremely dilute aqueous solution of the dyestuff, which is maintained in a saturated state by the presence of the solid dyestuff. Now the rate of diffusion of dyestuff into a fibre is determined in part by the concentration gradient across the fibre surface; if the



concentration of dyestuff in solution is low, then the rate will be slow. One way in which a dyeing assistant might increase the rate of dyeing would be by forming a complex with the dyestuff and so in effect increasing the solubility of the dyestuff in the aqueous phase. This would increase the concentration gradient across the fibre surface and so increase the rate of dyeing. At equilibrium more dyestuff would remain in solution than in the absence of assistant.

## 2. Aqueous Swelling of the Fibre

A second hypothesis is particularly applicable to water-soluble assistants such as phenol, in regard to which it may be assumed that the agent is of small molecular volume and has some affinity for the fibre. The agent diffuses into the fibre more rapidly than does a dyestuff, becomes attached to the fibre substance by Van der Waals attraction to the hydrophobic part of its molecules, and then attracts water into the fibre by virtue of its hydrophilic groupings. The water thus swells the fibre, opens the molecular structure and facilitates the entry of dyestuff molecules. On this hypothesis the agent need not interact with the dyestuff at all and may affect only the rate of dyeing.

## 3. Plasticization of the Fibre Structure

The mechanism outlined in (2) cannot be applied to hydrophobic dyeing assistants such as diphenyl or chlorobenzene. These compounds cannot attract water into the fibre, but they do cause fibre shrinkage and are effective in increasing the rate of dyeing. A possible explanation is that such agents act as molecular lubricants, becoming attached to the polymer molecules in the fibre and destroying existing cross-linkages. In a plasticized material of this kind, it is easier for the polymer molecules to slide over one another and accordingly easier for a bulky dyestuff molecule to force the chains apart and enter the fibre. On this hypothesis too, only the rate of dyeing will be affected by the agent.

## 4. Formation of New Dyestuff Sites

Finally the dyeing assistant may be such that it has high affinity for both dyestuff and fibre. It will diffuse quickly into the fibre by virtue of its small molecular size, become absorbed on the polymer molecules and then in turn form new sites for the absorption of dyestuff molecules. The defect of the hypothesis is that it does not readily account for an increase in the rate of dyeing but should have a greater effect on the equilibrium uptake of dyestuff. At first, the absorption of dyestuff would increase with increasing amount of assistant absorbed by the fibre, but if excess agent were present then the dyestuff would distribute itself between the agent inside the fibre and that in the aqueous solution and the amount of dyestuff taken up by the fibre might again decrease.

Vickerstaff then proceeded to evaluate several dye carrier materials both insoluble and water soluble. From the water soluble group, he chose oxalic acid, benzoic acid, and phenol. Water insoluble compounds



investigated were toluene, xylene, naphthalene and biphenyl.

From his work, Vickerstaff concluded:

1. Water solubility is not an attribute of a good polyester dye carrier; the water insoluble materials are approximately 50 times more effective than the water soluble ones.

2. Solubility of the dye in the carrier or formation of a dye/-carrier complex is not a good characteristic of a dye carrier. Dispersol Fast Scarlet B dye evaluated by Vickerstaff was quite soluble in high concentrations of oxalic acid; oxalic acid was nearly ineffective as a dye carrier. Hence, carriers do not carry the dye into the fiber.

3. Whereas the carrier efficiency of a compound is unrelated to the amount sorbed by the fiber, the carrier must be sorbed by the fiber to be effective. Vickerstaff showed that no oxalic acid was sorbed by Terylene under dyeing conditions where phenol and benzoic acid were quite soluble in the fiber. However, the fiber picked up more benzoic acid than phenol while phenol is a more effective agent.

4. Carriers do not work by increasing the number of dyesites in the fiber. The sorption of phenol by Terylene increases linearly as the concentration of phenol in the bath increases whereas dyestuff sorption by the fiber rises to a maximum and then decreases as the concentration of phenol increases. The phenol must be acting as a colorless dye and is actually competing for dyesites within the fiber. It has long been known that an excess of dye carrier will act as a retarder or levelling agent. Vickerstaff (14) noted that if dyeings were carried to equilibrium, more dye was absorbed without carrier than with carrier in the case of phenol.

5. The hypothesis that dye carriers reduce fiber-fiber Van der Waals forces was verified by showing that elongation of the fiber at any point on the stress-strain curve was increased. The measurements were made under dyebath conditions with and without carrier.

6. Using hot and cold methanol extractions of carrier treated fiber, Vickerstaff showed that the amount of carrier sorbed on the surface of the fiber is greater than the amount entrapped in the fiber. Thus, he concluded that the dyeing takes place not from an aqueous solution of dye, but from a thin layer of the carrier on the fiber.

7. The addition of a dye carrier to the bath serves the same purpose as raising the temperature of the bath.

He concluded that carriers work both by loosening up the intramolecular forces of the fiber and by providing a thin film of dye solvent around the fiber from which the dyeing can take place. Theoretically speaking, the small aromatic compounds would be the most efficient; but due to their volatility, higher molecular weight substances would have to be chosen.

Lyle, et al., (15) in their study of high temperature dyeing of Dacron remarked "actually, the absorption obtained at the higher temperature without a carrier is equal or superior to that obtained with benzoic acid, one of the better carriers for the application of acetate dyes to Dacron polyester fiber at 212°F." Their work showed that with Celanthrene Violet BCF better dye absorption was obtained at 250°F than at 212°F with 20 g/l benzoic acid as carrier. Both samples were dyed one hour at the respective temperatures.



Zimmerman and his colleagues (16) studied the effectiveness of several types of carriers when dyeing Dacron polyester fiber. They concluded that based on cost and efficiency, the best dye carriers are (used at 8 g/l) methyl benzoate and methyl salicylate. Further, they claim these materials increase the diffusion of the dyes in Dacron to such a degree that the fiber could now be dyed on any equipment below the boil. Two sets of dyeings were performed. One set evaluated the performance of the methyl benzoate esters of benzoic, anthranilic, meta-toluic, and salicylic acids when emulsified with dioctyl sodium sulfosuccinate (Aerosol OT). The other set evaluated the same esters unemulsified and confirmed earlier work (17) which determined that the unemulsified esters give spotty dyeings. However, the set dyed with the emulsified esters were level. The effect of various emulsifiers on emulsion stability is discussed in this paper. In addition, it is pointed out that excessive amounts of emulsifiers tend to retard the sorption of or "hold off" the dyestuff. This was found to be particularly true with the nonionic surfactants as they tend to increase the solubility of the nonionic disperse dyes, thereby giving the dyes higher affinity for the aqueous phase. Actually, the practice of using a nonionic surfactant as a leveler or retarder has long been used.

Zimmerman pointed out that the inclusion of water-solubilizing groups on dye carriers renders them ineffective on Dacron. He also found that the aromatic esters gave improved color yield whereas the aliphatic esters do not. Further, increasing the molecular weight of the acid or alcohol portion of the ester decreases the efficiency of the compound as

a dye carrier. All of these findings are in accord with those of Waters (18). It was determined that the hydrolysis products of the ester are not responsible for the carrier action shown by methyl benzoate.

The lightfastness of dyes is apparently not harmed by methyl salicylate as with carriers such as ortho-phenylphenol and phenylmethylcarbinol, thereby reducing the severity of afterscour needed when methyl salicylate is used as carrier. The use of methyl salicylate at 250°F does not improve on the performance obtained at 212°F (19).

Earlier, Zimmerman (20) proposed that carriers work by increasing the concentration of disperse dye in the monomolecular state, thereby increasing the diffusion of the dye into the fiber, or increasing the rate of dyeing.

Fern and Hadfield (21) proposed a mechanism for dye carrier action not covered by Vickerstaff (22). They cite the possibility that a dye carrier might work by forming a complex with the dye, internally neutralizing the forces on the dye and thereby allowing the complex to more easily enter the fiber than could the dye despite the increased molecular volume. This may be analagous to using salt in a direct dyeing process to lessen the electronegativity of the cotton substrate. Fern and Hadfield predicted that with the advent of high temperature dyeing equipment, interest in carrier dyeing would decline.

Schuler (23) examined the mechanism of carrier action when dyeing Dacron polyester fiber in an isoöctane dyebath system. His research led him to conclude that compounds more soluble in Dacron polyester fiber are more effective carriers. Earlier, Vickerstaff (24) noted that solubility of the carrier in the polyester fiber was a requisite of carrier action.



However, the carriers could not be ranked as most soluble, most effective, etc. Vickerstaff cites benzoic acid and phenol as examples.

A mechanism for the dyeing of Dacron polyester was advanced by Schuler. He claimed the dyeing progressed in three steps:

1. Equilibration of the surface layer of Dacron with organic carrier, water, and dye.
2. Diffusion of organic carrier and water into the fiber; this loosens the interchain forces.
3. Diffusion of dye through the somewhat more permeable fiber.

Fortess and Salvin (25) examined factors influencing the dyeing of acetate fibers with disperse dyes and determined from this and prior work that the mechanism of carrier action when dyeing cellulose triacetate followed three steps:

1. Increased rate of solution of dyestuff (or decreased dye particle size).
2. If the carrier is insoluble, the product forms a thin film on fiber surface by filtration and deposition.
3. Sorption of the carrier by the fiber.

According to Fortess and Salvin, step number three results in reduced inter-molecular fiber forces (swelling and plasticization) and solvation of dye molecules in the fiber.

It was shown that tri-propyl phosphate was a good dyeing accelerant for cellulose triacetate and was ineffective on polyester fibers. Tri-propyl phosphate is sorbed by cellulose triacetate and is not sorbed by polyester fibers. Also, it was noted that carrier action must primarily occur in the fiber phase.

Glenz et al. (26), noting that the difficulty in dyeing polyesters was diffusion of dye inside the fiber (which determined the dyeing rate), examined the diffusion coefficient as an index of dyeing rate of disperse dyes on polyester fibers. The diffusion coefficients were not measured directly but were calculated from the exhaustion curves. These researchers revealed several important findings when Dacron polyester fiber was dyed with carrier present (benzoic acid and trichlorobenzene). The use of carrier as a dyebath adjuvant increased dye rate 10-100 times when compared to non-carrier dyed polyester. The molecular nature of the dyestuff played a large role in the efficiency of the carrier; dyes with low dye rates were accelerated more than dyes with high rates of dyeing. It was also determined that the efficacy of a carrier is directly related to the increase in dye rate obtained under standard conditions. Schuler (27) pointed out that all carriers had the same effect when present in the fiber in equimolar concentrations; thus, Glenz (28) concluded that the activity for all carriers depended on the number of molecules of that carrier present in the fiber and that the chemical nature of the carrier was important only in determining the substance's partition coefficient between fiber and dyebath. Glenz (29) summarized that the more hydrophobic substances would be better dye carriers but that more hydrophilic grouping, e.g. hydroxyl, would be preferred to improve dispersion properties and reduce volatility. Interestingly, biphenyl is used in the United States in large quantities for dyeing polyester carpet, so hydrophobic hydrocarbons are not eliminated from use as they can be used in emulsion form.



Salvin (30) and his colleagues investigated the mechanism and principles for accelerant dyeing (carrier dyeing) hydrophobic fibers. They examined several facets of carrier dyeing including dye solubility in carrier, sorption of carrier by fiber, effect of surfactants and liquor ratio on carrier action, dye desorption in carrier presence, fiber pre-treatment with carrier, carrier effects on water imbibition, dye migration from carrier film and physical effects of carrier on fiber.

It was concluded by these workers that dyes diffuse through holes in the fiber surface so that the dye molecule may enter more easily.

Rawicz (31) and his co-workers examined the swelling action of carriers in dyeing polyethylene terephthalate fiber. His work indicates that water insoluble accelerants cause longitudinal shrinkage (lateral swelling) of polyethylene terephthalate fibers to a greater degree than do water soluble dyeing accelerants. Earlier, Taylor (32) showed that ortho-phenylphenol and other agents also produced shrinkage of polyethylene terephthalate fibers. Rawicz also noted that substances sorbed in negligible or small quantities do not swell the polyethylene terephthalate fiber and are ineffective as dyeing accelerants. Further, he showed that carrier treatment of the fiber with carrier substances disoriented the fiber as determined by x-ray analysis. Rawicz points out that the essential function of the carrier is "to reduce the attractive forces between the molecules." Two reasons for increased dye rate with carriers were given: greater mobility of the polymer chains allow for faster diffusion; and to a lesser extent, increased swelling gives a larger volume for the dye to diffuse through the fiber.

Brown and Peters (33) examined nineteen mono- and poly- halogenat-

ed benzenes as disperse dye carriers for polyester fibers. They found that in general 7.5-10 g/l of the carriers were needed for good dyebath exhaustion although exceptions were noted. The most effective carriers were found to be: ortho-chlorobromobenzene > ortho-dibromobenzene > 1,2,3 trichlorobenzene > para-bromochlorobenzene > ortho-dichlorobenzene > para-dichlorobenzene for maximum dyebath exhaustion. As for the influence of the halogen atom in the mono substituted compound, the following order was observed by Brown and Peters (disregarding concentration): bromo > iodo > chloro > fluoro. Ortho > para > meta was found to be the order of optimum steric arrangement for carrier activity in the di-substituted compounds. When all economic factors were considered, ortho-dichlorobenzene and the trichlorobenzenes were concluded to be the most satisfactory in the series studied.

Past and present dye carrier mechanisms were discussed. The same carriers studied in this paper were also evaluated for latent carrier activity by pretreating the fibers before dyeing.



## CHAPTER II

### INSTRUMENTATION, FIBER SPECIMENS AND CHEMICALS

#### Praxitest Dyeing Machine

The Praxitest Dyeing Machine is an instrument designed to give continuous flow of the dyebath through the material being dyed and a filter colorimeter. The instrument is coupled into a recording device whereby there is continuous intermittent recording of both dyebath temperature and per cent exhaustion. The Praxitest Dyeing Machine can be used to simulate mill dyeing conditions as dyeings can be carried forth at temperatures up to 130°C with very high and low bath ratios. This instrument is marketed in the United States by Brinkmann Instruments, Westbury, New York.

The Praxitest was used to evaluate dye rate and equilibrium sorption effects of the polyester dye carriers studied in this thesis. Figure 1 gives a typical view of the instrument during a dyeing. Figure 2 shows a test sample being fitted into the machine.

#### Polyethylene Terephthalate Fiber

Fortrel (Celanese Fibers Corporation) is representative of the polyethylene terephthalate class of polyester fibers and was the fiber chosen for this work. The fiber used in this study was a semi-dull, 16 denier/filament, four inch staple fiber. The fiber was spun into a 2/2 ply yarn and had subsequently been tufted into greige unbacked carpet.

The yarn was removed from the jute backing before dyeing so the weights given for the polyester do not represent any jute; thus, the weights are for 100 per cent polyester.

This study was carried forth utilizing polyester carpet yarn because this is a study of hydrophobic aromatic dye carriers. The carpet industry is perhaps the largest user of hydrophobic aromatic dye carriers, mainly biphenyl.

#### Poly(1,4-dimethylol)cyclohexyl Terephthalate Fiber

Tennessee Eastman's Kodel II polyester fiber represents the poly-(1,4-dimethylol)cyclohexyl terephthalate class of polyester fibers and was studied in this work.

The particular fiber studied was semi-dull, 15 d/f, four inch staple. The fiber had been spun into 1's singles yarn and tufted into unbacked, greige carpet. The yarn was removed from the jute back before dyeing.

#### Carriers Studied

For the structures and other properties of the compound studied in this work, please refer to Table 1, page

1. Benzene. Fishers certified reagent grade benzene was used in this study.
2. Toluene. Merck's reagent grade Toluene was used in this study.
3. Xylene. Baker's analyzed reagent grade xylene was used in this study. Meta-xylene makes up the largest percentage of a xylene mixture.

4. Naphthalene. Reagent grade naphthalene from Eastman Organic Chemicals was used in this study.

5. Methylnaphthalene. Evaluation of this particular compound as a new dye carrier was one of the main objectives of this study. A technical mixture of alpha- and beta- methylnaphthalenes (B.P. approximately  $240^{\circ}\text{C}$ ) from Ashland Oil and Refining Company was used in this experiment. This product was a clear colorless liquid which had minimal odor.

6. 1,2,3,4-Tetrahydronaphthalene. The tetrahydronaphthalene used in this work was a technical grade from Union Carbide Corporation. The product is 98% pure, low in odor and has a very pale, straw color.

7. Biphenyl. This chemical is currently used on polyester as a dyeing accelerant. A commercially emulsified form of biphenyl, Carolid ELF-C, was used.



## CHAPTER III

### PROCEDURES

#### Preparation of Fiber

The fiber specimens used in this work contained a water-soluble fiber manufacturers spin finish and a light water-soluble tint for identification purposes. Removal of these two contaminants was effected by a light scour with a crypto-anionic surfactant:

0.1%\* Seyco 8961-G (Seydel-Woolley and Company)

30/1 bath ratio with distilled water

55°C for 20 minutes

\*based on fiber weight

The fiber was then twice rinsed in 30 times its weight of distilled water and dried at 105°C until dry. The fiber was then allowed to regain its normal moisture content before use.

#### Emulsification of Carriers

Emulsification of the carriers was accomplished by stirring and warming 85 parts of each experimental carrier with 15 parts emulsifier. The emulsifier consisted of 75% phosphated ten mole ethoxylated nonyl-phenol and 25% dodecylbenzenesulfonic acid, this mixture being neutralized to pH 5.5-6.0 with isopropylamine to form the organic salt. Good emulsion bases were prepared by this technique with sufficient stability for the duration of the test. Finer emulsions with more "blossom" could

be obtained by the judicious use of certain nonionics and other water-soluble solvents, but for the purposes of this work, it was decided to keep variables at a minimum. Also, emulsion with extended dyebath stability could be prepared by increasing the amount of emulsifier in each carrier, but this would only increase the partition coefficient of the carrier for the aqueous phase thereby reducing the carrier's effectiveness. As is pointed out by Luttringhaus and Arcus (34), "too good" an emulsion is not desirable.

#### Preparation of Dyebath

C. I. Disperse Blue 60 (Latyl Blue BG, duPont) was chosen as the dye to be used in this experimental work. C. I. Disperse Blue 60 is known for its sensitivity to changes in dyebath variables.

A 2 g/l stock solution of the dye was made with distilled water each day for the dyeings to be run. The dyebath was prepared by mixing 100 ml of the dye stock solution with 350 ml of distilled water and adjusting the pH to 5.5 with reagent grade acetic acid. The necessary amounts of liquid carriers were then added with vigorous shaking and the volume was made to 500 ml with additional distilled water. Twenty grams of polyester fiber was dyed in this bath to give a 1% dyeing with a bath ratio of 25/1 which is usual for carpet dyeing. In the case of solid carriers (naphthalene and the control, Carolid ELF-C), these compounds were added at 80°C and 70°C respectively as the dyebath temperature was rising.

The previously scoured and dried fiber samples were placed in the Praxitest and the dyebath added. The colorimeter was adjusted for 0%

exhaustion (the instrument being previously calibrated for 100% exhaustion) and the heating started. The dyebath was started at 30°C and fifteen minutes was required to reach 95°C. The dyeings performed in this study were run with a colorimeter cell thickness of 10 mm and a red interference filter of  $\lambda = 650-700 \text{ m}\mu$ , Praxitest number F 1325/50.

After reaching 95°C, the dyeings were held for one hour, cooled and rinsed. It was found advantageous to run the bath flow in one direction only as reversal of the bath created swirls of air bubbles which caused erratic colorimeter readings. The sample holder on the Praxitest is vertical with the flow entrance/exit tubes at the bottom and top. The dyebath was run from the bottom up to keep air bubbles to a minimum. A dozen glass beads (typical boiling beads) were placed on top of the sample to keep the yarn from pressing against the exit filter, thus clogging the system and reducing bath flow. A bath flow of approximately 1 kg/cm<sup>2</sup> was used.



## CHAPTER IV

## DISCUSSION OF RESULTS

Dyeing Rate

The data indicate that the compounds investigated in this research, when applied at a similar concentration, have the following order of dye rate using one per cent (owf) C. I. Disperse Blue 60:

Biphenyl, Naphthalene > Methylnaphthalene > 1,2,3,4-Tetra-  
hydronaphthalene > Xylene > Toluene > Benzene

Earlier reports indicated that dye rate activity for all carriers was nearly equivalent when they are present in the fiber in equimolar concentrations. This would seem to indicate that, weight for weight, substances such as benzene would have nearly twice the activity of substances such as biphenyl since the molecular weight of benzene is nearly one-half that of biphenyl. However, it appears that even though there was a higher molar concentration of benzene, toluene and xylene in the dyebath, the activities were lower. This might indicate that these compounds reside in some phase other than the fiber. This might be explained as due to two reasons. First, toluene, benzene, and xylene have appreciably lower boiling points than do the other four compounds so there will be a tendency to vaporize into the dyebath atmosphere. Secondly, since benzene, toluene, and xylene have low molecular weights, under similar surfactant concentrations and temperatures, these three materials

will probably have a higher partition coefficient for the aqueous phase. Due to these two reasons, benzene, toluene, and xylene will be held out of the fiber and will have a lower dye rate under practical dyeing conditions. Also, biphenyl and naphthalene have melting points of 70°C and 80°C respectively, so these two products will not enter the fiber until the bath reaches this temperature. Once these two substances enter the fiber, the fiber begins accepting the dye at a rapid rate.

The dyeing rate appears to be slightly slower for all compounds when dyeing Fortrel as compared to Kodel. The specific gravity of Kodel II is lower than that of Fortrel which would mean that the interior of the Kodel II fiber would be more accessible and this would account for increased dye rate on the Kodel II fiber.

Increasing the amount of the individual carriers tended to increase dyeing rate until the dye could be made to exhaust in a matter of two or three minutes.

#### Equilibrium Exhaustion

The equilibrium exhaustions of the dye carriers examined when adjusted to approximately equal time of half dyeing were in the following order on Fortrel:

Methylnaphthalene > 1,2,3,4-Tetrahydronaphthalene; Biphenyl  
Naphthalene > Xylene > Toluene > Benzene

When Kodel II was dyed, the following order was observed:

Methylnaphthalene > 1,2,3,4-Tetrahydronaphthalene >  
Naphthalene, biphenyl > Xylene > Toluene > Benzene



It appears that Naphthalene is more effective when dyeing Kodel II polyester fiber than Fortrel. The higher molecular weight compounds give higher equilibrium exhaustions than the lower molecular weight products due in part to their higher dye rates. In addition, the decreased volatility and low water solubility of methylnaphthalene, naphthalene, biphenyl and 1,2,3,4-tetrahydronaphthalene would indicate that these materials would have high fiber solubility, therefore high equilibrium exhaustion of dye into the fiber.

#### Levelling

Methylnaphthalene: 1,2,3,4-tetrahydronaphthalene and biphenyl were examined for their dye transferring ability. This was accomplished by placing equal weights of dyed and undyed polyester in the Praxitest; then adding a bath consisting of 1 g/l, for each carrier, distilled water and 2 ml 10 per cent acetic acid. (Note: in each case the dyed polyester was dyed in a bath using one-half g/l of the respective carrier.)

The dye transfer test is a somewhat stringent test for dye carriers to pass but is thought to be an excellent indicator for levelling activity. In a true levelling test such as would be encountered under mill conditions, both samples would have been exposed to carrier. In the dye transfer test, the undyed sample has not been previously exposed to the carrier.

For dye transfer activity, the carriers examined were ranked as follows:

Methylnaphthalene, biphenyl > 1,2,3,4-Tetrahydronaphthalene.

After only 30 minutes at dyeing temperatures, biphenyl and methyl-naphthalene had transferred sufficient dye to the undyed sample so that both samples of fiber were the same depth of shade. At the end of one hour, 1,2,3,4-tetrahydronaphthalene had dyed the undyed sample to about three-fourths of the shade of the dyed portion.

#### Sources of Errors

The Praxitest colorimeter is designed to measure the concentration of dye in the test solution as a function of the initial concentration of the dye. Thus, intrinsic difficulties are associated with colorimetrically measuring the exhaustion of an aqueous dispersion of essentially insoluble dyes. This problem was overcome to a large extent by using a dilute dispersion of the dye (0.4 per cent at start). Dilute dispersions tend to behave as dilute solutions if kept well mixed and dispersed and it was found that the dye rate and equilibrium exhaustion could be followed colorimetrically.

The temperature rate of rise was found to be consistent and the temperature recorder was calibrated and found to be accurate  $\pm$  one centigrade degree. In addition, the heating system was able to maintain dyeing temperature  $\pm$  one centigrade degree for the duration of the dyeing cycle.

## CHAPTER V

### CONCLUSIONS

The data indicate that methylnaphthalene and 1,2,3,4-tetrahydronaphthalene would be as satisfactory as biphenyl for exhausting disperse dye onto polyester fibers using enclosed kettles at atmospheric pressure.

In addition, methylnaphthalene and 1,2,3,4-tetrahydronaphthalene did have two important advantages over biphenyl. First, biphenyl is a solid and must be added to the dyebath near its melting point ( $70^{\circ}\text{C}$ ) whereas both methylnaphthalene and 1,2,3,4-tetrahydronaphthalene are liquids and can be added to the dyebath at  $27^{\circ}\text{C}$ . Also, there would be no danger of crystals forming when the bath is cooled as there is with biphenyl.

Secondly, since methylnaphthalene and 1,2,3,4-tetrahydronaphthalene can be added to the bath at room temperature, the dyeing can start early, greatly minimizing unlevelness which might result from rapid dye strike when biphenyl is added hot.

1,2,3,4-tetrahydronaphthalene suffers slightly in dye levelling ability although this was not a serious defect.

Methylnaphthalene is a relatively unreactive aromatic compound similar to aromatics currently in use as dye carriers. It is believed that methylnaphthalene would be no more toxic than materials currently in use.



## CHAPTER VI

### RECOMMENDATIONS

While dye rate and equilibrium exhaustion at least comparable to commercially viable carriers is a prime requisite of any new dye carrier, any new product must be satisfactory in other respects. Effect on lightfastness and compatibility with a broad range of dyestuffs must be determined.

Methylnaphthalene and 1,2,3,4-tetrahydronaphthalene are relatively unreactive alkyl aromatics and would be expected to have no more effect on lightfastness than would biphenyl. However, since these products are coal-tar fractions, there may be impurities in commercial samples which would affect lightfastness and compatibility.

## APPENDIX

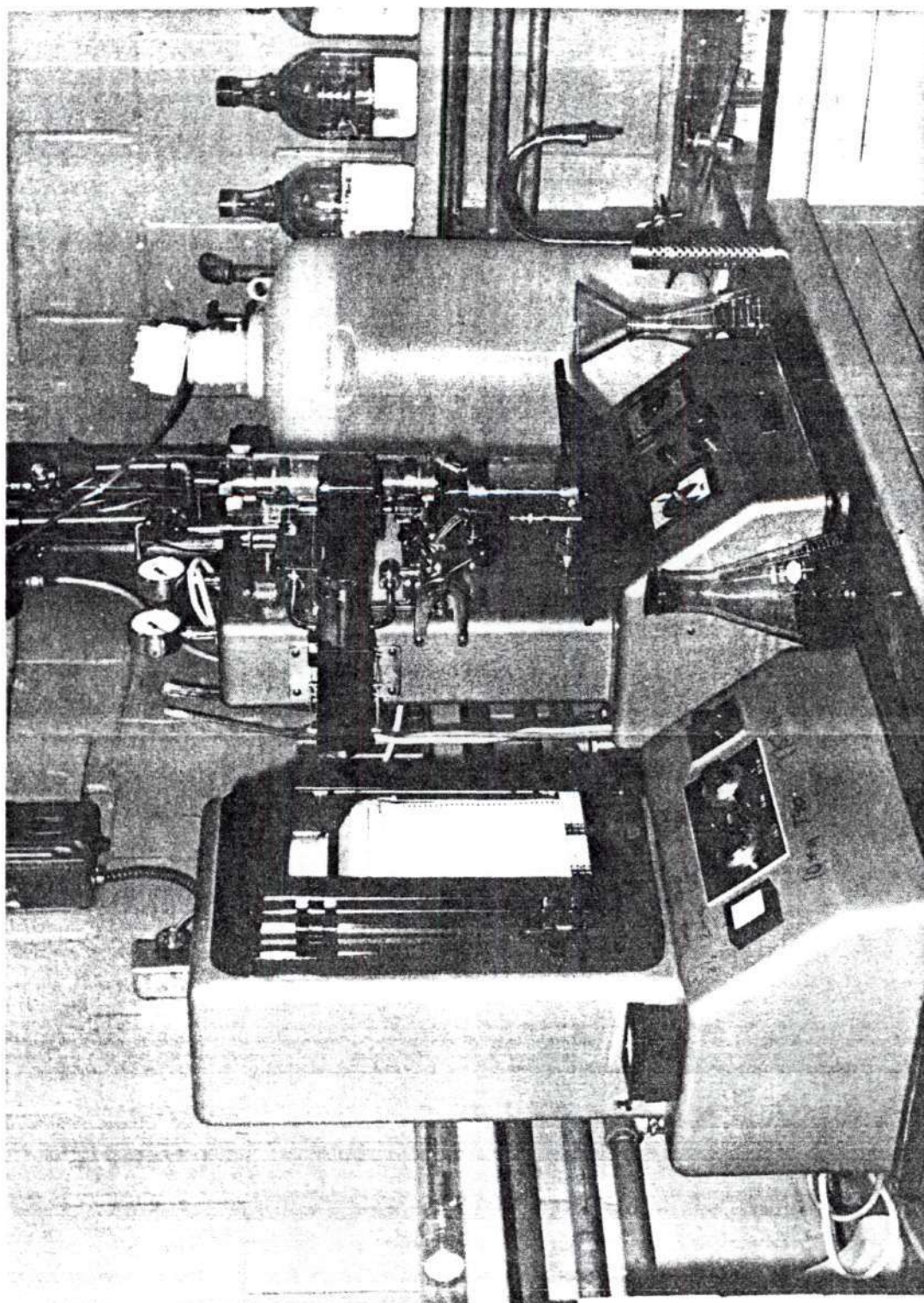


Figure 1. The Praxitest Dyeing Machine with Attached Recording Colorimeter.



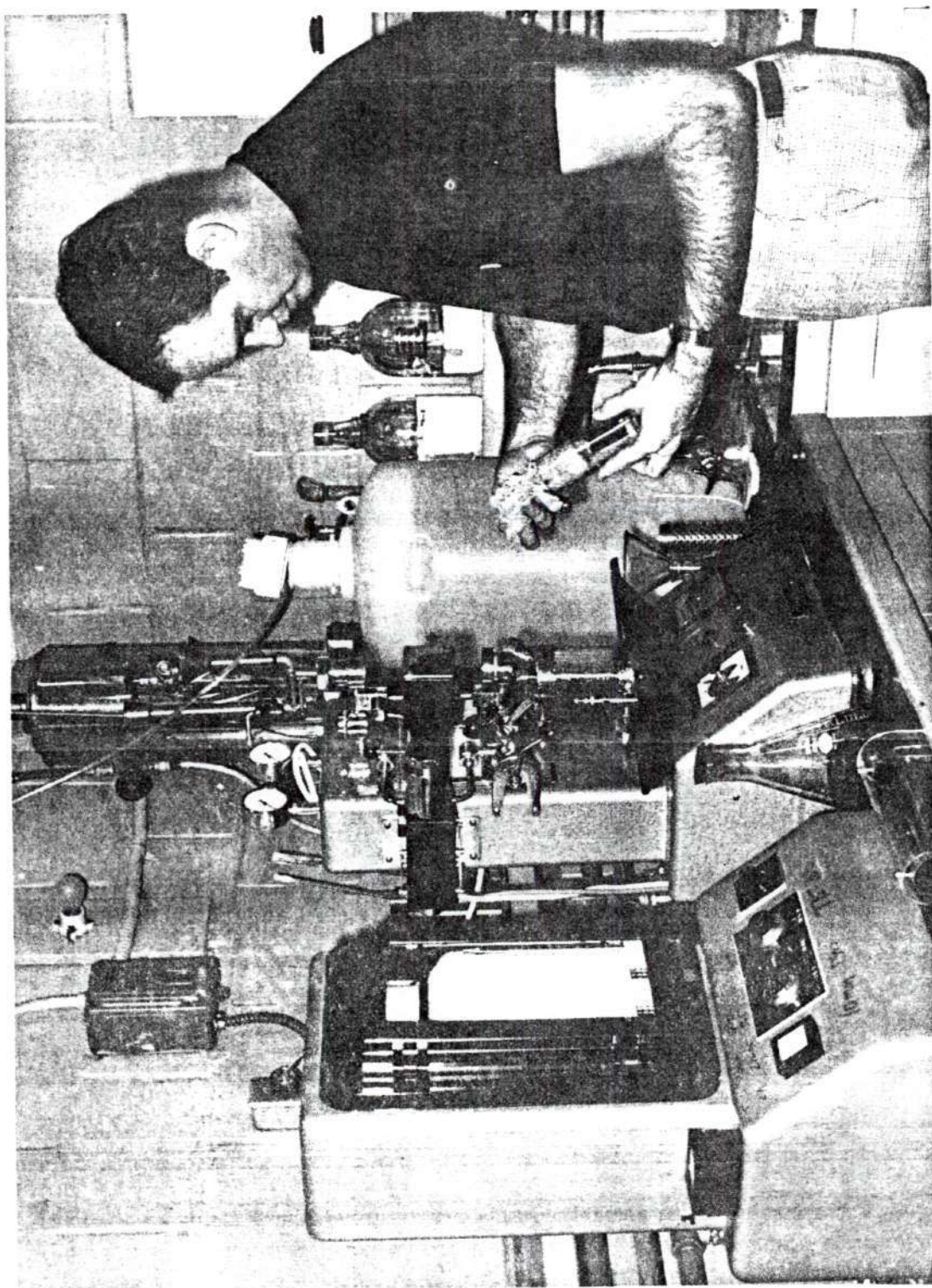


Figure 2. Fitting Test Sample into Praxitest Dyeing Machine

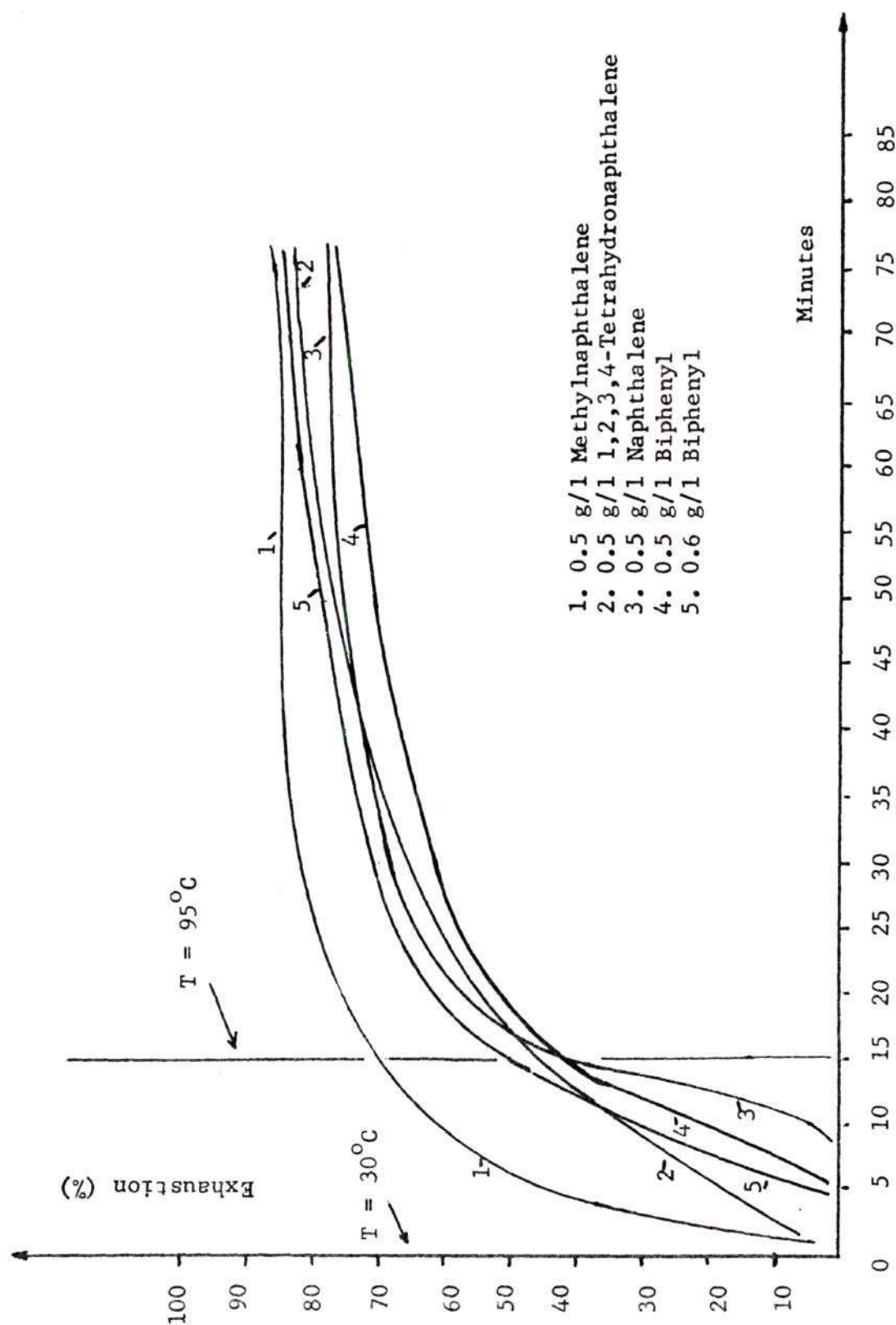


Figure 3. Exhaustion of 1% (owf) C. I. Disperse Blue 60 on Kodel II versus dyeing time.



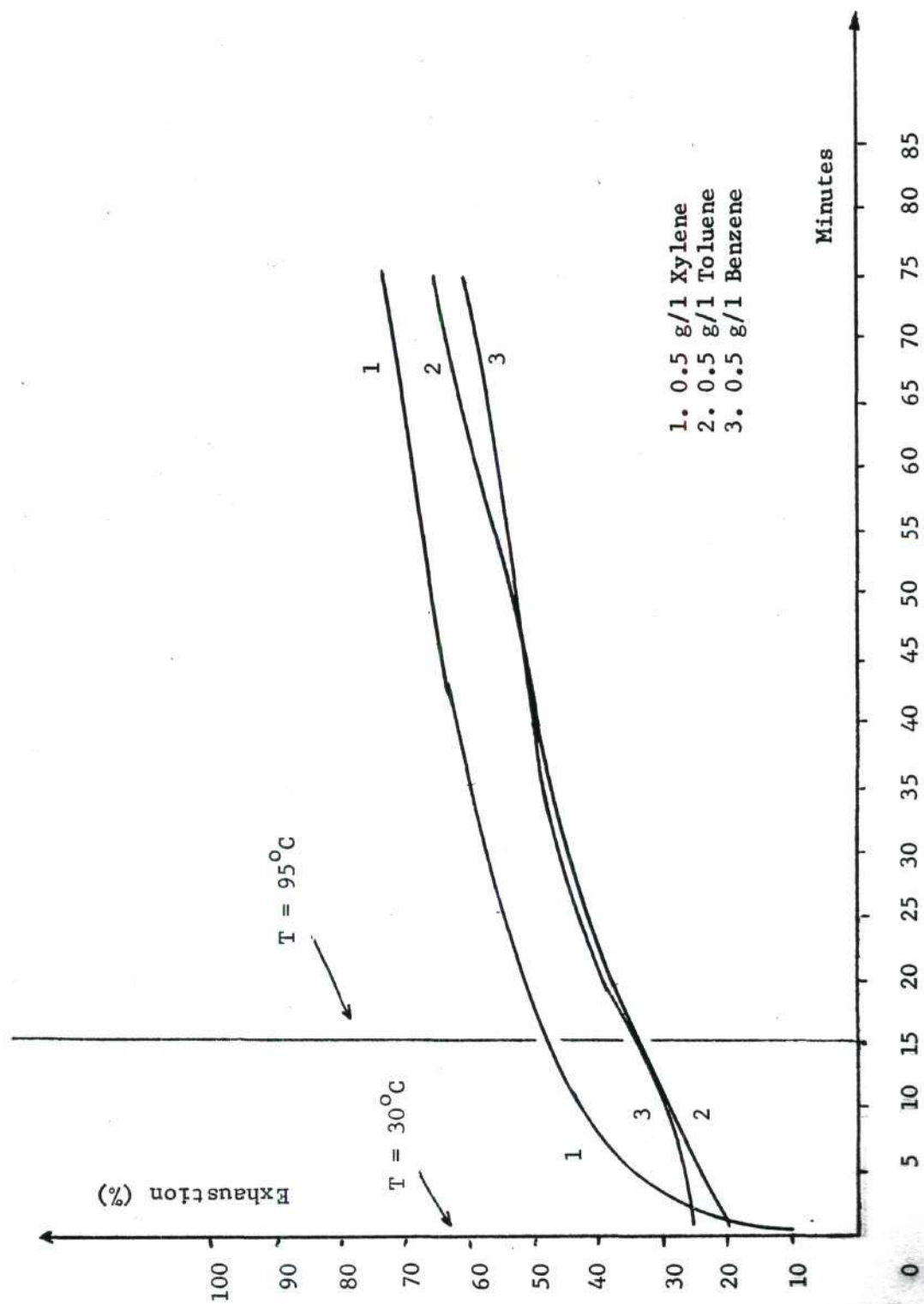


Figure 4. Exhaustion of 1% (owf) C. I. Disperse Blue 60 on Kodel II versus dyeing time.

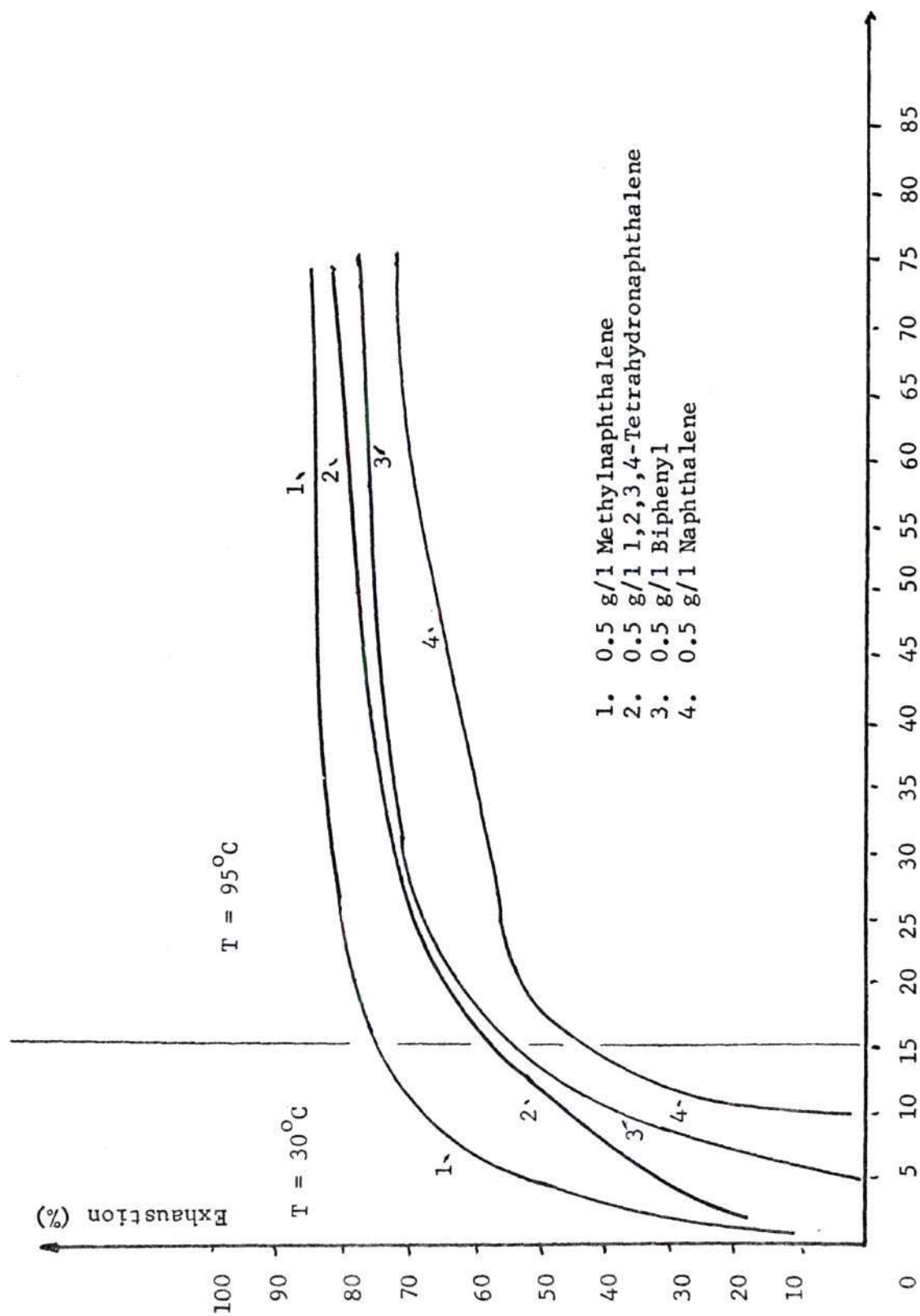


Figure 5. Exhaustion of 1% (owf) C. I. Disperse Blue 60 on Fortrel versus dyeing time.

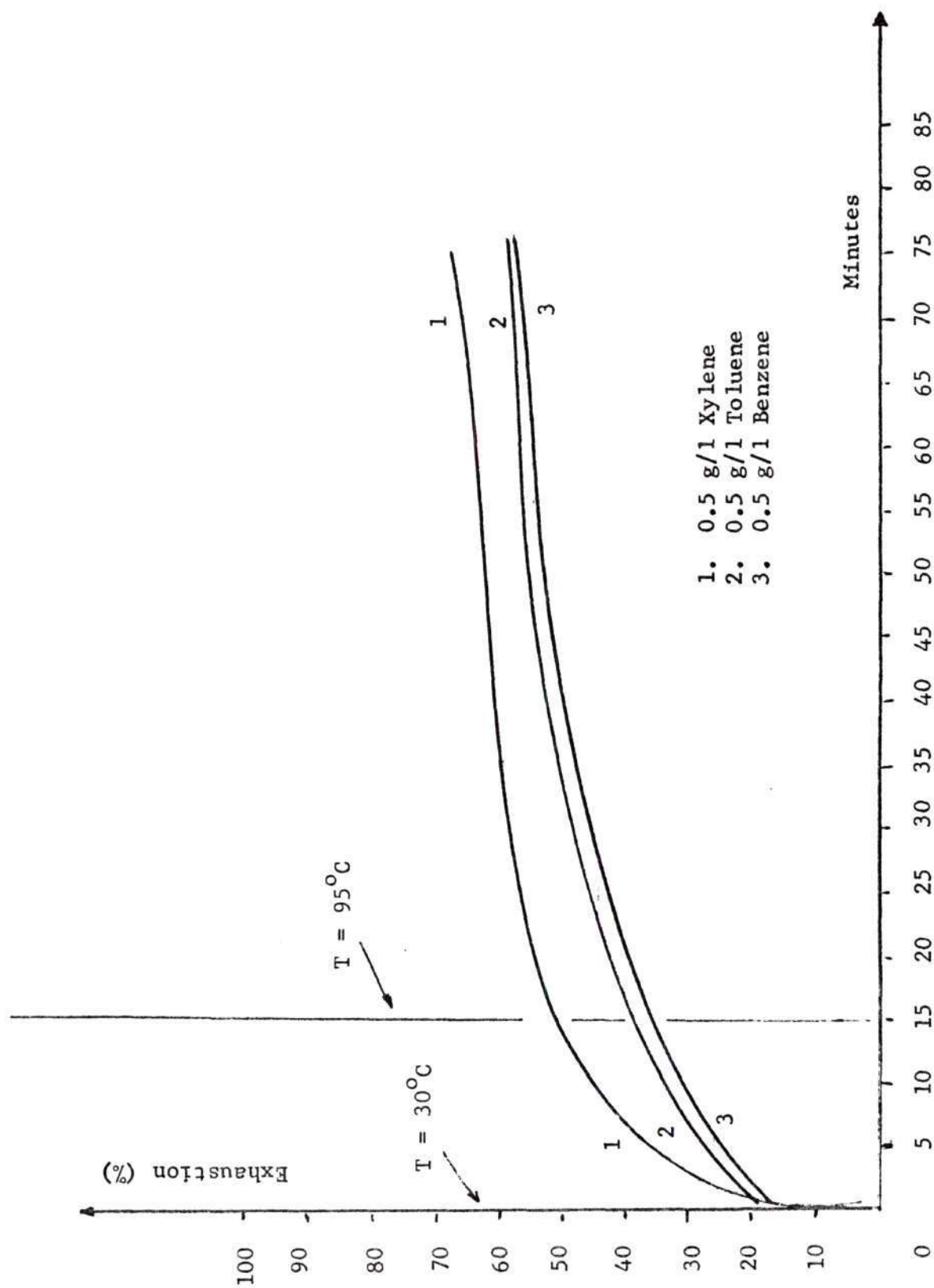


Figure 6. Exhaustion of 1% (owf) C. I. Disperse Blue 60 on Fortrel versus dyeing time.



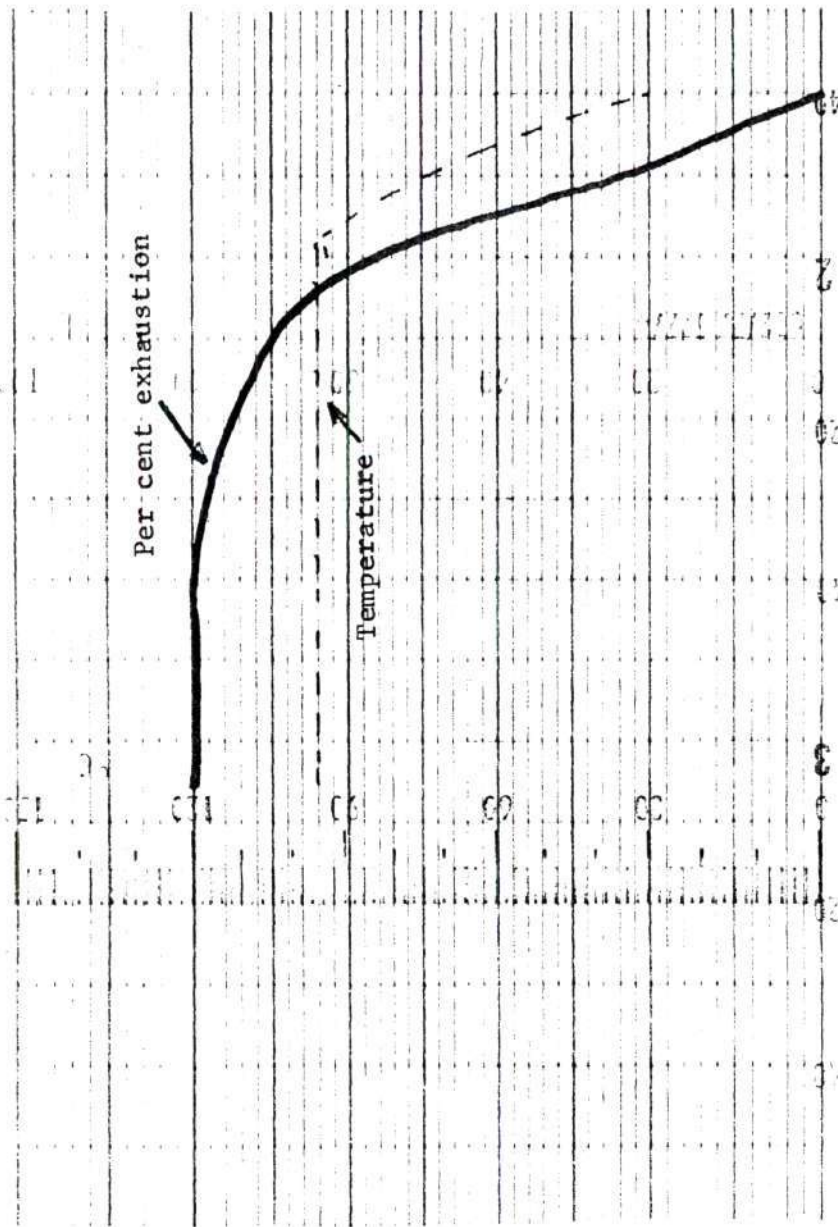


Figure 7. Typical Data Chart

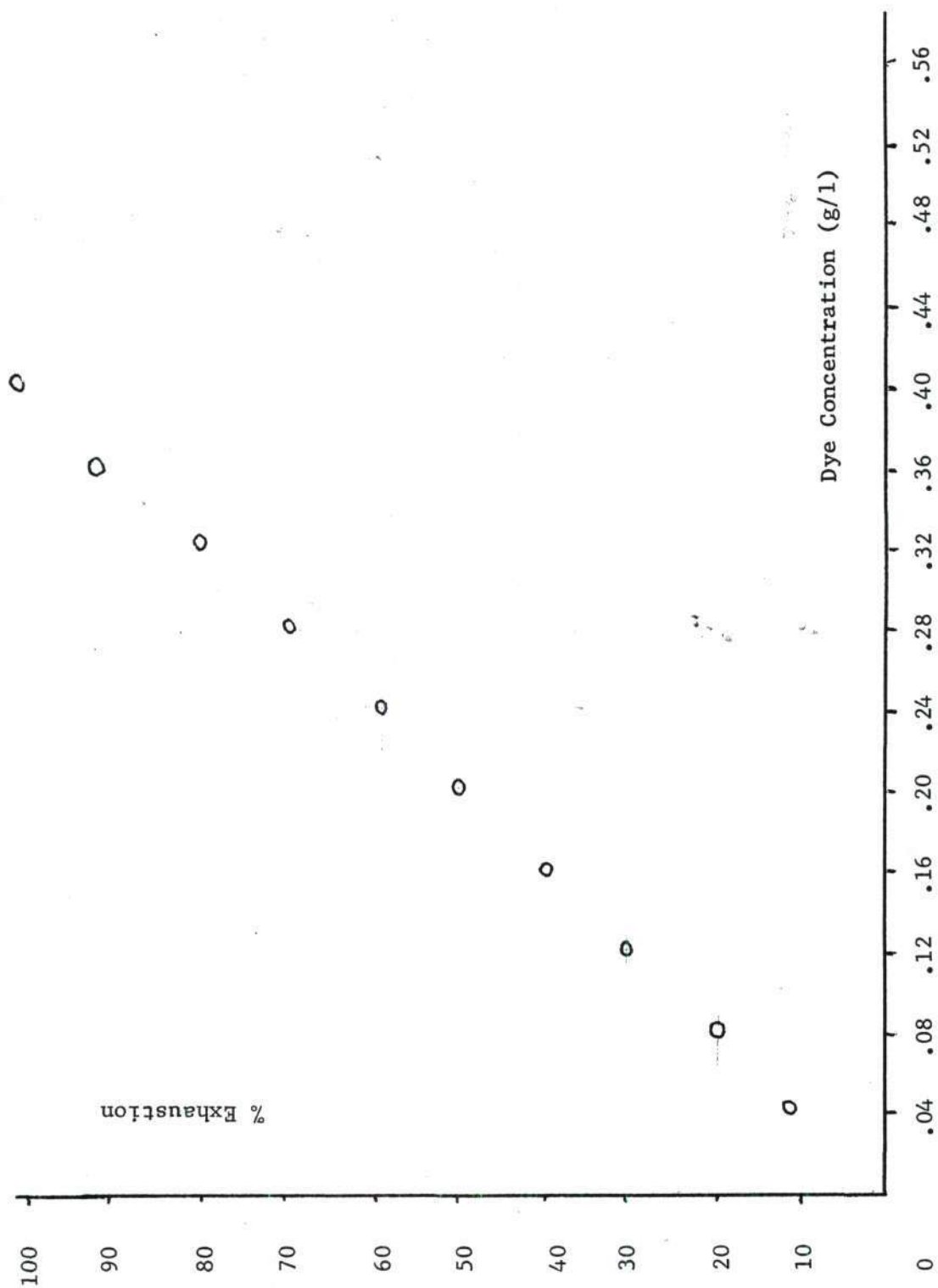


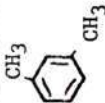

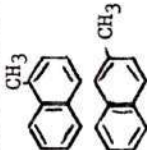

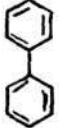


Figure 8. Calibration Curve for Latyl Blue BG

Table 1. Properties of Materials Investigated in this Research

Name and Formula	Mol.Wt.	Structure	m.p. (°C)	b.p. (°C)	Density (g/ml)	Conc. (g/l)	Equilibrium Exhaustion Kodel II	Equilibrium Exhaustion Fortrel
Benzene $C_6H_6$	78.1		6	80	0.879	0.5	60%	60%
Toluene $C_7H_8$	92.1		-95	111	0.867	0.5	64%	60%
Xylene <sup>2</sup> $C_8H_{10}$	106.2		-54	139	0.864	0.5	72%	66%
Naphthalene $C_{10}H_8$	128.2		80	218	1.145	0.5	77%	70%
Methyl-naphthalenes $C_{11}H_{10}$	142.2		-22 <sup>3</sup> 35 <sup>4</sup>	242 <sup>3</sup> 245 <sup>4</sup>	1.025 <sup>3</sup> 1.029 <sup>4</sup>	0.5	86%	86%
1,2,3,4-Tetrahydronaphthalene $C_{10}H_{12}$	132.2		-30	207	0.971	0.5	80%	80%
Biphenyl $C_{12}H_{10}$	154.2		70	254	1.180	1.0	76%	77%

<sup>1</sup> One per cent Latyl Blue BG-one hour at 95°C.<sup>2</sup> The given data is for meta-xylene.<sup>3</sup> Alpha-methylnaphthalene.<sup>4</sup> Beta-methylnaphthalene.



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