

FACTORS INFLUENCING FABRIC SOIL RELEASE
AND SOIL REDEPOSITION

A THESIS

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James William Wiley

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7/25/68

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DEDICATION

I gratefully dedicate this thesis to my fiancée, Janice,
for her love and encouragement.

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENT.	iii
LIST OF TABLES.	v
LIST OF ILLUSTRATIONS	vi
SUMMARY	vii
Chapter	
I. INTRODUCTION	1
Statement of the Problem	
II. SURVEY OF THE LITERATURE	4
Objections to Deposition Tests	
Soils for Testing	
Methods of Measurement	
Influences on Redeposition	
III. INSTRUMENTATION AND EQUIPMENT.	14
Launder-Ometer	
Color-Eye	
Hewlett-Packard Calculator	
Detergent	
Test Fabric	
Chemicals	
IV. EXPERIMENTAL PROCEDURES.	19
Preliminary Experiments	
Choice of Detergent	
Sample Preparation	
Measuring the Reflectance of Samples	
Test Method	
Calculation of Color-Difference	
V. DISCUSSION OF RESULTS.	26
VI. CONCLUSIONS.	31
VII. RECOMMENDATIONS.	32
APPENDIX.	33
BIBLIOGRAPHY.	46

LIST OF TABLES

Table	Page
1. Detergent Composition and Per Cent Ingredient	16

LIST OF ILLUSTRATIONS

Figure	Page
1. Effect of Optical Brighteners.	20
2. Effect Without Brighteners	21
3. Per Cent Acceptance vs Color Difference, From Davidson's Work	27
4. Effect of Detergent Concentration.	34
5. Effect of Water Hardness	35
6. Effect of Time	36
7. Effect of Temperature.	37
8. Effect of Liquor Ratio	38
9. Redeposition Build Up-Constant	39
10. Redeposition Build Up-Little Change.	39
11. Redeposition Build Up-Variable	39
12. Effect on Polyester.	40
13. Effect of Acetone in Liquor.	41
14. Effect of Dioxane in Liquor.	42
15. Effect of Methanol in Liquor	43
16. Effect of Polyethyleneglycol in Liquor	44
17. Effect of Perchloroethylene in Liquor	45

SUMMARY

The purpose of this research was to evaluate the factors influencing the trends in soil removal and redeposition by use of an improved method. This method was also used to determine the feasibility of a new detergent system of reduced liquor ratio and/or recoverable components. Such a system would help achieve better whiteness retention and a reduction in water pollution due to fabric laundering.

A commercially available standard soiled fabric was used in testing. The factors studied were time, temperature, detergent concentration, liquor hardness, liquor ratio, fiber blends, and water soluble additives in the liquor. Results were analyzed spectrophotometrically. Color difference values in terms of ΔE were determined using a computer program written for the Friele-MacAdam-Chickering color difference formula.

CHAPTER I

INTRODUCTION

Statement of the Problem

Soil redeposition during laundering or dry cleaning occurs when the soil that is removed from a soiled fabric becomes reattached to the surface of the textile fibers. One of the principal causes of this phenomenon is insufficient suspending power of detergents (1). This suspending power is generally influenced by the same factors influencing soil removal, some of which are time, temperature, mechanical agitation, detergent character and concentration, water hardness, bath ratio, the chemical nature of the fibers, and the nature of the soil. The latter factor is an important one, for most of the soil redeposited appears to be the result of colloiddally dispersed particles, ranging from 2 microns and smaller (2). These particles have high surface energy and deposit firmly on the surface of textile fibers which are of the order of 10 microns in diameter (3).

Soil redeposition is an aspect of detergency that is understood even less than soil removal itself. Knowledge about the latter certainly leaves much to be desired. In estimating the efficiency of detergents and detergent systems, too much attention has generally been paid to the relatively easier task of soil removal, while the much more difficult task of inhibiting soil redeposition has been largely ignored. Detergent manufacturers, aware of the problem, have added redeposition inhibitors

to their products. The equipment manufacturers have done less to combat the problem. Nevertheless, it is this very phenomenon of soil redeposition that causes much dissatisfaction with the results of home and commercial laundering because of the cumulative effect during several laundry cycles.

There have been many test methods developed by various investigators to study redeposition. Perhaps the obvious approach to a soil redeposition test was to simulate practice, washing clean cloth along with soiled, and determining the soil redeposited on the clean cloth. This is a true redeposition type test in that particulate soil is removed from cloth and redeposited. In such a test however, the amount of soil available in the wash liquor depends on the soil-removing ability of the detergent and the amount of soil present on the laundered fabric. Because this approach seemed to "stack the cards" against detergents with good soil-removing ability (2), many detergency workers turned to deposition type tests, in which a model soil, containing particulate soil, was added to the detergent bath and soil pick-up by the clean cloth determined. This approach permitted accurate control of the soil loading in the detergent bath.

In the absence of contradictory evidence, it has been generally assumed that deposition and redeposition type measurements give essentially equivalent qualitative results. Within the past few years deposition evaluations have been shown to be misleading and in some cases contradictory to redeposition evaluations (2,4,5,6). For this reason more work is needed in the area of realistic redeposition.

Methods for instrumentally measuring the apparent soil deposited

or redeposited are usually optical and are based on the reflectance principle, e.g. a comparison of the light reflected using a white standard and a redeposited sample. Quantitative results rely on a decrease in per cent reflectance. The charts and formulas utilizing this value make it obvious that redeposition is real. They do not however, indicate if it is perceivable, yet perception is the key to dissatisfaction with the results of laundering. For this reason an improved method for measuring redeposition should be developed which will indicate the degree of perception. The results of such a method would indicate whether the redeposition was critical enough to cause dissatisfaction.

The purpose of this research was to evaluate the factors influencing the general trends in soil removal and redeposition by use of an improved method. This method was also used to determine the feasibility of a new detergent system of reduced liquor ratio and/or recoverable components. If these studies are successful better whiteness retention may be achieved along with a possible reduction in water pollution due to fabric laundering.

CHAPTER II

SURVEY OF THE LITERATURE

Objections to Deposition Tests

In the past, more investigators have favored deposition type testing than redeposition testing. In deposition tests, the amount of soil in suspension can be controlled as well its type and particulate size. However in redeposition tests, the suspended soil load is a variable and dependent on the deterging efficiency of the surfactant and the nature of the soil. Some of the most recent studies have found considerable fault with deposition testing. Hensley (4) does not believe that the same kind of dispersion of a soil results when it is removed from a soiled fabric as when bulk soil is added to a cleaning solution. Stillo and Kolat (6) pointed out that the unrealistic conditions employed in deposition tests exaggerate the effect of an anti-redeposition agent, whose major action is on the soil. Hensley (4), using deposition tests, showed that polyvinyl alcohol and polyvinylpyrrolidone were much superior to sodium carboxymethyl cellulose (CMC) and a polyethylene glycol in improving whiteness retention. However, in redeposition tests only CMC was shown to be effective. He obtained further contradictory results in this study using various builders.

Perry and Schwartz (5) states that all the commonly used alkaline builders tend to increase soil redeposition in soft water. Hensley, above, pointed out that this statement by Perry and Schwartz was based on deposition tests and that he and his co-workers had obtained beneficial

results with redeposition tests. Smith, Wentz, and Martin (2), working with some 44 commercial detergents, showed conclusively that graying was much more severe in redeposition tests despite the fact that the equilibrium soil-concentration was 35% greater in related deposition tests.

Soils for Testing

Although there is no such thing as a standard natural soil, most detergency evaluations of this nature are based on artificial soils. The artificial soils which have been used in testing fabric detergency vary quite widely in composition, and in some instances, there is a large element of arbitrariness in their formulation.

Griesinger and Nevison (7) have reported that laboratory results from a simple vegetable oil-mineral oil-carbon soil can be correlated with practical results. Wagg (8) found that a high content of free fatty acid in an artificial soil based on oil and carbon will afford realistic results. Studies made using a mixture of street dirt, household dust, and air conditioner filter dirt were done by Sanders and Lambert (9). A test soil made up of carbon black and various types of proteins was used by Tomiyama and Iimori (10). Commercially available soiled cotton fabrics can be used for redeposition testing and are described by Harris (11).

Wagg (8) said that the nature of the soiling material was a most important factor contributing to the agreement between laboratory tests and laundry trials. He developed a soiling mixture with the oily component of which was formulated to give an analysis approximating that of natural soiling. Martin and Davis (12) objected to the use of

carbon black and graphite in soil redeposition studies because of lack of evidence that either material occurs to any significant extent in normal clothes soil. Their studies showed that clay was a better model soil, for it seemed to be the predominant particulate soil present.

Methods of Measurement

Nearly all reports of soil removal and redeposition have been based on the use of reflectance measurements to determine the amount of soil on a substrate. Small differences are readily detectable. The simplest method for measuring the results has been to show a change in per cent reflectance. In most cases the Y-tristimulus reflectance, which is related to lightness-darkness of a sample, has been used.

Kubelka and Munk (13) in 1931 developed a basic formula relating reflectance to the pigment content or concentration.

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

where

K = coefficient of reflectivity

S = coefficient of light scattering

R = observed reflectivity for monochromatic light

Harris et al. (14) and Martin and Davis (12) experimentally reaffirmed the Kubelka-Munk equation showing it to be essentially a linear function of soil concentration.

The application of this formula to the evaluation of detergency test swatches has been suggested by many. To calculate the per cent

soil removal from a soiled fabric, Bacon and Smith (15) applied it in the following form:

$$\% \text{ soil removal} = \frac{K/S \text{ for soiled fabric} - K/S \text{ for washed fabric}}{K/S \text{ for soiled fabric} - K/S \text{ for unsoiled fabric}} \times 100$$

Their equation for detergency was

$$S = K(CFT)^n$$

where

S = per cent soil removal

K = a constant

n = constant slope

C = concentration

F = force applied

T = time

In further work (16) they developed still another formula.

The reflectance of soiled cloth was correlated to the amount of soil present by Reich et al. (17) in the following equation:

$$\log \left[(1-R)^2 - (1-R')^2 \right] = n \log G + \text{Constant}$$

where

R = reflectance of soiled cloth

R' = reflectance of clean cloth

G = amount of soil present

n = slope

They reported that in most instances the slope was equal to one and

the equation merely became the Kubelka-Munk. The Bayley-Weatherburn equation (18) was strictly related to deposition. Suspending power, which is related to deposition, was estimated as follows:

$$\text{suspending power} = \frac{B_s - B_w}{B_o - B_w} \times 100$$

where

B_s = reflectance of deposition sample with a surfactant present

B_w = reflectance of deposition sample without a surfactant present

B_o = reflectance of unsoiled sample

Costanza (19), using three reflectance methods, investigated the ability of dyed carpet fibers to retard or hide soil. The first method made use of the Hunter-Scofield color difference formula. The second method utilized the Y-tristimulus reflectances in the following equation:

$$\text{apparent soil} = \frac{(1-R_{\text{soiled}})^2}{2R_{\text{soiled}}} - \frac{(1-R_{\text{unsoiled}})^2}{2R_{\text{unsoiled}}}$$

The third method employed the monochromatic filter close to the dominant wave length of the color in the same equation. This method proved to be the best for reducing the effect of colors.

Martin and David (12) (20) developed a test for soil removal called the "Soil Index." This test involved taking the reflectance of the residue on a filter paper after a constant volume of the wash liquor had been filtered. This reflectance value decreases proportionally with the quantity of soil in the liquor. With a known amount of

suspended soil in the liquor before testing, the amount removed by deposition was also estimated.

Several investigations (4) (20) were based on turbidimetric analysis. The soil concentration was calculated after measuring the transmittance of the suspension with a spectrophotometer. Again both soil removal and soil deposition were evaluated in this manner. Weeks et al. (14) also used turbidimetric analysis. They, however, had a different approach. They dissolved the fabric away then determined the amount of soil on it turbidimetrically.

In Martin and Davis's second work, already referenced, they were able to determine the amount of clay deposited by comparing the weight of clay residue before and after testing by evaporating aliquots of each bath to dryness. A more sophisticated method of measurement was that of Hensley et al. (21). They used soils tagged with radioactive isotopes to determine both soil removal and redeposition. Another highly sophisticated method (22) used fluorescent spectroscopy to detect the amount of soil on fabrics.

Influences on Redeposition

There are a large number of variables and possible interactions in aqueous systems containing surfactants, inorganic builders, particulate soils, multi-fiber fabrics, and antiredeposition additives. The two most important variables which are a function of dynamics are impact and friction (23). These generate high liquid velocities within the fabric which flush the soil released by the detergent and help keep it from being attached again to acceptor sites.

The redeposition and retention of soil on fabrics is influenced

by mechanical, chemical, and electrical forces (24). The first includes macro-occlusion, entrapment in interyarn spaces, and micro-occlusion, entrapment in fiber surface irregularities. Ionic effects and coordinate bonding, particularly hydrogen bonding account for important chemical forces. Electrical forces which cause attraction of soil for the substrate may be electrostatic, in which soil for substrate attraction is considerable, and results from dissimilarity of charge; van der Waal's or coulombic forces, which operate within molecular ranges; and electrokinetic forces largely associated with the double layer surrounding soil and substrate in aqueous systems (25).

The size of soil particles has a great influence on soil removal and redeposition. Soil particles range from 50 microns and smaller (26). Coarser particles are easier to remove than fine ones; particle release becomes more difficult as their diameter becomes less than 0.2 microns. As previously referenced, particles 2 microns and smaller are responsible for most redeposition. Demonstrating the importance of overall size, Reich (27) found that deflocculation was a controlling factor in preventing redeposition.

Soil redeposition is caused primarily by the presence of calcium and magnesium cations in natural waters and to a lesser degree by the relatively high concentration of sodium ions introduced with the washing composition. A most important function of builders in the washing process is to suppress the effect of calcium or magnesium ions. Use of inorganic electrolytes offers important detergency advantages but can cause an increase in soil redeposition (28, 29, 30, 31).

Ross et al. (31) and others (32, 25) found that when builders

were used in hard water, the observed minima in deposition (or maxima in whiteness of the swatch) were a consequence of the stoichiometric titration to form the Ca or Mg complex followed by the normal increase in deposition due to added sodium ions. Much information can be found in the literature concerning effects of builders. A good summary was presented by Powney and Noad (29). They found considerable differences in the effects produced by electrolyte builders upon the stability of soil suspensions. They found that the order of increasing effectiveness of the builders studied was sodium carbonate < sodium hydroxide-Na Cl < water < sodium metasilicate < trisodium (mono-di-ortho) phosphate < sodium oleate < hexametaphosphate plus sodium carbonate < tetrasodium pyrophosphate < sodium hexametaphosphate. Redeposition increases with increasing cation concentration and valence (30, 31). The effect can be minimized by choice of an anion and by use of monovalent metal salts.

Sodium carboxymethyl cellulose (CMC) has long been recognized and used as a redeposition inhibitor. Wagg (33), Vitale (30), and Ross (31) have demonstrated its effectiveness in reducing the electrolyte effect of detergent builders and neutral salts. It does not sequester or remove hardness ions to any marked degree (31). Several theories have been advanced to explain the action of CMC (as well as other inhibitors). Trost (1) suggested that its action is due to an increase in the electrostatic repulsion force that normally exists between the negatively charged soil and the negatively charged fiber. The CMC increases the negative potential at the fiber and has little or no direct electrical effect on the soil. Another theory (25) suggests that a thin film of

CMC on the fiber and/or soil make it difficult for the particles to enter fiber irregularities. Stillo and Kolat (6) noted the importance of steric hindrance in preventing redeposition. Other inhibitors have also been studied by various investigators (30) (34).

Review of the literature shows that redeposition while laundering synthetics has received little attention. Compton and Hart (35) studied the redeposition propensities of nylon. Deposition studies on polyester (36) indicate that soil is more easily deposited on polyester fabrics than on cotton fabrics. It has been shown that soil attaches to fine fibers more readily than coarse ones (26). Certain finishing agents used to impart permanent press properties have been shown to aggravate soil redeposition (37).

Rhodes and Brainard (38) found that extended washing times resulted in a pronounced decrease in suspending action, which they attributed to an increase in the degree of dispersion of the soil. Soil deposition prevention may be affected by a temperature change (39). Detergent solutions generally showed lower whiteness retention while soap showed better suspending power.

"Secondary deposition" has been shown to occur when a fabric or fibers are dried (40). The amount of soil retained by the fabric or fiber substrate is enormously increased, as is the tenacity with which the soil is held.

From an extensive literature survey it is obvious that most of the work done with this problem has been with deposition testing. As pointed out, results from unrealistic deposition tests are not always the same as these from realistic redeposition tests. Also it was

shown the methods of evaluation can be improved. Information based upon detergent systems (excluding dry cleaning) using a liquor other than water appears to be nil.

CHAPTER III

INSTRUMENTATION AND EQUIPMENT

Launder-Ometer

All soil removal and redeposition testing was done on a Launder-Ometer manufactured by the Atlas Electric Devices Company. All standard wash fastness tests of the American Association of Textile Chemists and Colorists are based upon the use of the Launder-Ometer.

The operating principle of this piece of equipment is simply a constant temperature bath in which a shaft carrying up to ten pint jars and/or up to ten stainless steel quart containers rotates at 42 r.p.m., providing reproducible mechanical agitation. The actual wash liquor is contained in each container or jar. Mechanical action can be increased by adding to each container a desired number of quarter inch stainless steel balls. Electric heating coils regulate the bath temperature, giving it a range of room temperature to 200° F, with control reliability being only to 190° F. A pre-heating tray preconditions containers to the proper temperature by means of a circulating system integral with the bath.

Preliminary work indicated that the pint jars could not be used under the conditions of this research. Soiled samples showed considerable unevenness in the amount of soil removed. This caused error in the evaluation of results. This unevenness was due to folds and creases in the samples caused by lack of mobility within the small volume. For

this reason all subsequent tests made use of the quart containers which provided greater free volume, more mobility, and thus even removal.

Color-Eye

All reflectance values were measured on a Signature Model Large Sphere Color-Eye, model number LSD-1, manufactured by Instrument Development Laboratories. With this instrument, the sample and standard were diffusely illuminated within an 18 inch diameter integrating sphere, with viewing about 8 degrees from the normal. It is equipped with three sources of illumination which are "A" tungsten, "C" daylight, and ultraviolet. An optional feature on the instrument used allowed a reduction of the sample and standard port to two and one-quarter inches in diameter with the Color-Eye viewing a target two inches in diameter.

This abridged spectrophotometer was designed to afford users with additional versatility of sixteen narrow band wavelength through the use of interference filters. These sixteen wavelengths run in twenty nanometer increments from 400 to 700 nanometers. In addition the Signature Model is a four filter colorimeter (X, Y, Z, and x'). The use of the x' filter gives closer matches to C.I.E. (Commission International de l'Eclairage) than is possible with a three filter colorimeter.

Hewlett-Packard Calculator

The C.I.E. recommended Friele-MacAdam-Chickering color-difference formula (41) was used in calculating all MacAdam color differences. All calculations were made using a program written for the Hewlett-Packard 9100A calculator. The size and nature of the program also required the 9101A Extended Memory, 9160A Marked Card Reader, 9120A Printer, and the

9102A Calculator Buffer. Figures 1 through 17 were drawn using a program requiring the above equipment plus the 9125A x-y plotter.

Detergent

About five pounds of Heavy Duty Laundry Detergent (DCP-2-376A) containing no optical brighteners was obtained from the Research and Development Department of Colgate Palmolive Company. The detergent had the composition as found in Table 1. The active ingredients were the first three compounds, giving the detergent an active ingredient concentration of 14%.

Table 1. Detergent Composition and Per Cent Ingredients

Composition	% Ingredient
Linear Tridecyl Benzene Sulfonate	10.0
Neodol 45-11 (C ₁₄₋₁₅ Primary Alcohol · 11 EO)	2.0
Soap (⁸⁰ /20 Tallow/coco)	2.0
Sodium Tripolyphosphate	34.0
CMC (Carboxy Methyl Cellulose)	0.5
PVA (Polyvinyl Alcohol)	0.2
Na Silicate (1:2.35 Na ₂ O : SiO ₂)	7.0
Sodium Sulfate (anhydrous)	33.5
Water	10.0
Brighteners (omitted)	(0.8)
	100.0%

Test Fabric

A study of this nature requires a fabric soiled to a uniform degree by various soil ingredients, with at least one being a particulate type. The United States Testing Company, Incorporated, Hoboken, N. J. produces a soiled fabric which meets these requirements better than any that could be produced in the allotted time in the A. French Textile Laboratory. For this reason, their Standard Soiled Cloth was used in this study.

The Standard Soiled Cloth is made from 56/52 cotton cloth called Indian Head which comes under the general heading of plain weave sheeting cloth. The cloth is processed in 18 inch widths. It is soiled by immersion in a soiling solution consisting of carbon black, vegetable oil, and mineral oil. The amount of soil is controlled by the reflectance reading on a Hunter Reflectometer, the limits for this reflectance being $25\% \pm 2\%$ relative to tristimulus green filter (Y) magnesium oxide-100%.

Immediately after the cloth passes through the soiling bath it enters a drying oven, exiting in a dry state. The cloth is then artificially aged for one week in an oven held at 140° F.

The white fabrics used in the redeposition tests consisted of 100% cotton and 50/50, 65/35, and 100/1 polyester/cotton blends. The ends and picks per inch were 96/86, 106/64, 104/68, and 112/88 respectively. Both the cotton and polyester-cotton blends contained optical brighteners as indicated by the Color-Eye and ultraviolet illumination. These brighteners were removed for the same reasons as will be indicated in the Procedure Section.

Chemicals

Reagent grade acetone, methanol, dioxane, and perchlorethylene were obtained from the Fisher Scientific Company. The polyethylene glycol used, had a molecular weight of 400 and was obtained from the Textile Department.

CHAPTER IV

EXPERIMENTAL PROCEDURES

Preliminary Experiments

Preliminary experiments were performed for essentially two reasons. First, a range for each of the variables time, temperature, liquor ratio, detergent concentration, and water hardness had to be determined. The Launder-Ometer is not quite the same as present day washers. Also the standard soiled fabric proved to be an extremely tough fabric to clean. Therefore, time and concentration, for example, were important variables.

The last reason was to determine what the effect would be if the detergent and/or the fabric contained optical brighteners. Because of the method of evaluation, this effect proved to be critical.

Choice of Detergent

Optical brighteners have become one of the most important components of modern laundry products. Their mechanism is as follows: Electronic excitation occurs by absorbing energy in the U.V. region between 250 and 400 nanometers, and emitting it in the visible region, generally between 400 and 500 nanometers (42). The x' and z reflectance values, two of the requirements for the color-difference formula, are taken in this region. Figures 1 and 2 are reflectance values for swatches laundered in a Sear's detergent containing brighteners, and the Colgate detergent without brighteners, respectively. It is seen that the x' and z values are higher due to brighteners. As a result they

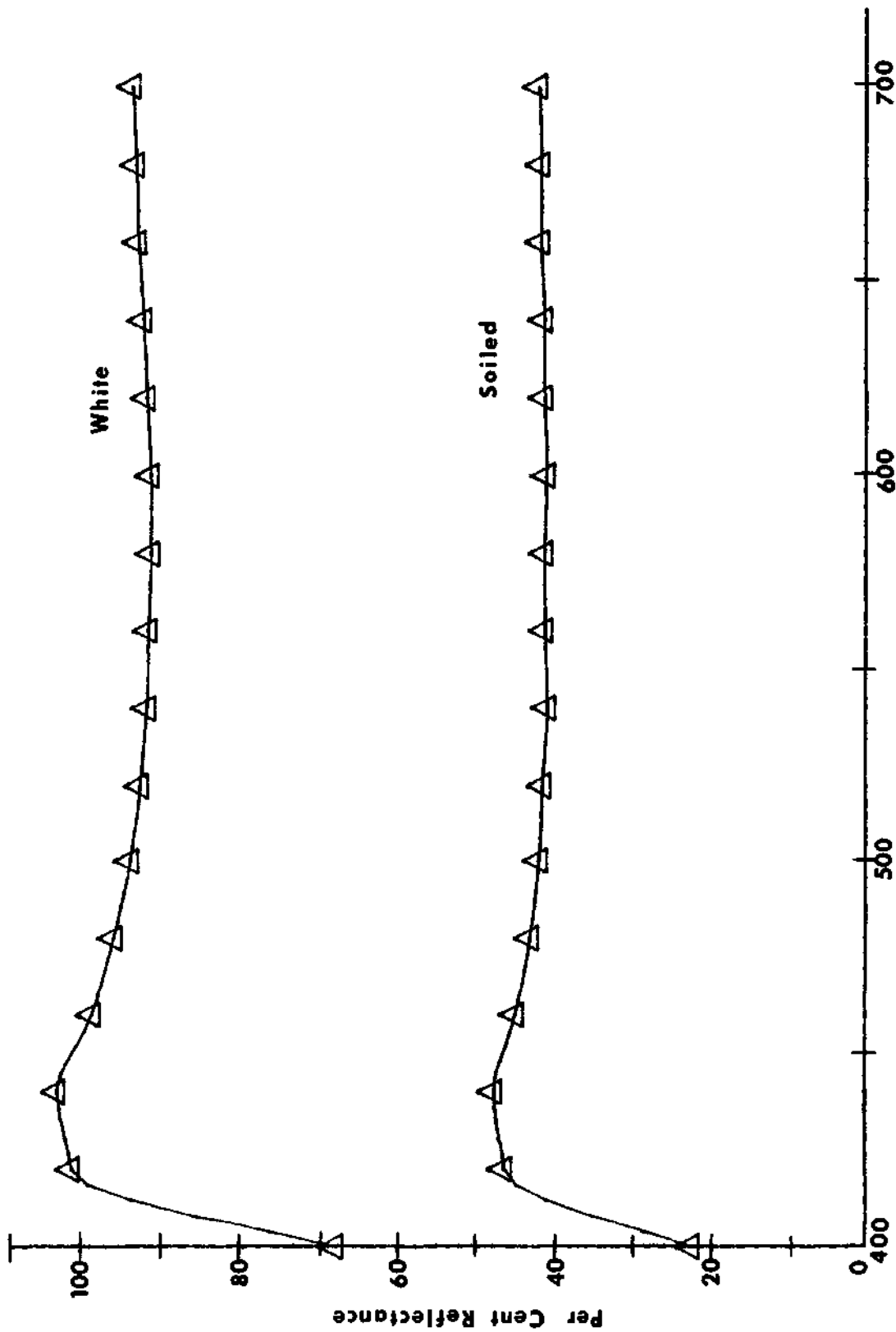


Figure 1. Effect of Optical Brighteners.

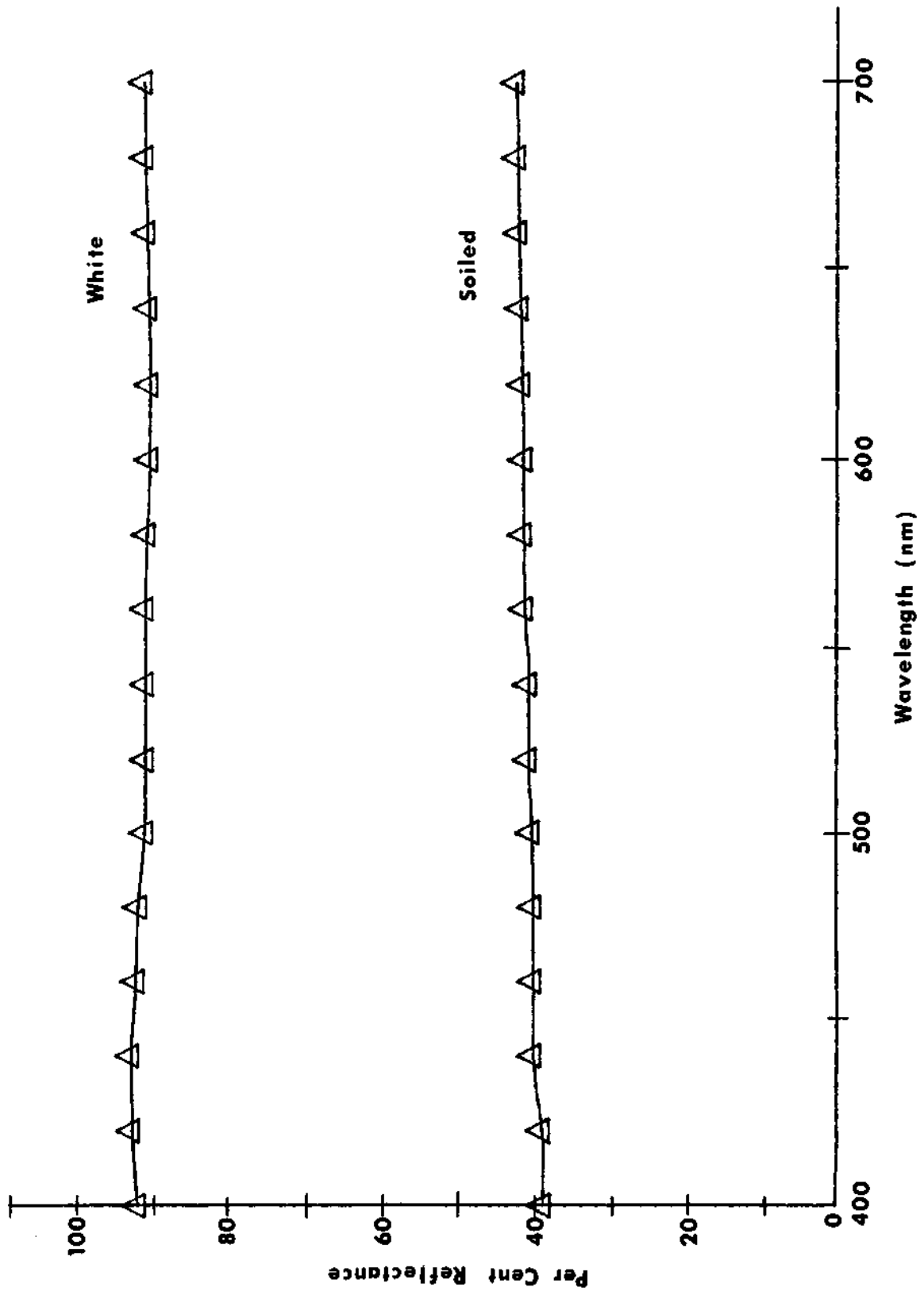


Figure 2. Effect Without Brighteners.

optically "hide" apparent soil. For this reason, brighteners could not be used with the color-difference formula.

Sample Preparation

The most commonly used cotton fabric brighteners can function as "direct" brighteners, behaving like direct dyestuffs (42). To remove them, a method recommended by Trotman (43) for stripping direct dyes from cotton was used. This method called for bleaching with a solution of sodium hypochlorite containing 1.5-2 g/liter of available chlorine. Approximately 90 grams of fabric were used per four liter volume, with the time being 45 minutes. This process was repeated as fabric was needed.

For removing the brighteners from the polyester and the polyester-cotton blends, a similar process was used. It called for boiling with 1-2% of sodium chlorite which has been brought to a pH between 3 and 4 with formic or acetic acid (43). In this case 30 gram samples were bleached in one liter baths brought to a pH of 3.5 with acetic acid. The time of the boil was 20 minutes. In both cases, proof of removal was made with the Color-Eye and U.V. illumination.

The white fabrics were cut into swatches using a 4.5" x 5" template. Each was trimmed down to 3 grams \pm .015 grams. The standard soiled fabric was cut using a 4" x 5" template and also trimmed down to 3 grams \pm .015 grams. The 3 gram size gave an area of fabric ideal for the stainless steel containers as well as for the Color-Eye viewing port.

Measuring the Reflectance of Samples

Reflectances for each and every swatch were determined before and

after each laundry cycle. Swatches were folded to give a four-fold thickness to ensure no error due to holder background. Each time reflectances were taken on the same fabric area, with the same orientation. This was achieved by notching one corner of the swatch.

The Color-Eye was calibrated according to the manufacturer's recommended procedure. Light source "C", high sensitivity and non-specular inserts were used for all measurements with "A" white vitrolite plate as the reference standard. Readings were taken to the nearest tenth of a per cent using the x' , X, Y, and Z filters.

Test Method

Preliminary experiments helped establish a range for the variables within which to work. They also helped establish the following standard from which to work:

Time - 100 minutes

Temperature - 140° Fahrenheit

Liquor Volume - 250 ml. (Liquor Ratio 42:1)

Detergent Concentration - .06%, Weight/volume active ingredients

Water Hardness - 60 ppm Ca ions

In the laundry procedure, the variable being studied was changed while the other four were held constant, based on the above so-called standard conditions. In the studies of different additives however, the temperature was elevated to 190° F, and percentages were based on volume.

The first step involved measuring out the desired volume of liquor brought to the desired hardness using a stock solution of 2740 ppm Ca^{++} , made from $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ and distilled water. To the liquor in each container were added the proper detergent concentration, ten quarter inch

stainless steel balls, one standard soiled swatch, and one white swatch. Each container was then preconditioned for 15 minutes in the pre-heating tray of the Launder-Ometer. Following this time, the containers were clamped on the rotor and laundered for the desired time.

After the run, both swatches were removed and vigorously rinsed in distilled water at a temperature of 110° F for approximately one and one-half minutes. Samples were then dried in a circulating-exhaust oven for 30 minutes at 160° F. Samples were ironed with a warm iron to remove wrinkles which might cause error. A hot iron was avoided because of the danger of scorching and yellowing.

Three tests were run under each set of conditions. This permitted an average for results and helped eliminate incorrect results due to experimental error. To develop more reliable trends, each white swatch was laundered five times, each time with a new soiled swatch. This was not necessary however, with the water soluble additives, for conclusions could be drawn quickly.

Calculation of Color-Difference

The reflectances from the Color-Eye were used to calculate ΔE , or color difference due to soil removal or soil redeposition. In each case, color difference was based on the original readings as being the standard and readings after laundering as being the sample. Using these values and a program for the CIE-recommended Friele-MacAdam-Chickering color-difference formula (41), color difference was calculated on the Hewlett-Packard 9100A calculator. This formula is:

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

where

$$\Delta C = K_1 \Delta C_1, \text{ and } \Delta L = K_2 \Delta L_2,$$

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

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

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

$$\Delta C_{yb} = \left[S\Delta L_1 / (P^2 + Q^2)^{1/2} \right] - \Delta S$$

$$\Delta L_2 = 0.279 \Delta L_1/a$$

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

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

$$a^2 = 17.3 \cdot 10^{-6}(P^2 + Q^2) / \left[1 + (2.73P^2Q^2) / (P^4 + Q^4) \right]$$

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

$$P = 0.724 X + 0.382Y - .098Z,$$

$$Q = -0.48 X + 1.37Y + 0.1276Z,$$

$$S = 0.686Z$$

X, Y, and Z are the tristimulus values for the standard, and ΔP , ΔQ , and ΔS are the differences (sample-standard) between the values P, Q, and S for two colors.

CHAPTER V

DISCUSSION OF RESULTS

In this work, the redeposition of a particulate soil on to white fabric was studied under various conditions of time, temperature, water hardness, detergent concentration, liquor ratio, fabric blends and liquor additives. The liquor additives, all water soluble, were acetone, methanol, dioxane, and a polyethyleneglycol. Redeposition, as well as soil removal, was analyzed spectrophotometrically and evaluated by use of the Friele-MacAdam-Chickering color-difference formula.

In order for the reader to clearly understand the results, he must be able to read the figures. It was seen that the color difference values were calculated in terms of ΔE . The larger the ΔE , the greater the color change based on the original sample. To understand the role of ΔE in soil removal and redeposition, look at Figure 4. With a detergent concentration of .02%, the redeposition curve shows a greater ΔE than at .20%. Therefore there is more redeposition at .02% than at .20%. Looking at the soil removal curve the larger ΔE at .20% than at .02% indicates more soil removal at the higher concentration.

To have some feel for the seriousness of redeposition when looking at certain values, comparisons can be made with Davidson's work (44), Figure 3. After some 12,000 tests of human responses with color differences, he was able to determine the size of acceptable color differences. Figure 3 is an interpretation of his results and shows what per cent of the people would accept different ΔE values.

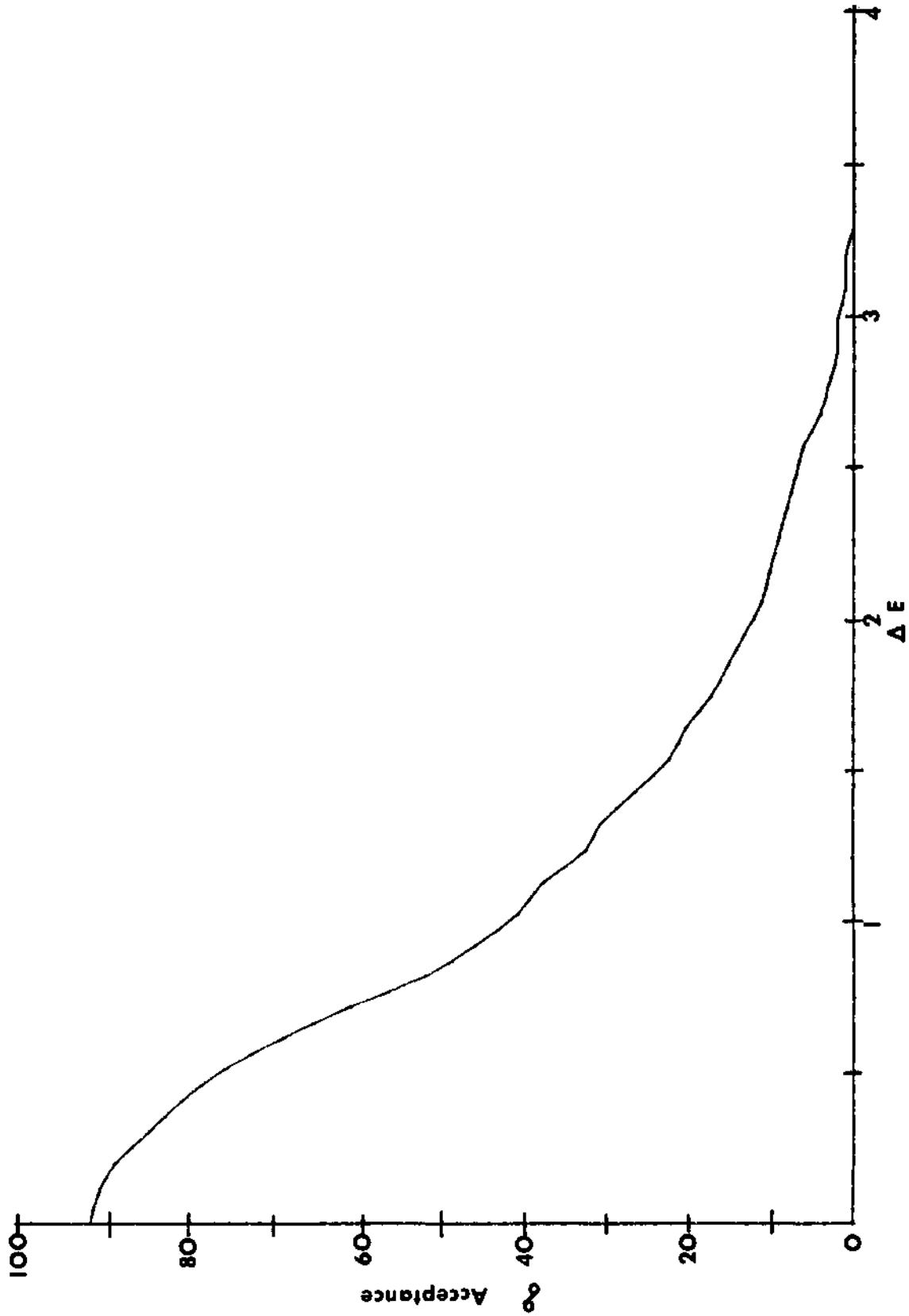


Figure 3. Per Cent Acceptance vs Color Difference, From Davidson's Work (44).

Each ΔE value for the redeposition curves in Figures 4, 5, 6, 7, and 8 is the value after the fifth wash and indicates the average amount of redeposition build up, based on three samples. Each ΔE value in these figures for soil removal is an average of soil removal, based on the three standard soiled swatches used in the first wash. This was reliable, for spot checking indicated values within the range.

Figure 4 shows that as the detergent was increased, soil removal increased. This held true up to a point, after which it leveled off. Redeposition decreased as the detergent was increased, in every case. Although more redeposition causing builders were present, so too was inhibitor. In the lowest concentrations, redeposition was very critical. Although less at the highest concentration, it was still not within a good acceptable range.

Figure 5 demonstrates that soil removal was seriously affected by water hardness, as expected. Redeposition was serious in hard water, but fairly acceptable in soft. This is in agreement with Hensley's (4) results and his statement contrary to Perry and Schwartz (5).

Figure 6 demonstrates how difficult the soiled fabric was to clean. Increased soil removal with time was as one would expect. Time increased redeposition. At the shortest time the redeposition was acceptably low but increased to severity at the longest time. This was probably due to more soil in the bath, some of which was the smaller, harder to remove particles, plus greater dispersion.

Figure 7 shows that soil was removed easiest at the highest temperatures. Redeposition was only slightly affected by an increase in temperature up to 160° . In each case however, it was severe. Con-

tradicting previous studies based on deposition (39), redeposition decreased to an acceptable degree at a higher temperature.

Figure 8 demonstrates the importance of a proper liquor ratio. Lack of liquor for high fluid velocities is clearly demonstrated. The slight decrease in removal at the greatest liquor ratio was attributed to the decrease in overall detergent concentration. Redeposition was increased as the soil became more concentrated in the smaller liquor volumes, and was very critical at these conditions. The ratios of present day washers run from 10:1 to 20:1, well within the ranges studied.

Figures 4, 5, 7, and 8 without a doubt prove that the amount of soil suspended in the liquor is not necessarily the controlling factor for good testing. In each case, the greatest redeposition occurred under conditions which caused the least soil removal hence low suspended soil in the bath.

Figures 9, 10, and 11 show the three main observed ways redeposition was built up under the studies made. Each represents a single swatch as it was traced through five washes. Figure 11 demonstrates that redeposited soil, like regular soil, can also be removed to a certain degree.

Figure 12 demonstrates that polyester was easier to build up soil redeposition than cotton. Although the redeposition on cotton was critical, it became even more critical on the all polyester fabric.

The water soluble components used in Figures 13, 14, 15, and 16 gave results which make their use as all or part of a wash liquor very unlikely with existing household detergents. The reason is obvious, a

serious decrease in soil removal. Redeposition was very small in each case, but keep in mind these results were from only one wash. This drop was not entirely due to the decrease soil in suspension. This was proven by adding two more soiled swatches to increase the soil content. Redeposition increased very slightly.

Figure 17 was plotted merely for curiosity. The results from it, although fairly good, were not unexpected, for the conditions under which the test was performed approach a dry cleaning system.

CHAPTER VI

CONCLUSIONS

Redeposition on the substrate during laundering was a real phenomenon. Its presence, when not hidden by optical brighteners, was readily detected by use of the color difference formula. This enabled comparisons to determine just how perceivable it was and how serious.

Comparisons with results from other investigators showed that deposition and redeposition tests do not always give the same results.

A system using the water soluble additives studied to reduce the pollution caused by laundering, is very unlikely unless a new detergent is formulated which will not be affected by their presence.

Redeposition occurred under all conditions studied but was reduced considerably with simple changes. Tests showed that redeposited soil has a behavior similar to ordinary soil in that both build up and each can be removed to a degree.

CHAPTER VII

RECOMMENDATIONS

Since the development of a detergent system with reusable components would be invaluable against pollution, additional work needs to be done with different possible liquors. Work should also be done in developing a workable detergent for such a system.

APPENDIX

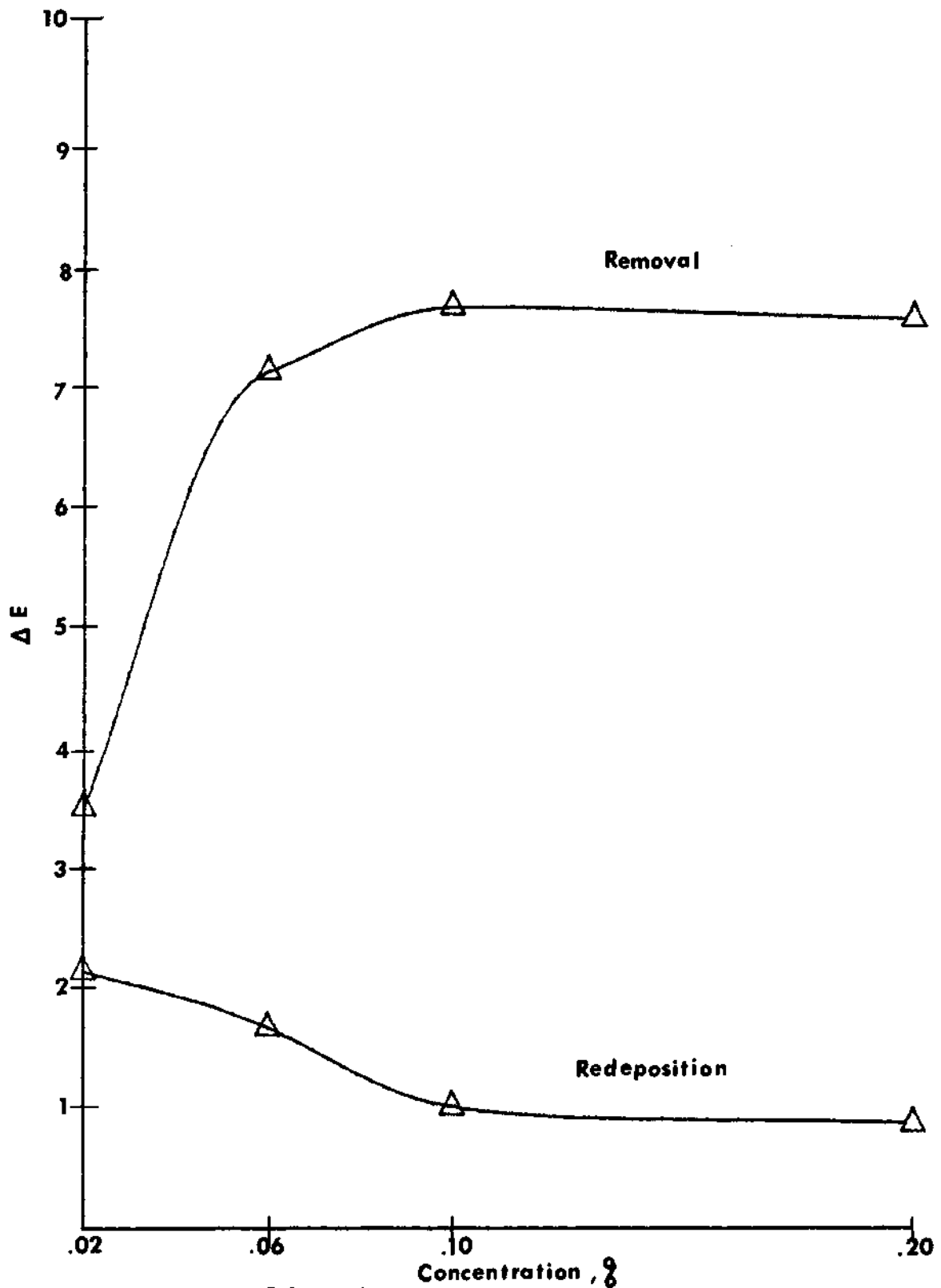


Figure 4. Effect of Detergent Concentration.

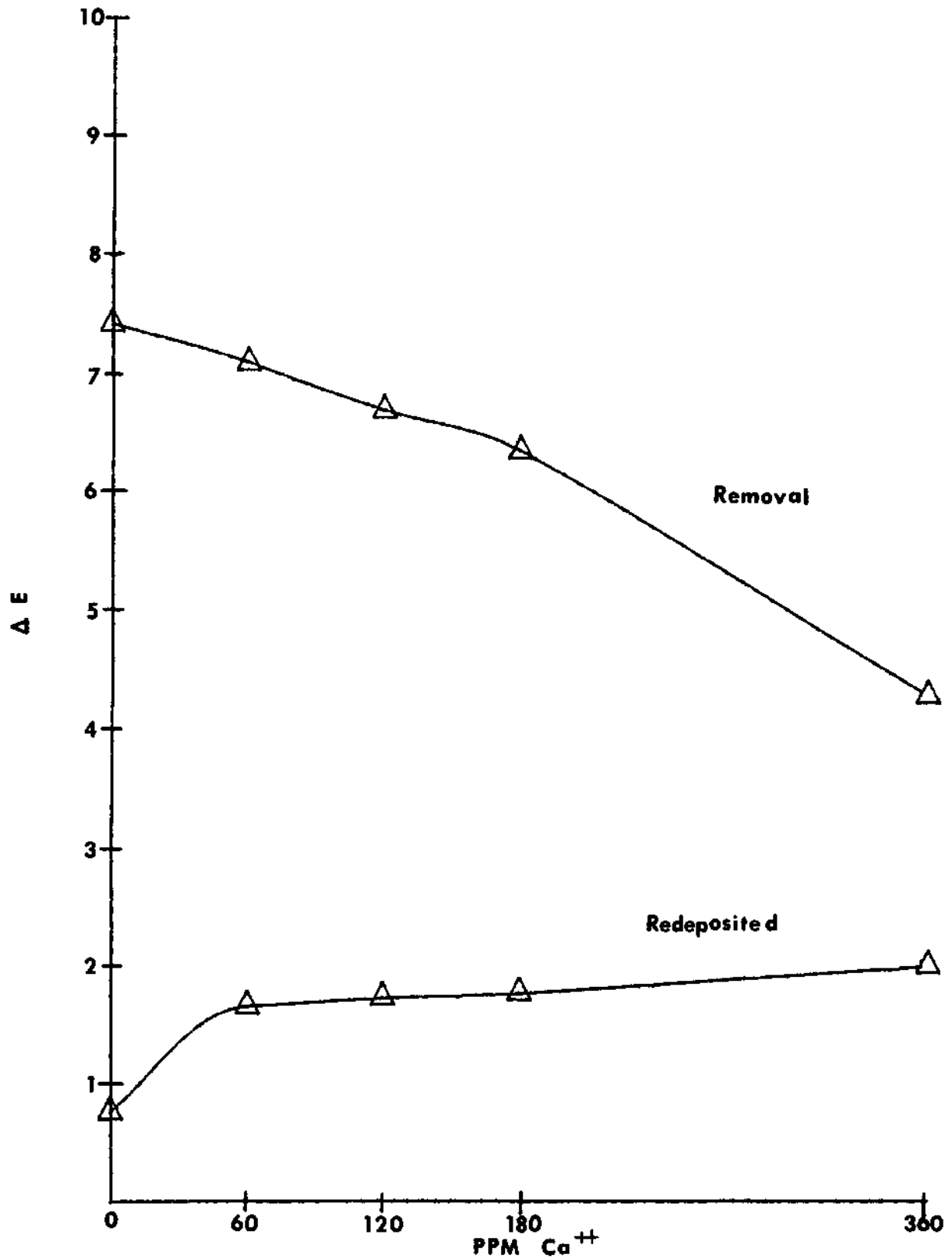


Figure 5. Effect of Water Hardness .

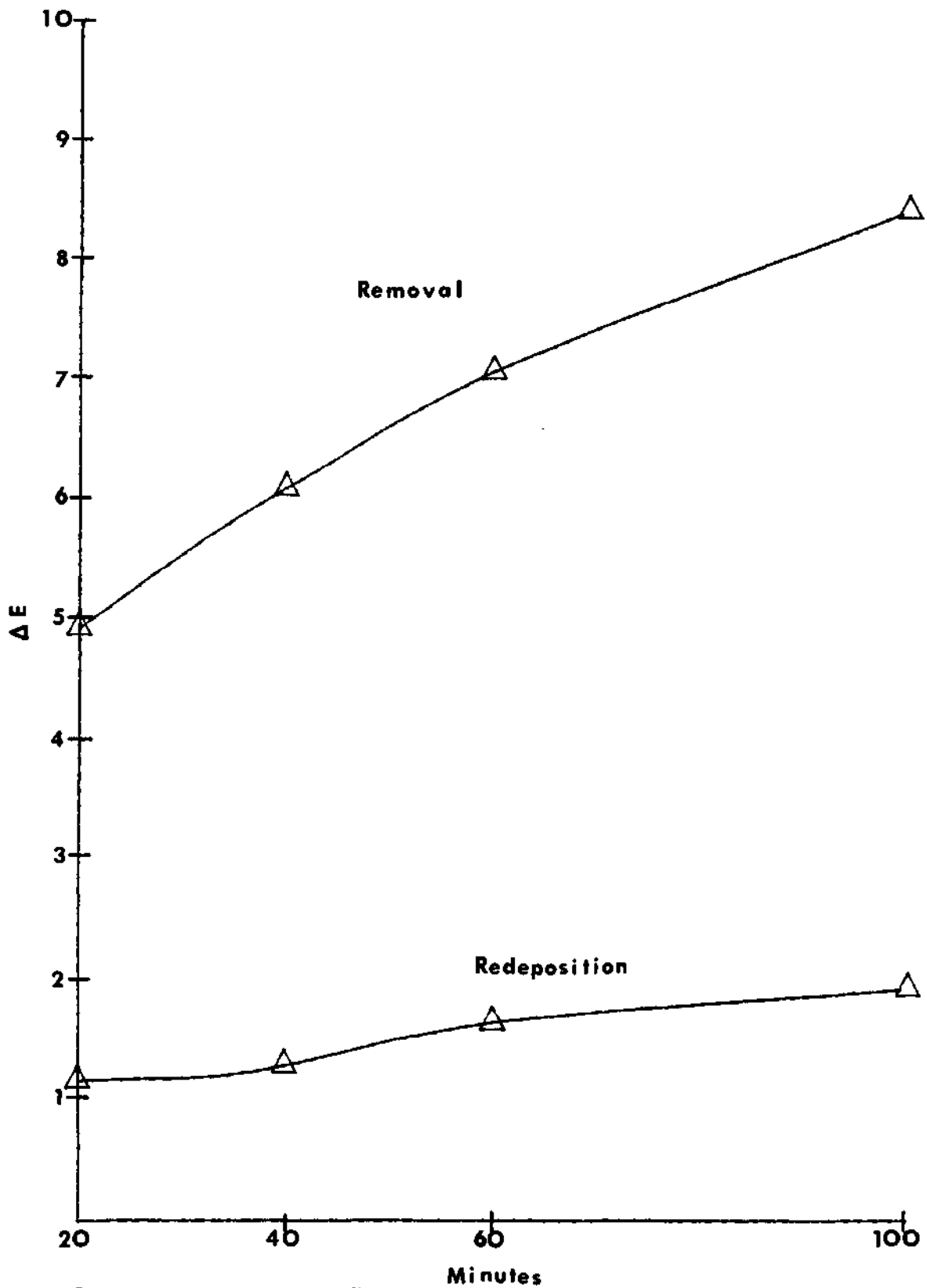


Figure 6. Effect of Time .

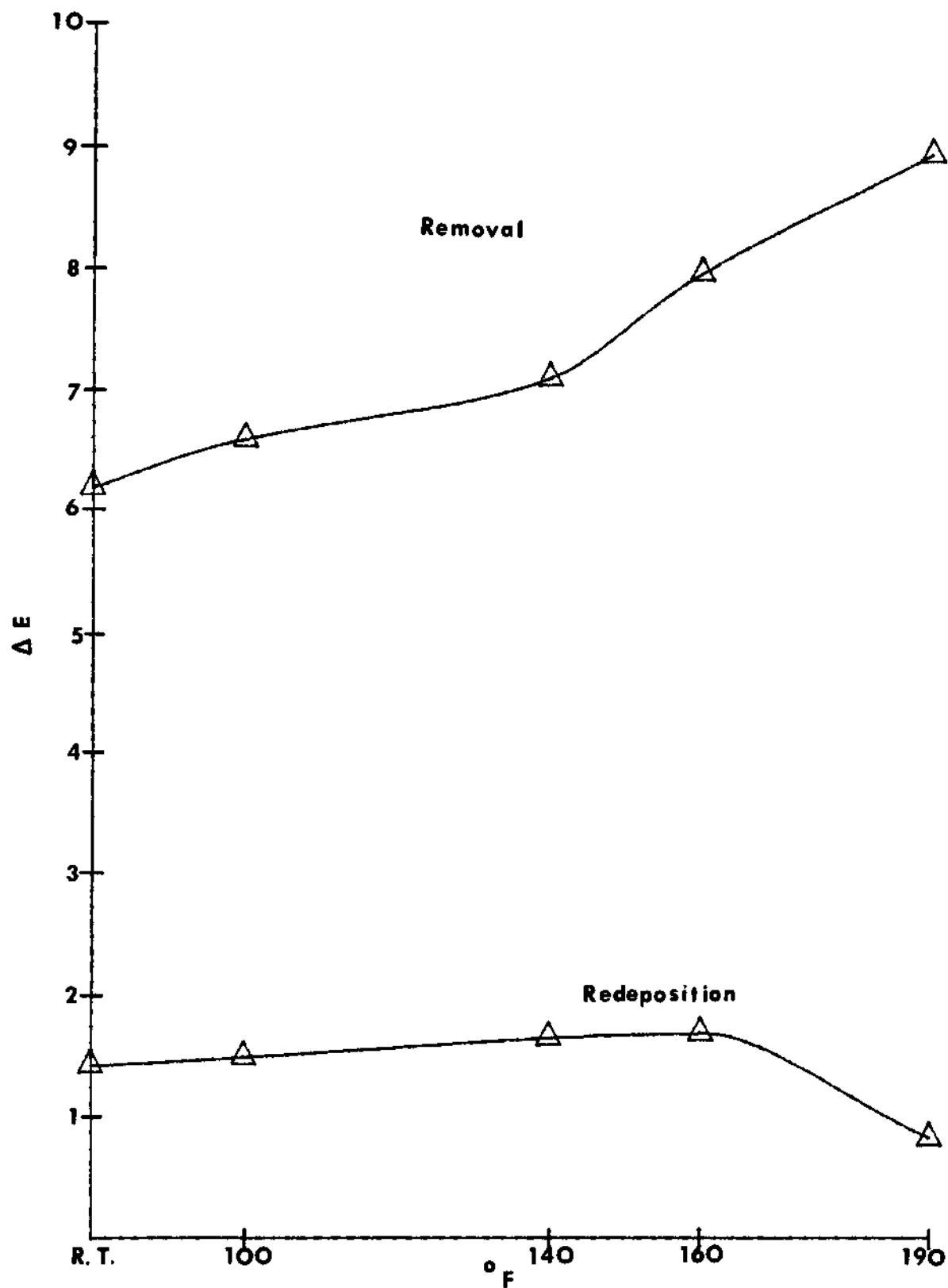


Figure 7. Effect of Temperature.

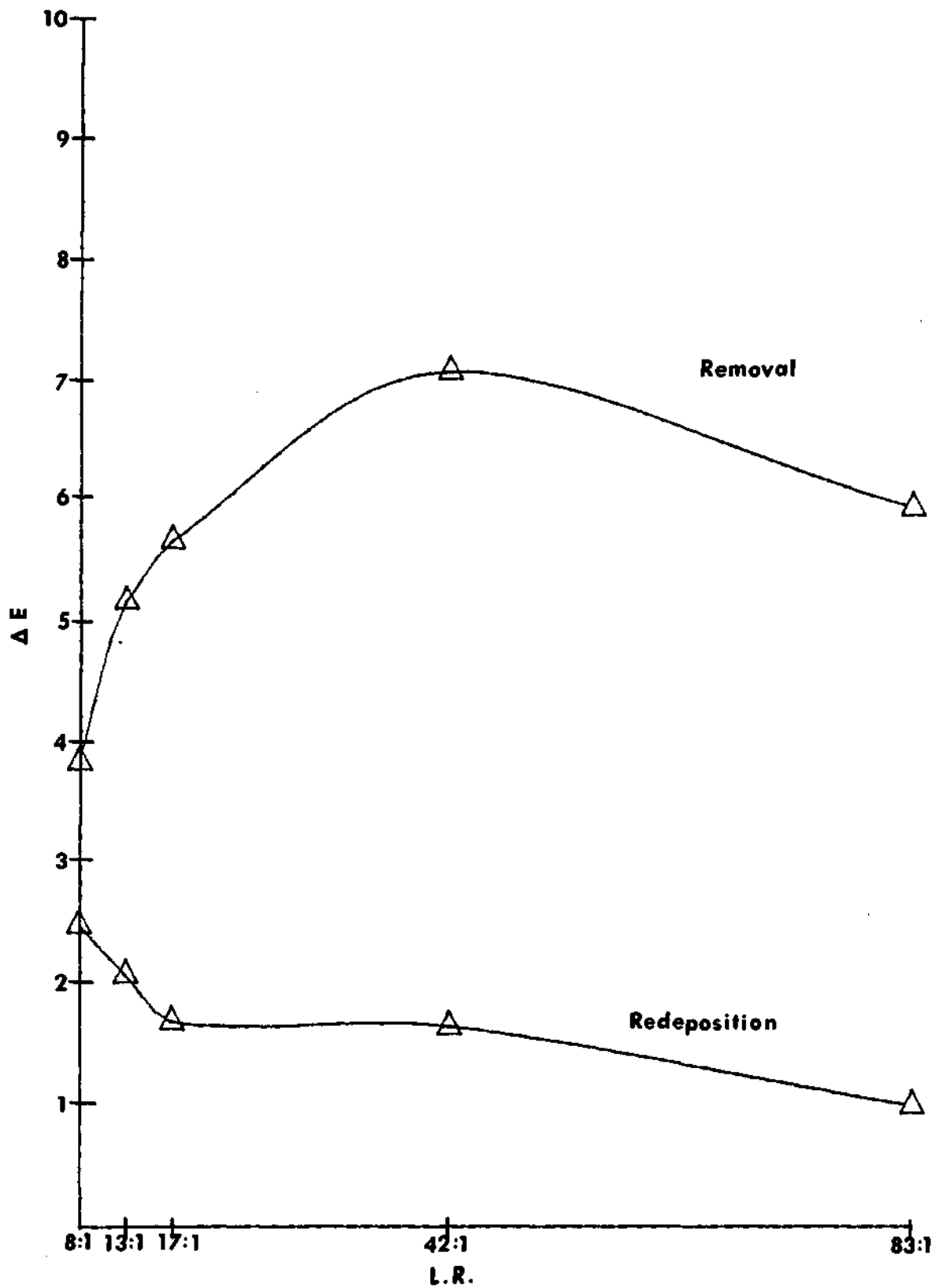


Figure 8. Effect of Liquor Ratio.

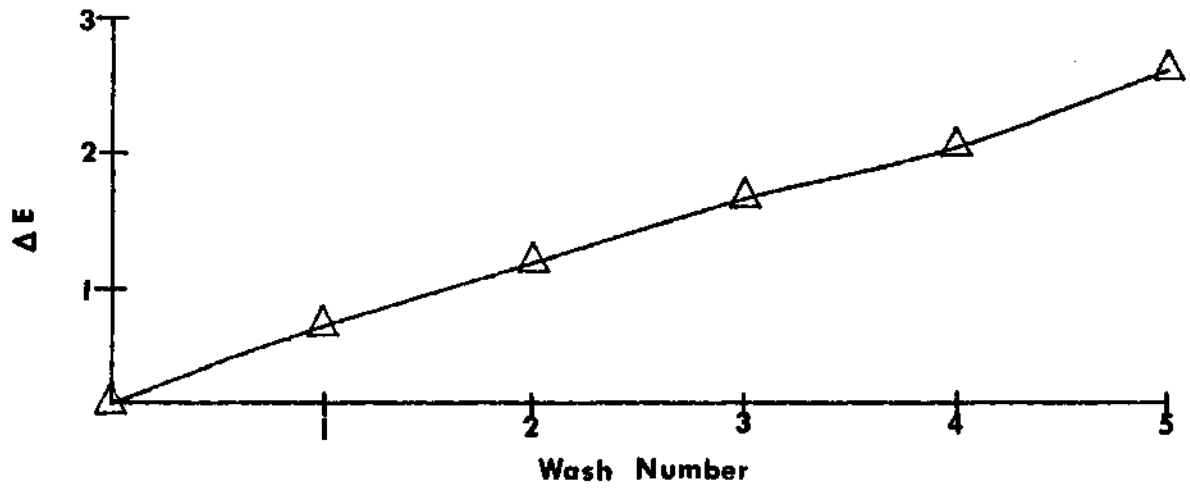


Figure 9. Redeposition Build Up - Constant.

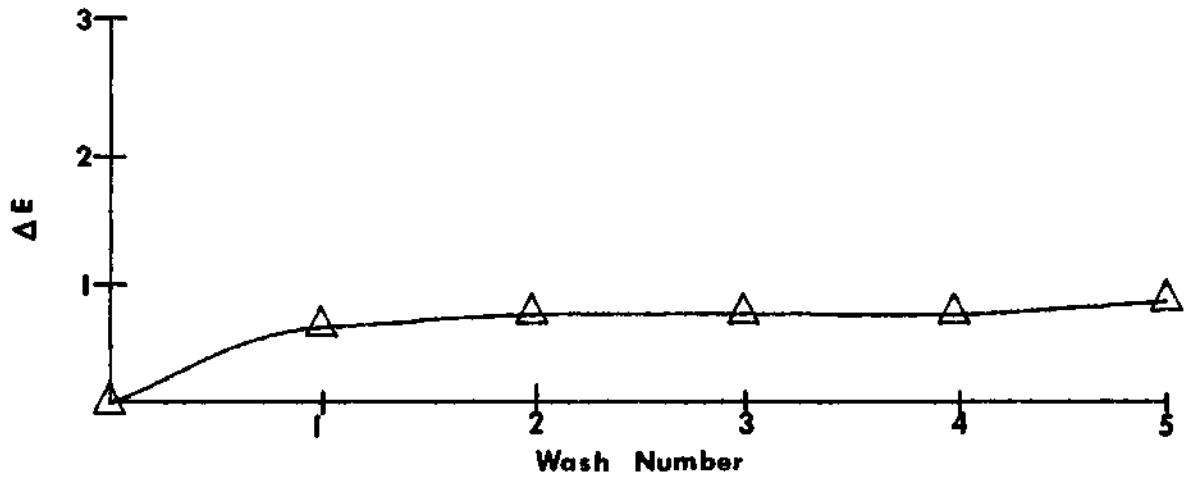


Figure 10. Redeposition Build Up - Little Change.

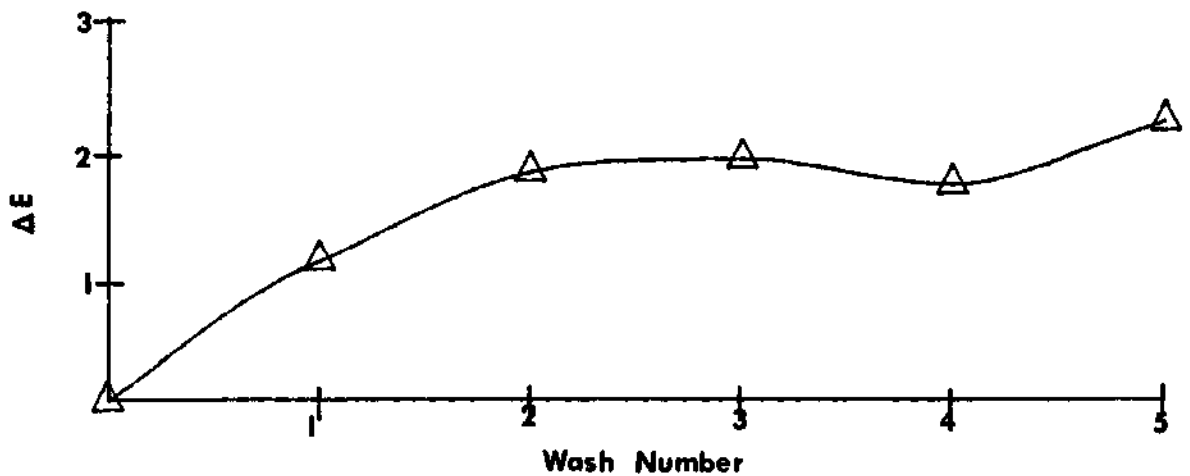


Figure 11. Redeposition Build Up - Variable.

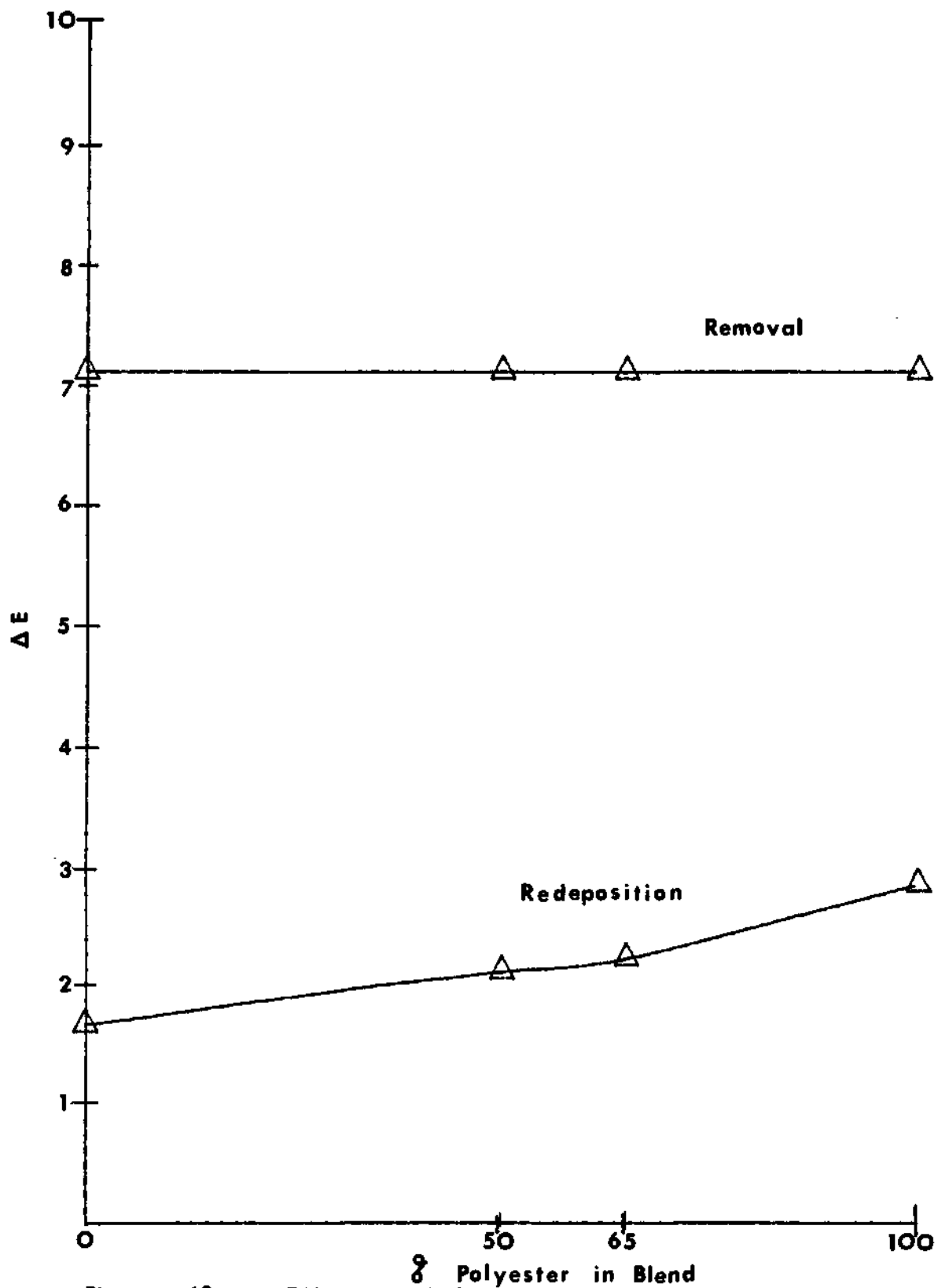


Figure 12. Effect on Polyester.

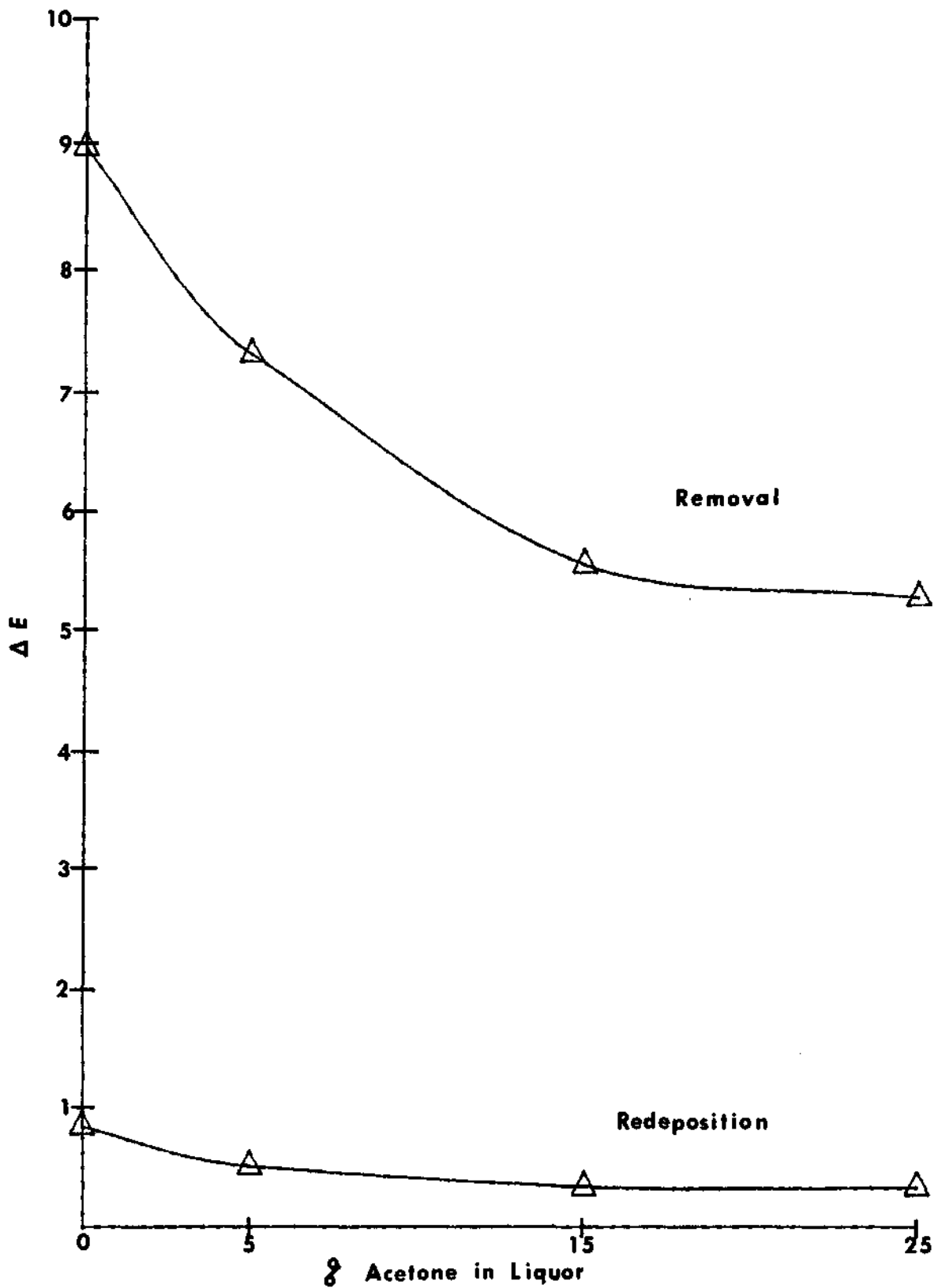


Figure 13. Effect of Acetone in Liquor.

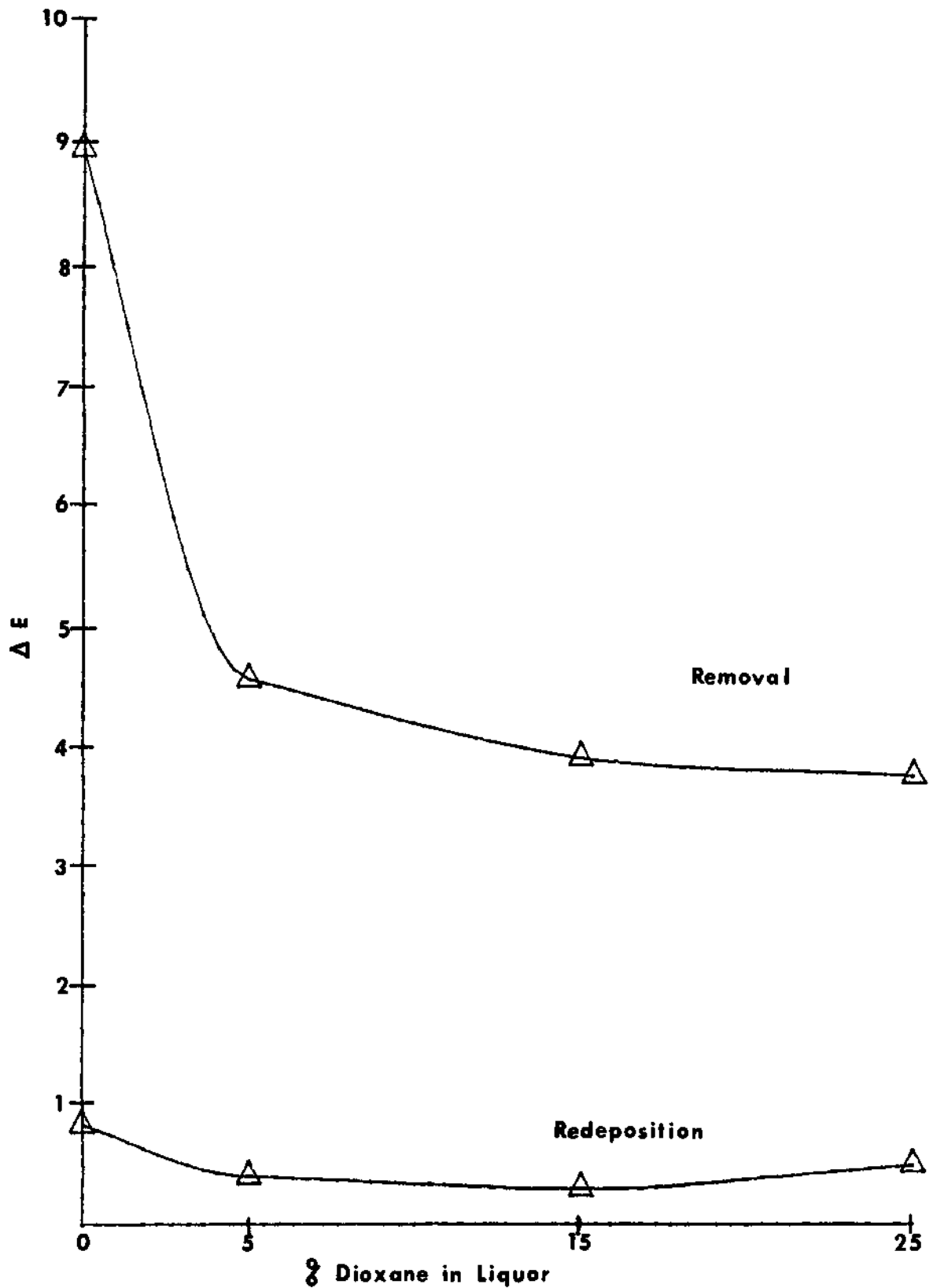


Figure 14. Effect of Dioxane in Liquor.

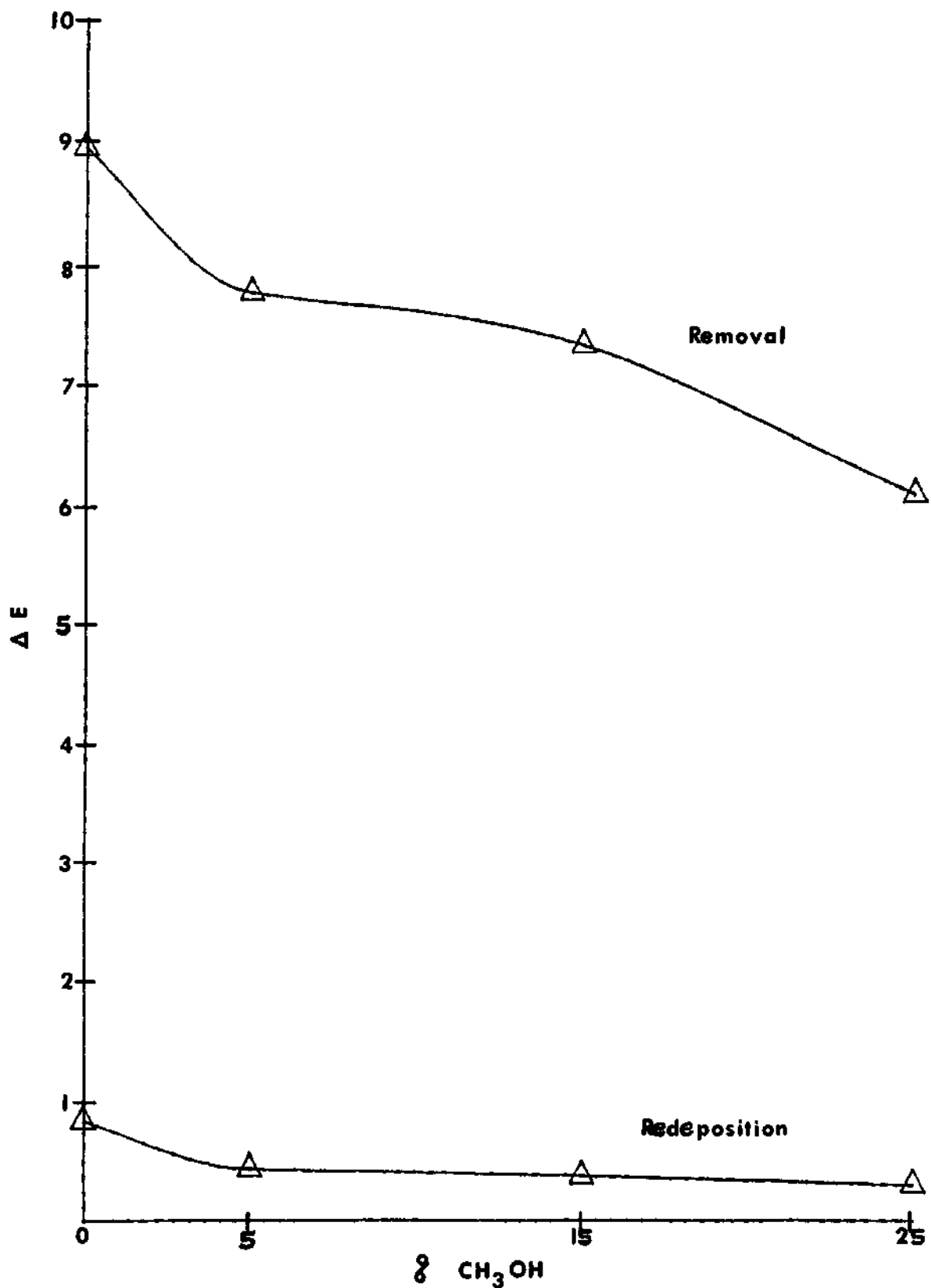


Figure 15. Effect of Methanol in Liquor.

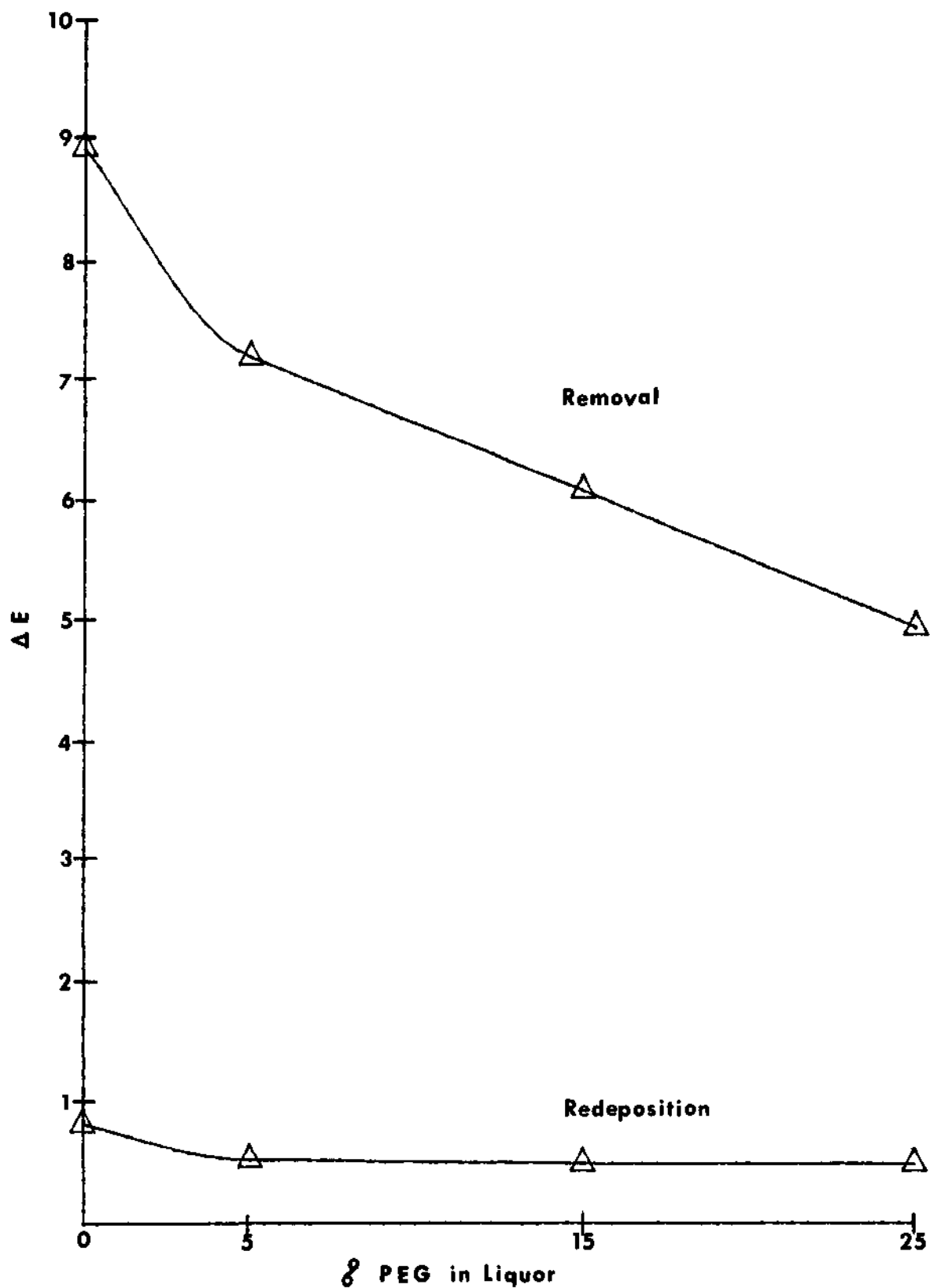


Figure 16. Effect of Polyethyleneglycol in Liquor.

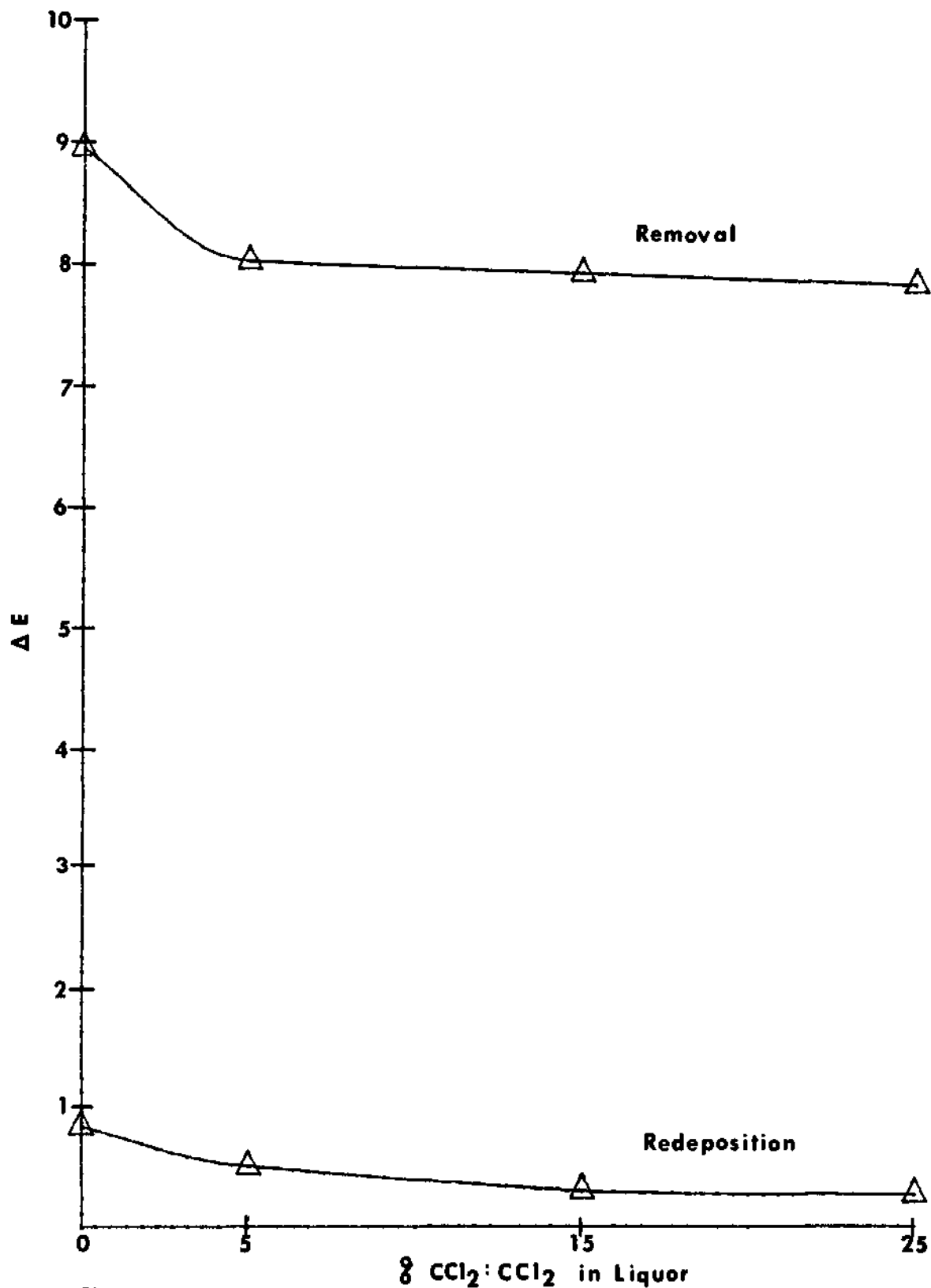


Figure 17. Effect of Perchlorethylene in Liquor.

BIBLIOGRAPHY

1. Trost, H. B., J. Amer. Oil Chem. Soc., 40, 669-674, (1963).
2. Smith, William H., Wentz, Manfred, Martin, Albert R., J. Amer. Oil Chem. Soc., 45, 83-86, (1968).
3. Powe, W. C., Text. Research J., 29, 879, (1959).
4. Hensley, James W., J. Amer. Oil Chem. Soc., 42, 993-997, (1965).
5. Schwartz, A. M., Perry, J. W., Berch, J., "Surface Active Agents and Detergents," Interscience Publishers, Inc., New York, P. 509 (1958).
6. Stillo, H. S., Kolat, R. S., Text. Research J., 27, 949, (1957).
7. Griesinger, W. K., Nevison, J. A., J. Amer. Oil Chem. Soc., 27, 96-100, (1950).
8. Wagg, R. E., J. Text. Inst., 43, T515-T516, (1952).
9. Sanders, H. L., Lambert, J. M., J. Amer. Oil Chem. Soc., 27, 153-9, (1950).
10. Tomiyama, S., Iimori, M., J. Amer. Oil Chem. Soc., 46, 357-359, (1969).
11. Harris, J. C., "Detergency Evaluation and Testing," Interscience Publishers, Inc., New York, p.83, (1954).
12. Martin, Albert R., Davis, Richard C., Soap Chem. Spec., 36, 79, (1960).
13. Kubelka, P., Munk, F., Z. tech. Physik., 12, 593, (1931).
14. Harris, J. C., Sullivan, M. R., Weeks, L. E., Industrial Eng. Chem., 46, 1942, (1954).
15. Bacon, O. C., Smith, J. E., Industrial Eng. Chem., 40, 2361-70, (1948).
16. Bacon, O. C., Smith, J. E., Amer. Dyestuff Rep., 43, 619-622, (1954).
17. Reich, Irving, Snell, Foster Dee, Osipow, Lloyd, Industrial Eng. Chem., 45, 137-141, (1953).

18. Bayley, C. H., Weatherburn, A. S., Text. Research J., 20, 510 (1950).
19. Costanza, Peter A., Text. Research J., 41, 134-138, (1971).
20. Martin, Albert R., Davis, Richard C., Soap Chem. Spec., 36, 49-52, (1960).
21. Hensley, J. W., Kramer, M. G., Ring, R. D., J. Amer. Oil Chem. Soc., 32, 138, (1955).
22. Richards, Susan, Morris, Mary Ann, Arkley, Thomas, H., Text. Research J., 38, 105-107, (1968).
23. Wollner, H. J., Soap Sanitary Chemicals, 26, 69, (1950).
24. Snell, F. D., Snell, C. T., Reich, I., J. Amer. Oil Chem. Soc., 27, 62, (1950).
25. Harris, Jay C., Text. Research J., 29, 99-117, (1959).
26. Leonard, E. A., Amer. Dyestuff Rep., 41, 323, (1952).
27. Reich, I., Ph.D. Dissertation, University of Southern California, June, (1956).
28. Fong W., Lundgrew, H. P., Text. Research J., 23, 769, (1953).
29. Powney, J., Noad, R. W., J. Text. Inst., 30, T157, (1939).
30. Vitale, Peter T., J. Amer. Oil Chem. Soc., 31, 341-344, (1954).
31. Ross, J., Vitale, P. T., Schwartz, A. M., J. Amer. Oil Chem. Soc., 32, 200-204, (1955).
32. Rutkowski, Beverly J., Martin, Albert R., Text. Research J., 31, 892-898, (1961).
33. Wagg, R. E., J. Text. Inst., 43, T325, (1952).
34. Fong, W., Ward, W. H., Text. Research J., 24, 881, (1954).
35. Hart, W. J., Compton, Jack, Text. Research J., 23, 164-167, (1953).
36. Shimauchi, Shiro, Mizushima, Haruo, Amer. Dyestuff. Rep., 57, 462-467, (1968).
37. Aliman, W. T., Dunlap, Robert K., Zybko, W. C., Amer. Dyestuff Rep., 57, 1086, (1968).
38. Rhodes, F. H., Brainard, S. W., Industrial Eng. Chem., 21, 60, (1929).

39. Vaughn, T. H., Smith, C. E., J. Amer. Oil Chem. Soc., 26, 733, (1949).
40. Institute of Text. Tech., Text. Research J., 24, 263-264, (1954).
41. Billmeyer, F. W., Smith, Roger, Color Eng., Nov.-Dec., 28-29, (1967).
42. Stensby, P. S., Soap Chem. Spec., 43, 41, (1967).
43. Trotman, E. R., "Dyeing and Chemical Technology of Textile Fibers," 3rd Edition, pp. 390-391, Charles Griffin and Co., Ltd., (1964).
44. Davidson, Hugh R., J. Optical Soc. Amer., 43, No. 7, 581-589, (1953).