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I am submitting herewith a dissertation written by Billie Jean Walters entitled "Formaldehyde Release from Durable Press Shirting Fabrics." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Home Economics.

Charles J. Noel

Charles J. Noel, Major Professor

We have read this dissertation
and recommend its acceptance:

Tyrone L. Vigo

M. H. Lietz

D B Easterwood

Accepted for the Council:

L. Evans Roth

Vice Chancellor
Graduate Studies and Research

FORMALDEHYDE RELEASE FROM DURABLE PRESS SHIRTING FABRICS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Billie Jean Walters

June 1981

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ABSTRACT

The objectives of this work were to determine the level of formaldehyde release from durable press consumer products, and to compare existing test methods for evaluation of formaldehyde release and content. Men's durable press dress shirts were purchased and analyzed for formaldehyde content and release, initially and after selected laundering intervals. Three different shirting fabrics were tested: 100% cotton, 60% cotton/40% polyester, and 65% polyester/35% cotton.

The shirting fabrics were analyzed for total formaldehyde, free formaldehyde, and formaldehyde in methylol groups. No free or methylol formaldehyde was detected by the analytical methods employed. Total formaldehyde ranged from 4,000 to 13,000 ppm. Very little of the total formaldehyde was released in tests designed to evolve hydrolyzable formaldehyde from durable press fabrics. The two standard tests for formaldehyde evaluation, the Japanese test and the AATCC test, were performed to assess the effect of laundering on formaldehyde release. The greatest amount of formaldehyde was released from unwashed fabrics; thereafter, the fabrics quickly reached a limiting value for formaldehyde release, which was unaffected by further washing.

The two test methods for formaldehyde evolution as well as two different colorimetric procedures for formaldehyde determination, were compared. The two test methods differed significantly only at low levels of formaldehyde release. There were also significant differences

between the two procedures for formaldehyde determination (acetylacetone and chromotropic acid). The latter method, CTA, proved to be more precise, perhaps because absorbance values for this reagent were in the range of minimum error.

Further comparison between the Japanese and AATCC tests was made by determining activation energies for the evolution of formaldehyde from the 100% cotton shirting fabrics. These activation energies were 21.0 kcal and 15.8 kcal respectively.

TABLE OF CONTENTS

CHAPTER		PAGE
1.	INTRODUCTION	1
	Definitions	3
	Objectives of the Study	4
	Assumptions	4
	Limitations	5
2.	REVIEW OF LITERATURE	6
	Development of Durable Press Finishes	6
	Reaction and Hydrolysis Mechanisms	9
	Testing for Formaldehyde and Formaldehyde Release	15
	Formaldehyde as a Consumer Issue	22
3.	PROCEDURE	27
	Shirting Fabrics	27
	Laundering	28
	Formaldehyde Analysis	28
	Physical Tests	33
	Data Analysis	33
4.	RESULTS AND DISCUSSION	35
	Shirting Fabrics	35
	Formaldehyde Content	35
	Formaldehyde Release	37
	Regression Analysis	39
	Physical Properties	58
	Comparison of Test Methods	58
	Determination of Temperature Coefficients	66
5.	SUMMARY AND CONCLUSIONS	71
LIST OF REFERENCES		75
VITA		83

LIST OF TABLES

TABLE		PAGE
1.	Descriptive Properties of Shirting Fabrics	36
2.	Formaldehyde in Shirting Fabrics	38
3.	Exponential Regression Model Values (Standard Error of Estimation)	41
4.	Physical Properties of Shirting Fabrics	59
5.	Linear Regression Values for Wrinkle Recovery Angle (Standard Error of Estimation)	60
6.	Analysis of Variance for Test Methods on 100% Cotton Shirts	62
7.	Analysis of Variance for Test Methods on 60% Cotton/ 40% Polyester Shirts	63
8.	Analysis of Variance for Test Methods on 65% Polyester/ 35% Cotton Shirts	64
9.	Coefficients of Variation for Formaldehyde Analyses	65
10.	Temperature Coefficients for Formaldehyde Evolution from 100% Cotton Fabric (Standard Error of Estimation)	70

LIST OF FIGURES

FIGURE		PAGE
1.	Total Formaldehyde in 100% Cotton Shirts	42
2.	Total Formaldehyde in 60% Cotton/40% Polyester Shirts	43
3.	Total Formaldehyde in 65% Polyester/35% Cotton Shirts	44
4.	Formaldehyde Extracted from 100% Cotton Shirts (Acetylacetone Analysis)	45
5.	Formaldehyde Extracted from 60% Cotton/40% Polyester Shirts (Acetylacetone Analysis)	46
6.	Formaldehyde Extracted from 65% Polyester/35% Cotton Shirts (Acetylacetone Analysis)	47
7.	Formaldehyde Extracted from 100% Cotton Shirts (Chromotropic Acid Analysis)	48
8.	Formaldehyde Extracted from 60% Cotton/40% Polyester Shirts (Chromotropic Acid Analysis)	49
9.	Formaldehyde Extracted from 65% Polyester/35% Cotton Shirts (Chromotropic Acid Analysis)	50
10.	Formaldehyde Released from 100% Cotton Shirts (Acetylacetone Analysis)	51
11.	Formaldehyde Released from 60% Cotton/40% Polyester Shirts (Acetylacetone Analysis)	52
12.	Formaldehyde Released from 65% Polyester/35% Cotton Shirts (Acetylacetone Analysis)	53
13.	Formaldehyde Released from 100% Cotton Shirts (Chromotropic Acid Analysis)	54
14.	Formaldehyde Released from 60% Cotton/40% Polyester Shirts (Chromotropic Acid Analysis)	55
15.	Formaldehyde Released from 65% Polyester/35% Cotton Shirts (Chromotropic Acid Analysis)	56
16.	Temperature Coefficient for Japanese Test	67
17.	Temperature Coefficient for AATCC Test	68

CHAPTER 1

INTRODUCTION

Currently there is widespread concern over environmental and occupational health, as evidenced by the many regulations of the Occupational Safety and Health Administration and by the recently passed Toxic Substances Control Act (TSCA). This Act, being implemented by the Environmental Protection Agency, caters to the emphasis on prevention as it seeks to identify and regulate potentially hazardous substances before they are manufactured and sold.

Because of its large use of chemicals the textile industry will be affected by TSCA. One reason is that the recent publicity given to the flame retardants Tris and Fyrol and to benzidine dyes has focused attention on chemicals in textiles for consumer use. This was further emphasized by the fact that, in the case of Tris, it was established that harmful substances could be absorbed through the skin (78). Therefore all chemicals on textile products must be evaluated in the light of TSCA.

One of the chemicals currently under investigation is formaldehyde (10, 57, 62, 89). It is estimated that between 60%-80% of all apparel fabric has been treated with chemicals which contain formaldehyde (90). Its biggest use, and the most important from a market standpoint, is in durable press resins used to produce easy care fabrics. These resins, formed from formaldehyde in combination with base compounds such as urea, melamine, cyclic ureas, or carbamates, act by crosslinking the

cellulose in cotton and cotton blend fabrics. After such resin treatment, fabrics may contain an amount of residual, or readily hydrolyzable, formaldehyde which may represent a potential health risk to consumers. Further, liberated formaldehyde can migrate from treated to untreated fabrics during storage (82).

The Japanese have designated formaldehyde to be a consumer hazard and have limited the level permissible in textile products. Their standard requires that no trace of formaldehyde be detected in clothing and bedding for children under age two, and limits formaldehyde in underwear, sleepwear, gloves, and hosiery to 75 parts per million (ppm). In addition the textile industry in Japan has voluntarily adhered to levels of 300 ppm for blouses, shirts, and skirts, and 1000 ppm for outerwear.

The range of toxic effects of formaldehyde, both known and suspected, is being catalogued. The acute toxic effects are fairly well established: at concentrations above 3 ppm, it is irritating to the eyes and upper respiratory tract; higher levels cause burning sensations, coughing, and tearing; dermatitis or skin discoloration may result from direct contact (25, 39). Recently physicians have linked formaldehyde with a mysterious ailment affecting people who live in mobile homes (54). Excess formaldehyde emitted from building materials (plywood, chipboard, and urea-formaldehyde foam insulation) caused headaches, nausea, and irritation of the eyes and nose.

More ambiguous is the area of the genetic toxicology of formaldehyde. Since the 1940s studies have consistently shown formaldehyde to be a

mutagen in fruit flies at sublethal levels (11, 12, 40, 41, 44). The agent has been shown to produce stable methylene crosslinks in DNA molecules (69, 85). However, the carcinogenicity of the chemical is still somewhat questionable (13).

Should a move toward regulation of formaldehyde in the United States develop in light of the above, information regarding the extent of the problem will be needed for adequate assessment of consumer risk. Such information includes measurement of the level of formaldehyde content of typical consumer products, as well as investigation of current test methods.

Definitions

The formaldehyde content of durable press fabrics includes formaldehyde in several forms:

Free formaldehyde is unattached or adsorbed formaldehyde.

Formaldehyde as methylol groups is formaldehyde releasable from methylol amides via hydrolysis of the carbon-nitrogen bond.

Total formaldehyde includes the free and methylol formaldehyde as well as formaldehyde which exists as methylene ether groups.

In durable press fabrics formaldehyde may be released from either the methylol groups or the methylene ether groups. Formaldehyde release is the relative propensity of a finished fabric to release formaldehyde. The amount of formaldehyde released is stated in parts per million of formaldehyde on the weight of fabric and depends on the specific test method employed. The Japanese test method requires extraction of a

fabric specimen in water for one hour at 40°C (24). Formaldehyde released in this test is usually referred to as extractable formaldehyde (8). The test procedure of the American Association of Textile Chemists and Colorists (the AATCC method) involves incubation of the specimen in a sealed jar over water for 20 hours at 49°C (3). This formaldehyde is termed releasable formaldehyde.

The wrinkle recovery angle is a measure of the ability of a fabric to recover from deformation and thus is an indication of the effectiveness of a finish.

Objectives of the Study

1. To determine the formaldehyde content of representative durable press consumer products, both initially and after selected laundering intervals.

2. To compare Japanese and AATCC test methods for formaldehyde release with determination of free, methylol, and total formaldehyde.

3. To determine if representative consumer products in the United States pass the voluntary Japanese standard of 300 parts per million of formaldehyde.

Assumptions

1. Fabrics purchased were representative of consumer products on the market.

2. All garments purchased of one type were similar with regards to finish.

Limitations

1. Only three products were examined.

2. The history of the fabric in terms of resin/catalyst system employed, and processing conditions were not known.

CHAPTER 2

REVIEW OF LITERATURE

This chapter reviews pertinent literature concerning formaldehyde-based durable press finishes under the headings: development of Durable Press Finishes, Reaction and Hydrolysis Mechanisms, Testing for Formaldehyde and Formaldehyde Release, and Consumer Implications of Formaldehyde in Textiles.

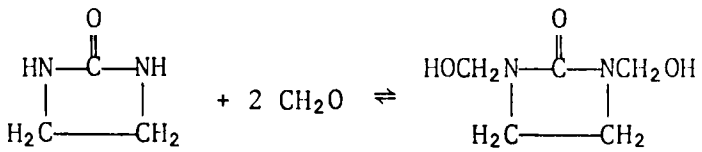
Development of Durable Press Finishes

The first finishes to alter the recovery behavior of cellulosic fabrics were applied at the Tootal Broadhurst Lee Co. Ltd. in the United Kingdom in the 1920s. Researchers reacted formaldehyde with urea to form a methylol compound which was then applied to cotton fabric. The fabric was padded with a solution of methylol urea and a catalyst, dried, and then baked at a high temperature. The small molecules penetrated to the inside of the fiber and once inside were polymerized by the baking (curing) step to form an insoluble resin. It was reasoned that the interstitially deposited resin would cause the fiber to spring back from any deformation, making it crease resistant (52).

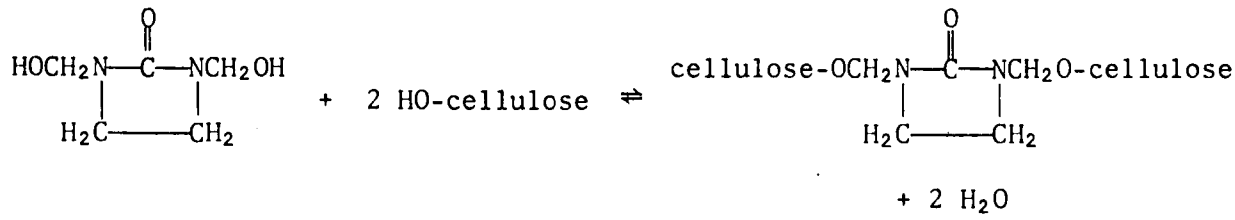
Later when the chemical constitution and molecular structure of cotton became known, it was established that the methylol compounds were capable of forming crosslinks between adjacent cellulose molecules (21, 88). Cameron and Morton (21) conducted a series of experiments on viscose rayon which led them to conclude that at least a portion of the

anticreasing agent applied to the fiber was involved in crosslinking. Their results were confirmed by Steele (76) who determined that crosslinking explained the changes in the chemical and mechanical properties of fabrics treated with crease resistant finishes more adequately than did the theory of resin deposition.

As the synthetics, with their inherent no-iron properties, began to penetrate the fiber market, the requirements for crease resistant cellulosics became more stringent. Fabrics must not only resist creasing, but must exhibit smooth drying properties after washing. The necessary technology to keep the cellulosics apace was supplied by the application of dimethylolethyleneurea (DMEU), a compound formed by reaction of formaldehyde with ethyleneurea (2-imidazolidinone):



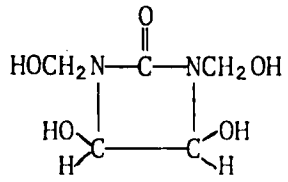
DMEU had been used to produce permanently pleated and embossed fabrics, and it was surmised that if the agent could permanently crease fibers, it could also permanently uncrease them (37, 76). As DMEU contains no free NH groups to react with methylol groups on other molecules, it does not form thermosetting resins as earlier agents had. Therefore the crease resistant properties produced by DMEU are primarily due to formation of covalent crosslinks (67, 76, 84). The methylol compound reacts with the hydroxyl groups of cellulose to form methylene ether bridges:



Strictly speaking this compound is not a resin or a potential resin as it does not polymerize; but the term "resin" has continued to be applied to finishes that are primarily reactive crosslinking agents.

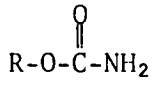
The 100% cellulosic wash-and-wear fabrics so produced exhibited an unacceptably low degree of abrasion resistance. Thus the early 1960s saw the marketing of "durable press" fabrics. This development made use of the naturally crease resistant and abrasion resistant thermoplastic fibers (22, 23). Blends of cotton and polyester (either 65% polyester/35% cotton or 50% polyester/50% cotton) were treated with reagent systems containing reactive crosslinking agents. The resultant fabrics exhibited crease retention and absence of seam puckering, and maintained a smooth appearance throughout repeated launderings.

A desirable processing innovation at the time was the delayed curing of durable press garments. In this process, the fabrics were "sensitized" with the durable press agent, then shipped, cut and sewn, and finally cured in garment form. The DMEU finish was not stable on the sensitized fabric, decomposing to release formaldehyde. It was determined, however, that a related compound, 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), possessed the stability necessary for delayed curing:

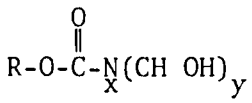


This methylol compound is tetrafunctional and so again will crosslink cellulose molecules. It was, and is, widely used to produce durable press fabrics, and in terms of quantities consumed is currently the most important crosslinking agent used in resin finishes (66).

A later class of compounds which have also been employed for durable press finishing are the carbamates, which have the general formula:



When a carbamate is reacted with formaldehyde, the permethylolated compound is obtained:



where (x + y = 2)

Reaction and Hydrolysis Mechanisms

Throughout the development of durable press finishes, it has been accepted that the best finishing agents were the N-methylol compounds. They had an irresistible combination of advantages: outstanding properties, low price, and easy application (1, 65, 67). However, a constant problem with these finishes has been hydrolysis of the finish, with subsequent release of formaldehyde.

Such release of formaldehyde is due to the reverse of the reactions which formed first the N-methylol agent, and then the condensation product with cellulose. The methylolation of NH-containing compounds such as melamine and cyclic or acyclic ureas, is an acid- or base-catalyzed equilibrium reaction. DeJong and DeJong (27) studied the formulation of monomethylol urea and formaldehyde. The reaction followed second order kinetics and the rate was proportional to the hydrogen or hydroxyl ion concentration, with the latter more effective as a catalyst.

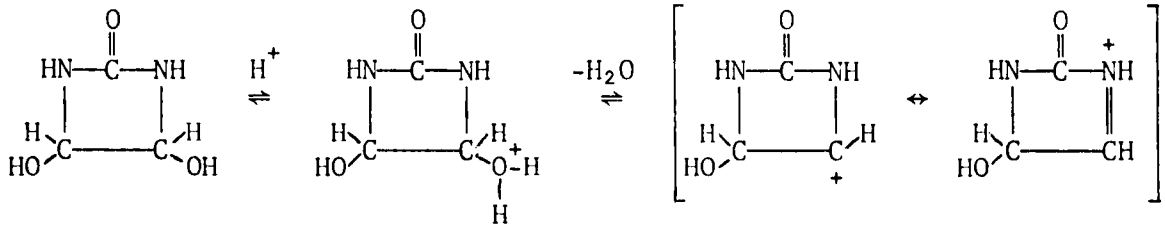
The rate of methylolation of different NH-containing compounds is dependent on the electron density at the nitrogen atom (64). As the reaction mechanism is a nucleophilic substitution, the most rapidly methylolated compounds are those with high electron densities at the nitrogen atom of the NH group.

Electron density is in turn affected by the existence of resonance forms of the molecule, as well as by the electron donating or withdrawing action of neighboring groups (70). With electron withdrawing groups, a negative inductive effect (-I) is observed compared to hydrogen, while alkyl groups produce an electron-releasing effect relative to hydrogen, (+I). When a methyl group replaces a hydrogen at the nitrogen atom, the electron density, and the methylolation rate, are increased. Ethyleneurea has an ethylene group, whose effect is electron-releasing, attached to the nitrogen atom, which has a high electron density.

Electron density is also affected by the existence of resonance forms which delocalize the electron density at the nitrogen atom, and thus influence the methylolation rate of various compounds. Ethyleneurea

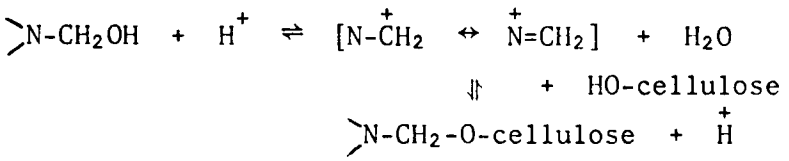
has a planar structure which essentially precludes any coplanarity of the nitrogen unpaired electrons with the carbonyl double bond. Consequently, this compound exhibits a higher degree of nucleophilicity and is more easily methylolated than are other cyclic ureas such as propyleneurea and butyleneurea, where the ring arrangement brings the carbonyl group into a position favorable for mesomerism with the nitrogen electrons (64, 65).

Other groups on the ring may affect resonance as well. In the case of 4,5-dihydroxyethyleneurea, the two hydroxy groups, which differentiate it from ethyleneurea, have a great effect on the methylolation rate under acid or neutral conditions. The hydroxy group is protonized and water is split off, forming a secondary carbonium ion. An equivalent imonium resonance structure can be drawn, whereby the electron density at the nitrogen atom of the NH group is delocalized, thus causing the methylolation rate of the dihydroxyethyleneurea to be more than 100 times less that of ethyleneurea (64).



This delocalization does not occur in alkaline media, and under those conditions the methylolation rates of ethyleneurea and 4,5-dihydroxyethyleneurea are comparable.

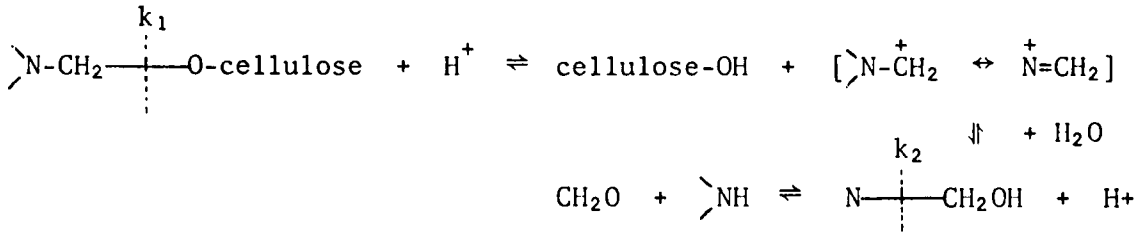
In durable press finishing, the methylolated compound is applied to cellulosic fabrics along with a catalyst to effect crosslinking of the cellulose chains. The reaction with the cellulose hydroxyl groups is an acid catalyzed equilibrium reaction. The mechanism involves addition of a proton to the oxygen of the methylol group and the splitting off of water. This forms a resonance stabilized carbonium-iminium ion which reacts with the nucleophilic hydroxyls of cellulose:



Petersen (65) studied the reaction rates of model compounds with mercaptans as analogous to the reaction with cellulose. Factors which affected the reaction rate included electron density at the nitrogen atom, the ability of the carbonyl group to coordinate protons, the presence of other basic centers in the molecule, and steric hindrance. DMEU, with a high electron density at the nitrogen atom, was very reactive with electrophiles, whereas DMDHEU, with a lower electron density, reacted more slowly.

In actual situations the ether bond formed by condensation of the N-methylol compound with cellulose, and the carbon-nitrogen bond of the methylol compound itself, can be broken, resulting in release of formaldehyde. Much research has been devoted to determination of the mechanisms of hydrolysis (59, 65, 70, 81). Nordhoy and Ugelstad (59) studied the acid hydrolysis of alkoxymethyl ureas and asserted that the

first step was the hydrolysis of the ether to give methylolurea and an alcohol; the methylolurea then decomposed to release urea and formaldehyde. They found, too, the first step to be much faster than the second. The reverse reactions of condensation and methylolation are apparently operative:



This path was confirmed by Vail and Pierce (81) who followed via nuclear magnetic resonance spectra the hydrolysis products as they were formed. They concluded that the carbon-oxygen bond was cleaved initially, yielding a methylol compound and a hydroxy compound.

Further investigation of model compounds has revealed k_1 to be much greater than k_2, and therefore the demethylolation reaction does not occur until hydrolysis of the ether (64, 65). Petersen (64) carried out acid catalysis of model N-methyoxymethyl compounds, and followed the reaction by determining the concentration of methylol groups (k_1) and the concentration of formaldehyde (k_2). The latter value was always smaller, but the ratio k_1/k_2 varied with different compounds. In the case of ethyleneurea, the ratio was 1000, but decreased as the reactivity of the compound declined.

Reeves et al. (70) examined the factors that influence the hydrolysis stability of the several N-methylol compounds. Formation

of the carbonium ion, which is the rate determining step, is increased by high electron density at the ethereal oxygen. And here the surrounding groups affect the electron density and enhance or inhibit cleavage of the carbon-oxygen bond.

Once the ether bond is cleaved the chemical constitution of the methylol compound comes into play in the hydrolysis of the carbon-nitrogen bond to form the NH compound and formaldehyde. The definitive factor in the demethylolation rate is the electron density at the nitrogen atom of the amino compound (64, 70). Those compounds which have a low electron density at the nitrogen atom, due to mesomerism or inductive effects, are more stable to hydrolysis. A relative rating of the stability of the commonly used finishing agents established DMDHEU and the permethylolated carbamates as the most resistant to hydrolysis (64, 65). These compounds have two electron-withdrawing alkoxy groups attached to the nitrogen. The dimethylol compounds or urea and propyleneurea were least stable. Intermediate stability was exhibited by the substituted propyleneureas.

It should be noted that, as the carbon-oxygen bond which is cleaved first is stable to aklaline hydrolysis, then both bonds can be considered stable to alkali, as long as there is no hydrogen attached to the nitrogen atom (65).

Much of the work on hydrolysis mechanisms was done when the concern was with development of objectionable odors and with the durability of resin finishes to laundering, not with the health effects of formaldehyde released from fabrics. But recently researchers have tried to reconcile

formaldehyde release conditions with known hydrolysis mechanisms (6, 7, 8, 15, 47).

Testing for Formaldehyde and Formaldehyde Release

The original impetus for testing for formaldehyde in durable press fabrics was concern over odor problems. Under hot humid conditions these fabrics often developed objectionable formaldehyde and amine odors. Accordingly the RA68 Committee of the American Association of Textile Chemists and Colorists (AATCC) was charged with devising a test method to measure the relative propensity of resin treated fabrics to release formaldehyde under simulated storage conditions. The problem was a double one: (1) how to cause the evolution of the formaldehyde, and (2) how to measure it.

For the problem of evolution the committee surveyed existing methods for formaldehyde liberation. The pioneering Tootal Boradhurst Lee Co. had opted for a water extraction, under which conditions results varied with extraction times (43). Reid et al. (72) stored samples in glass jars containing vials of water for 16 hours at 80°C. They found satisfactory comparison between this accelerated test and an actual storage test at 40°C for up to 10 weeks, and so concluded that the sealed jars adequately simulated hot, humid storage conditions.

The AATCC Committee likewise concluded that glass jars were the best containers to determine odor development, but they adopted the Dan River test which required storage in sealed jars for 20 hours at 120°F (60). Investigating this procedure, Lathrop et al. (48) adjusted the

pH to various values during incubation in the jars and found that a low pH increased the development of formaldehyde odor. This result was predictable as the hydrolysis is acid catalyzed.

The Committee also sanctioned a steam extraction method which had been developed by West Point Manufacturing Co. The sample was placed in a tube and steam was blown through it. Then an aliquot of the distillate was tested for formaldehyde content.

The Japanese government has in effect a standard for formaldehyde levels in durable press fabrics for consumer use. This law (112-73) specifies a water extraction test: one hour at 40°C (24). These extraction conditions are said to be milder than the sealed jar conditions (8).

Scientists at the Southern Regional Research Center in New Orleans have investigated various conditions for formaldehyde release and the available test methods with reference to existing information on hydrolysis (8, 9, 47). Concerning the sealed jar test they discovered that free formaldehyde continued to be evolved from fabric samples after incubation regardless of whether the fabric had been washed after treatment. Further, samples treated with DMDHEU were tested for methylol amide groups both before and after sealed jar incubation. Concentration of methylol groups decreased and free amide groups increased, indicating that the simulated storage tests are hydrolyzing the carbon-nitrogen as well as the carbon-oxygen bonds. This was confirmed by preparing samples with a resin compound incapable of dimethylolation and determining the quantity of amidomethylol groups before and after sealed jar incubation.

As this moiety decreased to 0 parts per million (ppm) after incubation, it was concluded that the methylol amides released formaldehyde, which did not then recombine with free amide.

Before the concern over formaldehyde was based on toxicity, researchers were not as concerned with analytical methods for absolute determinations of formaldehyde as they were with whether or not any formaldehyde (and hence odor) at all was released from durable press fabrics (48). Existing analytical methods (the majority colorimetric) were used in analyzing the extraction or release samples. Agents used to form colored compounds with formaldehyde for colorimetric or photometric analysis included hydroxylamine hydrochloride (43), Schiff's reagent (60), and phenylhydrazine (72). However, two substances, chromotropic acid (CTA) and acetylacetone (AA), have emerged as the most frequently employed in determining formaldehyde for toxicity concerns.

Acetylacetone has long been used for formaldehyde determination where mild reaction conditions were required. The analysis is based on the reaction of formaldehyde with AA and ammonium salt to give the yellow compound diacetyldihydrolutidine, which has a maximum absorbance at 412 nm (83). Nash worked out the test procedure in 1951 (58). He prepared the AA reagent with 159 g of ammonium acetate, 3 ml of acetic acid and 2 ml of redistilled AA in one liter of water. The ammonia concentration was more important than the AA concentration, as there was no difference in color between reagents prepared with 10 ml of AA, and those prepared with 2 ml. However, the smaller volume was decided on

because (1) the zero absorbance was less, (2) the resulting reagent was more stable, and (3) it was less toxic to living material.

For analysis, the reagent is mixed with an equal volume of test solution containing not more than 8 μg of formaldehyde. The rate of color development is dependent on temperature. Nash estimated times for 99% completion by assuming a first order reaction. The estimated times were 5 hours at 20°C, 40 minutes at 37°C, and 5 minutes at 58°C.

The AA test is specified in the Japanese law limiting formaldehyde in textile products. The extraction sample is compared to a reagent blank, a sample blank, and a formaldehyde standard of known concentration.

The other analytical technique which has figured prominently in the determination of formaldehyde in durable press fabrics is the colorimetric analysis with CTA (1,8-dihydroxynaphthalene,3,6-disulfonic acid). Formaldehyde can be detected by the intense red-violet color which develops on heating with CTA in the presence of strong sulfuric acid (83). The test was first reported by Eegriwe who studied it qualitatively. Boyd and Logan (18) subsequently adapted the method for quantitative determination using a colorimeter. The color produced was proportional to concentration within 2% provided the unknown differed from the standard by not more than 50%. The method required addition of CTA, sulfuric acid, and water to the test solution, and heating in a boiling water bath to develop the color.

Bricker and Johnson (19) and MacFayden (51), working independently, applied spectrophotometric techniques to the CTA method to determine formaldehyde. They found that transmission, measured at 570 nm, followed

Beer's Law. MacFayden noted that the concentration of sulfuric acid should be approximately 9.5-10M in the final solution, and should not be less than 9M. The absorbance spectrum showed maxima at 380, 480, and 570 nm. Since a solution of aceraldehyde reacted with CTA showed a maximum at 400 nm, 570 nm was the wavelength chosen for the quantitative analysis of formaldehyde. Bricker and Johnson recommended addition of 0.5 ml of CTA reagent to the test solution along with 5 ml of concentrated sulfuric acid, and heating in a boiling water bath for 30 minutes.

The Bricker and Johnson method was later used by Roff (74) to determine formaldehyde in textile finishes hydrolyzed by strong sulfuric acid. Finished fabrics were soaked in 12N sulfuric acid, and samples of the hydrolyzate were tested for formaldehyde at selected time intervals. Roff concluded that 16-24 hours were sufficient for complete hydrolysis of the finishes. After that time the increase in formaldehyde determined was the same as that for untreated fabrics.

Roff also investigated the critical factors in the CTA reaction to arrive at an optimum procedure. He recommended addition of 1.0 ml of a 5% CTA solution and 5 ml of concentrated sulfuric acid to the test sample, boiling for 30 minutes, and dilution with water before reading the absorbance at 570 nm.

Bricker and Vail (20) altered the method somewhat to eliminate reaction of formaldehyde with other compounds in strong sulfuric acid. They found that CTA retained formaldehyde when evaporated to dryness before addition of sulfuric acid. Following that procedure they claimed that the linearity of the calibration curve was extended beyond that of

previous methods. From further experiments they determined that the minimum ratio of reagent to test solution was 100 mg to one ml. Larger volumes of sample required proportionally larger quantities of CTA reagent. Bricker and Vail experimented with acids other than sulfuric, but found lower absorbances with phosphoric acid and hydrochloric acid.

Lee (49) later noted that reaction under anhydrous conditions increased the sensitivity of the CTA test. Altshuller et al. (2) eliminated the 30 minute heating step before dilution, merely depending on the heat of dilution at high acid concentrations to effect color formation. They compared results from unheated samples, and those heated for 15 and 30 minutes, and found very little change in absorbance.

Recently several attempts have been made to tailor the reaction conditions to optimize the absorbance response for CTA and formaldehyde (43, 61). The technique of simplex optimization was applied by Houle et al. (42) who recommended addition of 3.3 ml of CTA reagent (0.33 g of CTA in 100 ml of sulfuric acid) to 3.0 ml of sample. The heat of solution was sufficient to effect reaction. The authors claimed that the average sensitivity of the method was 0.294 $\mu g\ ml^{-1}$, and that the detection limit was 0.018 $\mu g\ ml^{-1}$.

Simplex optimization was also applied by Olansky and Deming (61) to CTA analysis of formaldehyde. They added CTA and sulfuric acid separately and so could vary the amounts of the two reagents in their statistical procedure. Absorbance values at 570 nm for 4 µg samples of formaldehyde were highest at the ratio of 0.30 ml of CTA to 2.8 ml of sulfuric acid. Absorbance readings were taken exactly 10 minutes after mixing of the reagents.

Throughout the period of wash-and-wear and durable press fabrics, textile scientists have also analyzed the formaldehyde content of these fabrics in any of its several forms: free formaldehyde, methylol formaldehyde, and total formaldehyde (52, 64). Free formaldehyde (unbound or adsorbed formaldehyde) has usually been determined by the sodium sulfite volumetric method (83). The method involves the quantitative liberation of sodium hydroxide when sodium sulfite is reacted with formaldehyde to form the addition product $CH_2(NaSO_3)OH$. The test sample is added to a solution of sodium sulfite and the resulting mixture is titrated with standard sulfuric or hydrochloric acid.

A modification of the method was introduced by Morath and Woods (56) in 1958, and employed by Reid et al. (71) to determine formaldehyde released from fabric. The reaction is carried out in the presence of acid, which neutralizes the liberated base, and the excess acid is then titrated with standard base using thymolphthalein indicator. If the sample contains methylol compounds as well as free formaldehyde, the reaction is carried out at 4-5°C to prevent hydrolysis of the methylol compounds, and hence a higher formaldehyde yield.

Donnally (29) used the principle of sulfite addition to formaldehyde but measured the consumption of sulfite in a different manner. He destroyed the unreacted sulfite with iodine, then added carbonate to decompose the formaldehyde addition product and titrated the liberated sulfite with standard iodine solution.

Bille and Petersen (15) carried out this analysis directly on durable press fabric samples. They placed a one g sample in 50 ml of

ice water, and then performed the sulfite addition and iodine titration recommended by Donnally. An unfinished sample was run and the formaldehyde content determined from the difference.

DeJong (26) proposed a method for determination of methylol formaldehyde. It is based on the alkaline hydrolysis of the methylol compound and reaction of the liberated formaldehyde with cyanide to form a cyanohydrin, according to the procedure of Pfeil and Schroth (68). The excess cyanide is then titrated with mercuric nitrate using diphenylcarbazone as an indicator. Petersen (67) adapted this method also for direct application to fabrics with N-methylol finishes.

The total formaldehyde in a resin system or in a fabric crosslinked with resin finishes is usually determined after hydrolysis with a strong acid (38, 74). Roff (74) hydrolyzed resin finished fabrics with 12N sulfuric acid and then determined the formaldehyde content using the CTA method of Bricker and Johnson (19). He found that the formaldehyde liberated from fabrics treated with N-methylol agents increased at a faster rate than for untreated fabrics up to 20 hours of hydrolysis, but thereafter the yield was the same for treated and untreated fabrics. He concluded that after approximately 20 hours the finish was completely hydrolyzed.

Formaldehyde as a Consumer Issue

Interest in the safety of consumer products has brought formaldehyde to the fore as a consumer issue (57, 78, 87, 90). Actions of government and industry groups signal a concern over both the acute and chronic

effects of this chemical which is used in building materials, cosmetics, and textiles (32, 45, 57).

Formaldehyde has long been a cause of irritation of the upper respiratory tract, with individuals exhibiting different degrees of sensitivity (25, 39). The irritant effects have been highlighted recently by cases of people suffering health problems attributable to formaldehyde released from urea-formaldehyde insulation and from plyboard where formaldehyde resins have been used as binders (50, 54, 57). The adverse effects included headaches, nausea, drowsiness, and irritation of the eyes, nose, and throat. The symptoms were especially apparent in residents of mobile homes, due to the small enclosed living spaces. What is important about these cases is that they stem from consumer products containing compounds similar to those on durable press fabrics. Significantly one state, Massachusetts, has banned the use of urea-formaldehyde foam for insulation.

Although they have not been as notorious, complaints of irritant effects directly associated with clothing have occurred (17, 73). Complaints of "burning, stinging eyes," headaches," and a "suffocating odor" are recorded. Two researchers determined the concentration of formaldehyde gas in dress shops from which complaints had been received and found that the air contained from 0.13 to 0.45 ppm of formaldehyde (17).

The adverse health effects of formaldehyde are also considered in the workplace and environment. The Occupational Health and Safety Administration (OSHA) regulates the amount of formaldehyde permissible

in finishing plants and the Environmental Protection Agency (EPA) regulates the substance as a hazardous water pollutant. The former agency proposed in 1976 that the permissible level of formaldehyde in plants be lowered from 3 ppm to 1 ppm, but a derivative standard has not yet been promulgated.

Add to the above, investigations into the mutagenicity and carcinogenicity of formaldehyde and the breadth of the problem becomes apparent. When the toxicity of the flame retardant, Tris, was revealed, the Consumer Product Safety Commission (CPSC) specifically stated that hazardous substances could be absorbed through the skin from clothing fabrics (78). Therefore the use of formaldehyde in textile finishers is subject to the same reasoning.

The question of the genetic toxicology of formaldehyde has been investigated for many years, as the substance had been frequently used as a preservative and disinfectant. In the late 1940s, Kaplan (44) and Herskowitz (40, 41) reported elevated nonlethal mutation rates in fruit flies fed food containing formaldehyde. Auerbach (11) however found no sublethal mutations in flies exposed to formaldehyde vapor, and concluded that the effective agent in mutagenesis was a compound resulting from a reaction of the formaldehyde with the food. The same researcher (12) later determined that indeed the formaldehyde was bound by the food and then gradually released in small doses causing the observed mutations. The absence of mutagenic effects when the flies were exposed to formaldehyde gas was due to the high lethal toxicity of the method.

Feldman (3K), in his review of formaldehyde effects on nucleic acids, differentiates between a primary reaction and a secondary reaction, giving the following sequence:

$$RNH_2 + CH_2O \rightleftharpoons RNH\text{-}CH_2OH \quad (1)$$

$$RNH\text{-}CH_2OH + R'H \rightleftharpoons RNH\text{-}CH_2\text{-}R' + H_2O \quad (2)$$

The formation of methylol derivatives (reaction 1) serves to fix thermally induced denaturation of nucleic acids. In this case formaldehyde might be considered as a "passive" rather than an "active" denaturing agent. Formation of stable methylene crosslinks (reaction 2) on the other hand fixes native ribonucleic acid (RNA) or nucleoprotein. Crosslinks may be formed during synthesis of deoxyribonucleic acid (DNA), inhibiting mitosis. Investigation of bacteria exposed to formaldehyde confirmed the formation of crosslinks between DNA strands (69, 85).

The carcinogenicity of formaldehyde is not as clearly documented. Auerbach (11) stated in 1977 that the problem arose because of the frequent association between mutagenesis and carcinogenesis, but there was no direct evidence of the latter. This was echoed by Dr. Harry Plotnik, an industrial disease expert with the National Institute of Occupational Safety and Health (NIOSH) (54). Dr. Robert Harris of the Environmental Defense Fund (EDF) is concerned about the suspected carcinogenicity of formaldehyde and is seeking definitive test data in that area (70). Two industry groups, the American Textile Manufacturers Institute (ATMI) and the Chemical Institute of Toxicology (CIT) have given formaldehyde top priority in their testing programs (10, 78).

The first results from a study being done for the latter group by the Formaldehyde Institute of New York indicate presumptive evicence of carcinogenicity (32, 57). Thirty-seven of 200 rats exposed to a formaldehyde concentration of 15 ppm developed nasal tumors after 18 months. But rats exposed to lower levels of formaldehyde (2 and 6 ppm) and mice exposed to all levels showed no evidence of cancer. However the result of this study is in some doubt as the rat colony was infested with a virus, the effect of which was not determined.

It has been suggested that formaldehyde is not actually a carcinogen, but at high concentrations is a cause of tissue damage (57). Rapid cell growth then readily follows such tissue damage.

Whether irritant, mutagen, or carcinogen, formaldehyde is the focus of attention by the CPSC. The agency has published a proposed rule which would require installers of urea-formaldehyde insulation to inform purchasers of the possibility of the release of formaldehyde gas into the home. Also, in 1980 the CPSC formed a formaldehyde panel to study the health effects of formaldehyde in consumer products. Further, formaldehyde is one of six priority chemicals on the testing agenda of the Interagency Regulatory Liaison Group which coordinates the activities of government regulatory agencies.

CHAPTER 3

PROCEDURE

The purpose of the present study was to determine the formaldehyde release from typical durable press fabrics and to examine the current test methods for formaldehyde evolution. This chapter outlines the experimental design, analytical methods, and data analysis.

Shirting Fabrics

Men's durable press, long-sleeved, white broadcloth dress shirts were purchased from local department stores in Knoxville, Tennessee. Three shirt types were purchased:

1. Shirts of 100% cotton with a Sanfor-Set finish.
2. Shirts of 60% cotton/40% polyester with a durable press finish.
3. Shirts of 65% polyester/35% cotton with a durable press finish.

Physical properties of the shirting fabrics were determined as follows:

Fabric weight. Fabric weight was determined as specified in ASTM Method D1910-64 (4). Five randomly selected 5.0 × 5.08 cm squares were conditioned and weighed on a Mettler balance. The weight in grams cm^{-2} was converted to ounces per square yard.

Fabric count. Fabric count was determined as specified in ASTM Method D1910-64 (4). The mean number of ends and picks of five randomly selected one-inch areas of conditioned fabric were recorded.

Laundering

The shirts were laundered under simulated home laundry/drying conditions. Five shirts of each type were washed and dried together and one shirt was withdrawn for testing at each of six wash intervals; after 0, 5, 10, 15, 20, and 25 launderings. The shirts were washed in a Kenmore washing machine and dried in a Kenmore dryer. Filler fabric of 100% cotton knit (no finish) was added to maintain all wash loads at four pounds, as outlined in AATCC Test Method 143-1975 (3). The "Permanent Press" wash cycle with warm water and warm rinse, and the "Permanent Press" drying cycle for a drying time of 40 minutes were employed. The only laundering aid used was 90 g of AATCC detergent for each wash load. The pH of wash water with detergent was 8.77.

Formaldehyde Analysis

Shirts from each laundering interval (0 through 25) were evaluated for formaldehyde content and formaldehyde evolution. Formaldehyde content was determined as free formaldehyde, methylol formaldehyde, and total formaldehyde. Formaldehyde evolution from shirting fabrics was tested by extraction and release methods.

Determination of free formaldehyde. Free formaldehyde was determined by (1) a modification of the method of DeJong and DeJonge (28, 67); and by (2) the method of Reid et al. (71).

1. By the first method, a one g fabric sample was cut into pieces and placed in a flask with 50 ml of distilled water at 0°C.

One ml of 0.5N sodium sulfite was added along with 3-4 drops of thymolphthalein indicator. Several drops of 2N sodium carbonate were added until the solution turned blue. The solution was neutralized to colorless with 0.3N hydrochloric acid, and the neutralized solution allowed to stand in an ice bath at 0°C for seven minutes. The solution was acidified to pH = 4 with five ml of 1N acetic acid, and several milliliters of starch indicator were added. The excess sulfite was back titrated with 0.1N iodine. The formaldehyde-bisulfite compound was destroyed with 10 ml of ice cold 2N sodium carbonate, and the liberated sodium sulfite titrated with 0.10N iodine. Free formaldehyde was calculated according to the equation:

$$CH_2O\ (\%) = \frac{3 \times \text{ml of } 0.01N\ I_2}{200 \times \text{sample weight in g}}$$

2. By the second method, a one g fabric sample was cut into pieces and placed in a flask with 100 ml of ice cold distilled water. The flask was placed in an ice water bath, several drops of thymolphthalein indicator were added, and then dilute sodium hydroxide was added dropwise until a blue color appeared. Ten ml of standardized 1.000N hydrochloric acid, and 50 ml of 1M sodium sulfite, were added. The solution was immediately titrated to the blue endpoint with standardized 1.000N sodium hydroxide. Formaldehyde was calculated in the following manner:

$$CH_2O\ (\%) = \frac{(\text{meq HCl} - \text{meq NaOH}) \times 3}{\text{sample weight in g}}$$

Determination of methylol formaldehyde. Methylol formaldehyde was determined by the method of Nordhoy and Ugelstad (59) modified by Petersen (67). A one g fabric sample was cut into pieces and placed in a flask with 50 ml of distilled water. Ten ml of 2N sodium hydroxide, and 10 ml of 0.100N potassium cyanide were added and the flask placed in a water bath at 50°C for 10 minutes. The mixture was cooled to 0°C, 4-6 drops of diphenylcarbazone indicator solution were added, and then 2N nitric acid until the color just disappeared. The sample was immediately titrated with 0.100N mercuric nitrate to the weakly violet endpoint. Formaldehyde was calculated according to the equation:

$$CH_2O\ (\%) = \frac{(\text{meq KCN} - \text{meq } Hg(NO_3)_2 \times 3}{\text{sample weight in g}}$$

This determination gives the total amount of free and methylol formaldehyde, as the sodium hydroxide breaks down methylol groups to the NH-containing compound and formaldehyde. The concentration of methylol groups is then found by subtraction of the methylol formaldehyde from the free formaldehyde.

Determination of total formaldehyde. Total formaldehyde was determined by Roff's method of hydrolysis (74). A one g fabric sample was cut into pieces and placed in a flask with 100 ml of 12N sulfuric acid. The flask was stoppered, shaken, and allowed to stand for 20 hours. After this time, the formaldehyde content of the extraction liquid was determined by the chromotropic acid (CTA) procedure.

The CTA procedure used was that recommended by Olansky and Deming (61), who optimized the absorbance response for the CTA-formaldehyde reaction. By this procedure, 5.6 ml of concentrated sulfuric acid were dispensed from a buret into a clean dry styrofoam cup containing a magnetic stirring bar. Six-tenths ml of CTA solution (20 g l^{-1}), and 4 ml of the test solution were added in rapid succession, and stirring was initiated. Absorbance readings of the solution were taken 10 minutes after mixing on a Pye-Unicam SP600 spectrophotometer, set at a wavelength of 570 nm. Formaldehyde concentration was read from a regression equation previously determined with standard formaldehyde solutions, and reported as ppm of formaldehyde on the weight of the fabric.

Determination of extractable formaldehyde. The extraction procedure specified in the Japanese formaldehyde standard was used to assess formaldehyde evolution (24). A one g fabric sample was cut into pieces and placed in a flask with 100 ml of distilled water. The flask was placed in a 40°C water bath for one hour. After cooling, the liquid was filtered and 5 ml of the filtrate placed in a test tube, to which was added 5 ml of Nash (acetylacetone) reagent. The Nash reagent was prepared with 150 g of ammonium acetate, 3 ml of glacial acetic acid, and 2 ml of acetylacetone, diluted to one liter. The test solution, a filtrate blank, a Nash reagent blank, and a standard formaldehyde solution with 5 ml of Nash reagent were placed in a 40°C water bath for 30 minutes, cooled to room temperature, and the absorbance read at 412 nm. Extracted formaldehyde was calculated by:

$$CH_2O \text{ (ppm)} = \frac{K(A - A_o)\ 100}{A_s \text{ (sample weight in g)}}$$

where

$K = 4\ \mu g\ ml^{-1}$,

A = sample absorbance - absorbance of Nash blank,

A_s = standard absorbance - absorbace of Nash blank, and

A_o = absorbance of filtrate blank - absorbance of distilled water.

The formaldehyde content of the extraction liquid was also determined by CTA analysis, as described above.

Determination of releasable formaldehyde. Releasable formaldehyde was determined by the AATCC sealed jar test (3). A one g fabric sample was folded and suspended with polyester thread over 50 ml of distilled water in a sealed Mason jar. The jar was placed in an oven at 49 ± 2°C for 20 hours. After removal of the fabric, a one ml aliquot from the jar was mixed with 10 ml of Nash reagent in a test tube, and heated in a water bath at 58°C for 6 minutes. After cooling, the absorbance of the solution was read at 412 nm. Concentration of formaldehyde in the liquid was taken from a regression equation determined with standard formaldehyde solutions, and reported as ppm of formaldehyde on the weight of the fabric.

Determination of formaldehyde in the liquid from the jar was also made using the CTA method.

Physical Tests

Shirting fabrics were also subjected to two physical tests: wrinkle recovery angle and tearing strength.

Wrinkle recovery angle. Wrinkle recovery angle was determined after each laundering interval according to AATCC Test Method 66-1978 (3). Twelve specimens 15 × 40 mm were cut: six with their long dimension parallel to the warp and six with their long direction parallel to the filling. Three of the specimens from each direction were marked "face" and three were marked "back." The specimens were conditioned overnight at 65 ± 2% RH and 70 ± 2°F. The specimens were creased under a load of 500 g for 5 min ± 5 sec, and the angle of recovery from deformation measured after 5 min ± 5 sec. The face and back readings were averaged, and then the warp and filling angles summed to give a total wrinkle recovery angle.

Tearing strength. Tearing strength was determined by ASTM Method D1424 (4). Five warp specimens and five filling specimens 102 × 75 mm were cut with a die from each shirt both before laundering and after 25 launderings. The specimens were conditioned overnight at 65 ± 2% RH and 70 ± 2°F, and then torn on a falling pendulum Elmendorf Tear Tester with a capacity of 3200 g.

Data Analysis

Correlation values between formaldehyde content and release results were calculated. All dependent variables were regressed against number

of washings to determine variation in formaldehyde release and content, and wrinkle recovery with laundering. Both linear and exponential regression models were employed. An analysis of variance was performed for each fabric at 0 and at 25 launderings to assess any differences in formaldehyde release or analysis methods. Data were taken to be significant at the 0.10 probability level. Computations were carried out on an IBM 360-65 Computer, using S.A.S. programs.

CHAPTER 4

RESULTS AND DISCUSSION

The purpose of the present study was to determine the formaldehyde content and evolution from durable press consumer products and to assess the effect of laundering on such values. A further objective was to compare existing test methods for formaldehyde in durable press fabrics.

Shirting Fabrics

Three types of men's long-sleeved white broadcloth dress shirts were purchased in the market. Descriptive properties of the shirting fabrics are presented in Table 1.

Formaldehyde Content

The formaldehyde content of the shirting fabrics was determined as free formaldehyde, as formaldehyde in methylol groups, and as total formaldehyde. The free and methylol analyses of the shirting fabrics gave anomalous results. In most cases, however, the analyses showed no free or methylol formaldehyde present. Conceivably, the volumetric analysis methods were not sensitive enough to detect very small amounts of free or methylol formaldehyde which might have been present, even after washing of the shirts. As Vail and Reinhardt (82) have pointed out, at low formaldehyde levels, the volumetric methods are of little value. If the titrant is too dilute, endpoints are difficult to see. More concentrated solutions on the other hand increase the analytical

Table 1. Descriptive properties of shirting fabrics

Fiber content	Fabric weight (oz/yd^2)	Fabric count (Warp × fill)
100% cotton	3.68	120 × 68
60% cotton/40% polyester	3.09	113 × 72
65% polyester/35% cotton	2.85	114 × 73

error in that one drop of titrant may be equivalent to 50-100 ppm formaldehyde.

Research carried out at the Southern Regional Research Center in New Orleans has determined that a large source of formaldehyde released in extraction or incubation tests is the methylol groups (>CH_2OH), which were present at significant levels in fabric finished with dimethyloldihydroxyethyleneurea (DMDHEU) (8, 82). Methylating DMDHEU however eliminates or decreases the number of methylol groups in the finish. If the finish on the shirts in the present study were a methylated agent, then very little methylol formaldehyde would be present.

The values for total formaldehyde for the different shirting fabrics are presented in Table 2. Of the three fabrics, the 60% cotton/40% polyester fabric contained the largest amount of formaldehyde. This was predictable. The 100% cotton shirts, while having a higher cotton content, were finished by the Sanfor-Set process. In this weight fabric (3.7 oz yd^{-2}) the finish (treatment of the fabric with liquid ammonia) is generally augmented with a small amount of durable press resin (30). The presence of such a resin was confirmed by the formaldehyde found by analysis. But there was less resin finish than in the case of the 60% cotton/49% polyester fabric. The shirting fabric containing only 35% cotton contained the least amount of total formaldehyde.

Formaldehyde Release

The results of the formaldehyde evolution tests, evaluated by both acetylacetone (AA) and chromotropic acid (CTA) analysis, are presented

Table 2. Formaldehyde in shirting fabrics

Fabric and wash interval	Formaldehyde released (ppm)				
	Total	Japanese (AA)*	Japanese (CTA)**	AATCC (AA)*	AATCC (CTA)**
100% cotton					
0	6905	50	309	151	160
5	5903	110	146	46	67
10	5949	12	224	14	46
15	4529	28	193	106	34
20	4434	33	93	11	23
25	4287	8	91	13	23
60% cotton/40% polyester					
0	9183	259	333	347	291
5	9164	27	76	169	156
10	9938	12	68	128	140
15	8797	34	83	202	87
20	8877	42	49	59	79
25	13799	26	90	59	91
65% polyester/35% cotton					
0	6094	106	146	72	96
5	5942	44	51	23	45
10	5155	22	23	25	36
15	5646	31	32	35	35
20	3905	24	33	33	46
25	4837	17	37	12	38

*Acetylacetone analysis.

**Chromotropic acid analysis.

in Table 2. Very little of the total formaldehyde content is released by the AATCC test or extracted by the Japanese test. Both the unwashed 100% cotton and the 60% cotton/40% polyester shirts would have failed the Japanese voluntary standard of 300 ppm as analyzed by CTA.

The largest amount of formaldehyde was released by the 60% cotton/40% polyester fabric, which the total formaldehyde analysis had revealed to have the greatest formaldehyde content. The 100% cotton shirts released the next largest amount of formaldehyde, and the 65% polyester/35% cotton, the least amount. The evolution values for all three fabrics decreased with washing.

A correlation analysis revealed significant relationships between wash interval and total, released, and extracted formaldehyde. In addition, total formaldehyde was correlated with released and extracted formaldehyde for the 100% cotton shirts and for the 65% polyester/35% cotton shirts.

Regression Analysis

As the correlation coefficients indicated a decrease in formaldehyde content and release with washing, each of the different analysis variables was regressed against laundering interval. Data were fit to both a linear decay model and an exponential decay model. The former model implies zero-order kinetics for the loss of formaldehyde with laundering. By contrast, exponential decay to an asymptote implies first-order kinetics and a leveling off of formaldehyde loss.

The exponential decay model accounted for more of the scatter in the data. This indicates that the hydrolysis of the N-methylol finish with washing is a pseudo-first-order reaction. The specific model used was:

$$\text{Formaldehyde (ppm)} = A + B \cdot \exp(-KW)$$

where

W = number of washings, and

A = the limiting value for formaldehyde content or release.

The exponential regression model values for the best fit to the data for each shirting fabric are presented in Table 3. The R^2 values were calculated from the total corrected sums of squares in the following manner:

$$R^2 = \frac{\text{Total Corrected Sum of Squares - Residual Sum of Squares}}{\text{Total Corrected Sum of Squares}}$$

The exponential regression curves for each fabric are shown in Figures 1-15. The A value represents an amount of releasable or extractable formaldehyde which is not affected by further washing. A large K value indicates a steep slope for the initial curve and, derivatively, that the fabric will quickly reach its limiting (A) value for formaldehyde release or content. A small K value indicates a more gradual slope, and signals a greater number of launderings before the limiting value is reached. Generally the K value for total formaldehyde was smaller than the K value for released or extracted formaldehyde.

Table 3. Exponential regression model values (standard error of estimation)

Fabric and test method	PPM = A + B*exp(-KW)			
	A	B	K	R^2
100% cotton				
Total	2815	4082	0.0443	0.8610
	(1663)	(1576)	(0.0298)	
Japanese/AA*	-1600	1665	0.0011	0.1803
	(249483)	(249469)	(0.1820)	
Japanese/CTA**	-78	356	0.0291	0.5290
	(521)	(356)	(0.0599)	
AATCC/AA*	36	114	0.5461	0.5989
	(11)	(26)	(0.6642)	
AATCC/CTA**	24	135	0.2087	0.9917
	(2)	(3)	(0.0139)	
60% cotton/40% polyester				
Total	7477	2021	0.0114	0.0354
	(50168)	(50015)	(0.3174)	
Japanese/AA*	28	231	3×10^{8}	0.9506
	(5)	(13)	(0.0000)	
Japanese/CTA**	73	260	0.8738	0.9624
	(6)	(14)	(0.8241)	
AATCC/AA*	84	253	0.1537	0.7475
	(29)	(40)	(0.0658)	
AATCC/CTA**	82	207	0.1758	0.9605
	(8)	(11)	(0.0252)	
65% polyester/36% cotton				
Total	2495	3692	0.0248	0.5717
	(6877)	(6730)	(0.0621)	
Japanese/AA*	22	84	0.2772	0.7999
	(6)	(11)	(0.1048)	
Japanese/CTA**	33	109	0.3777	0.8843
	(5)	(10)	(0.1261)	
AATCC/AA*	25	47	378.73	0.7150
	(3)	(7)	(0.0000)	
AATCC/CTA**	39	57	0.4621	0.9392
	(2)	(4)	(0.1356)	

*Acetylacetone analysis.

**Chromotropic acid analysis.

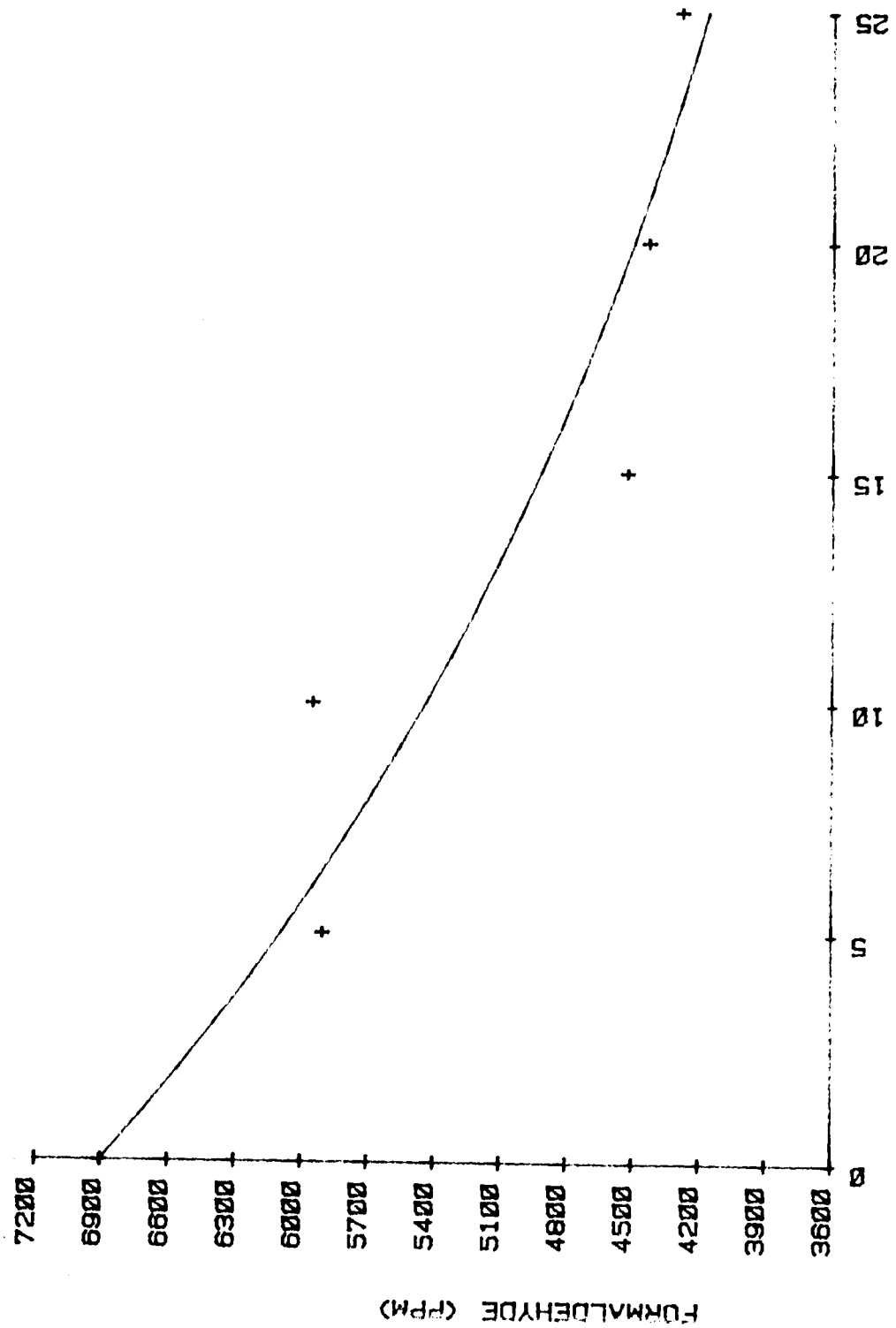


Figure 1. Total formaldehyde in 100% cotton shirts.

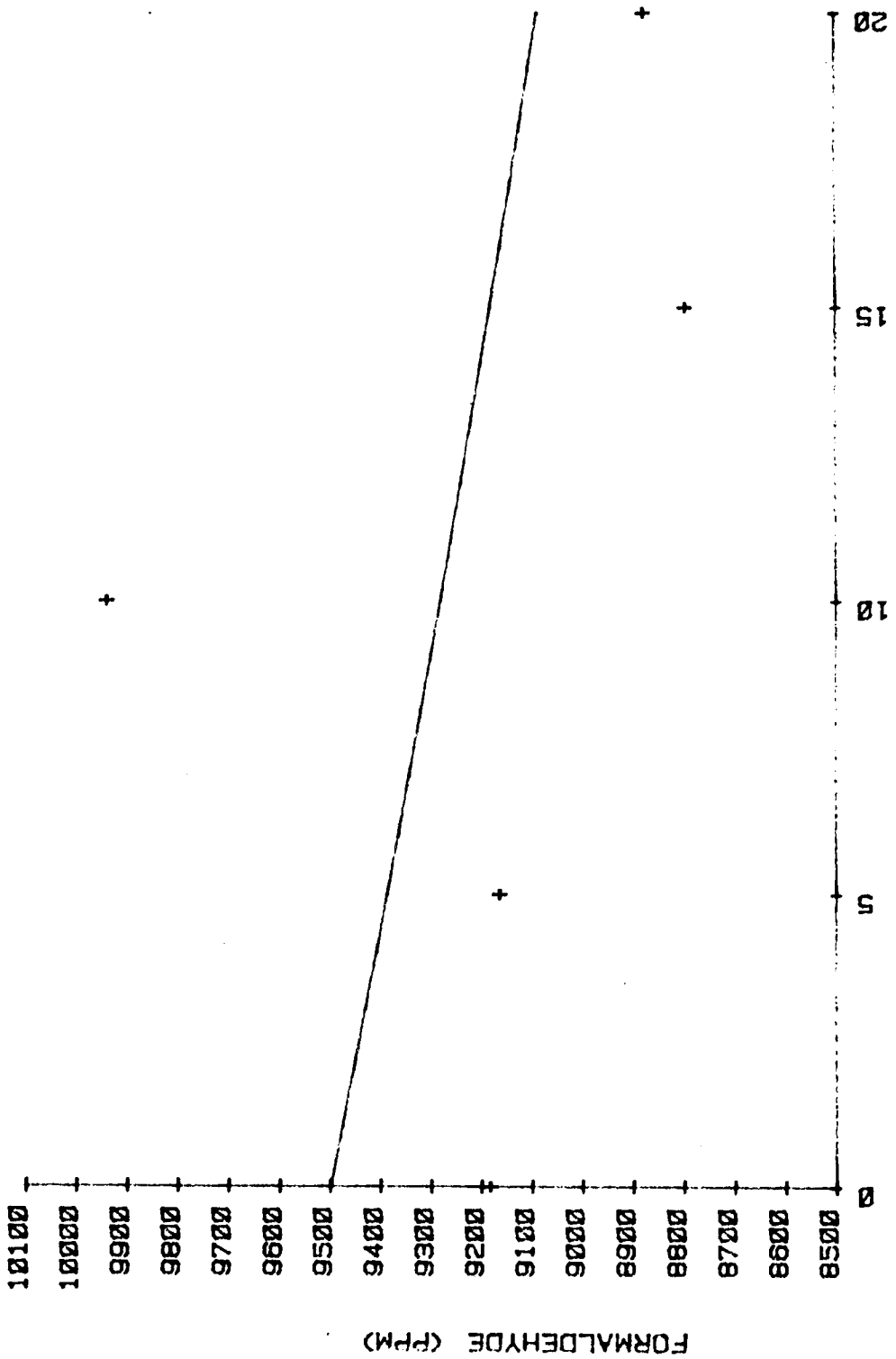


Figure 2. Total formaldehyde in 60% cotton/40% polyester shirts.

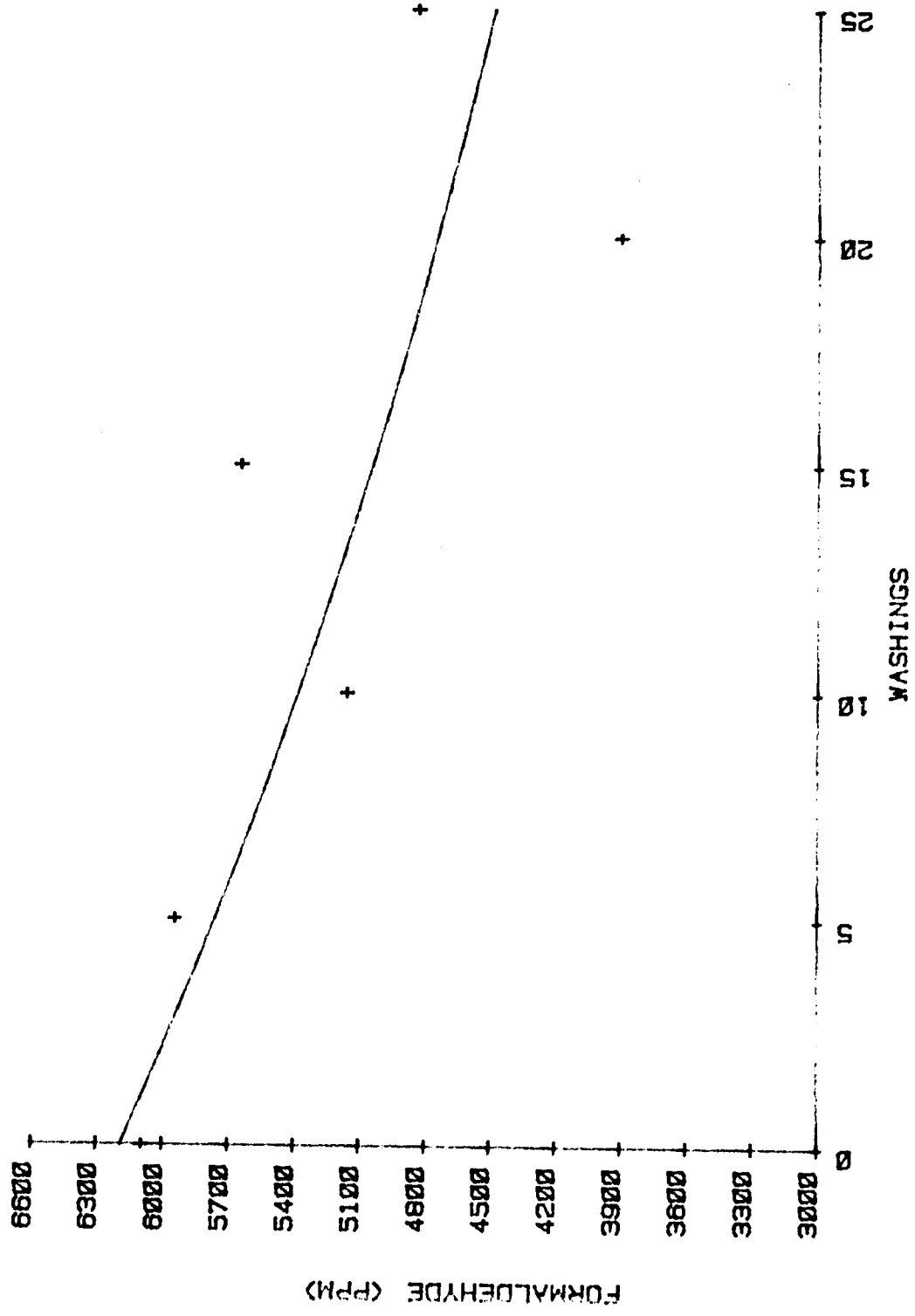


Figure 3. Total formaldehyde in 65% polyester/35% cotton shirts.

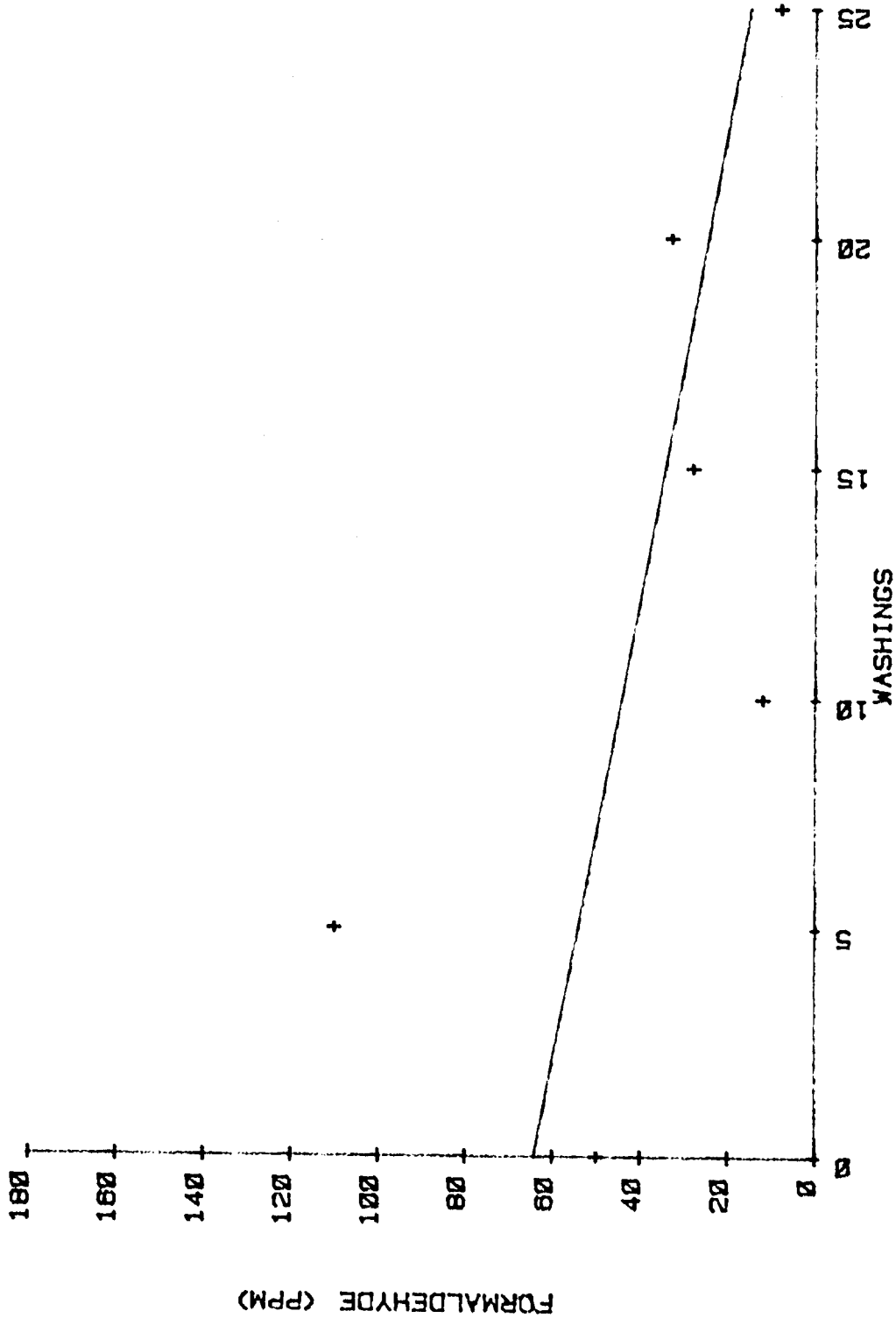


Figure 4. Formaldehyde Extracted from 100% cotton shirts (acetylacetone analysis).

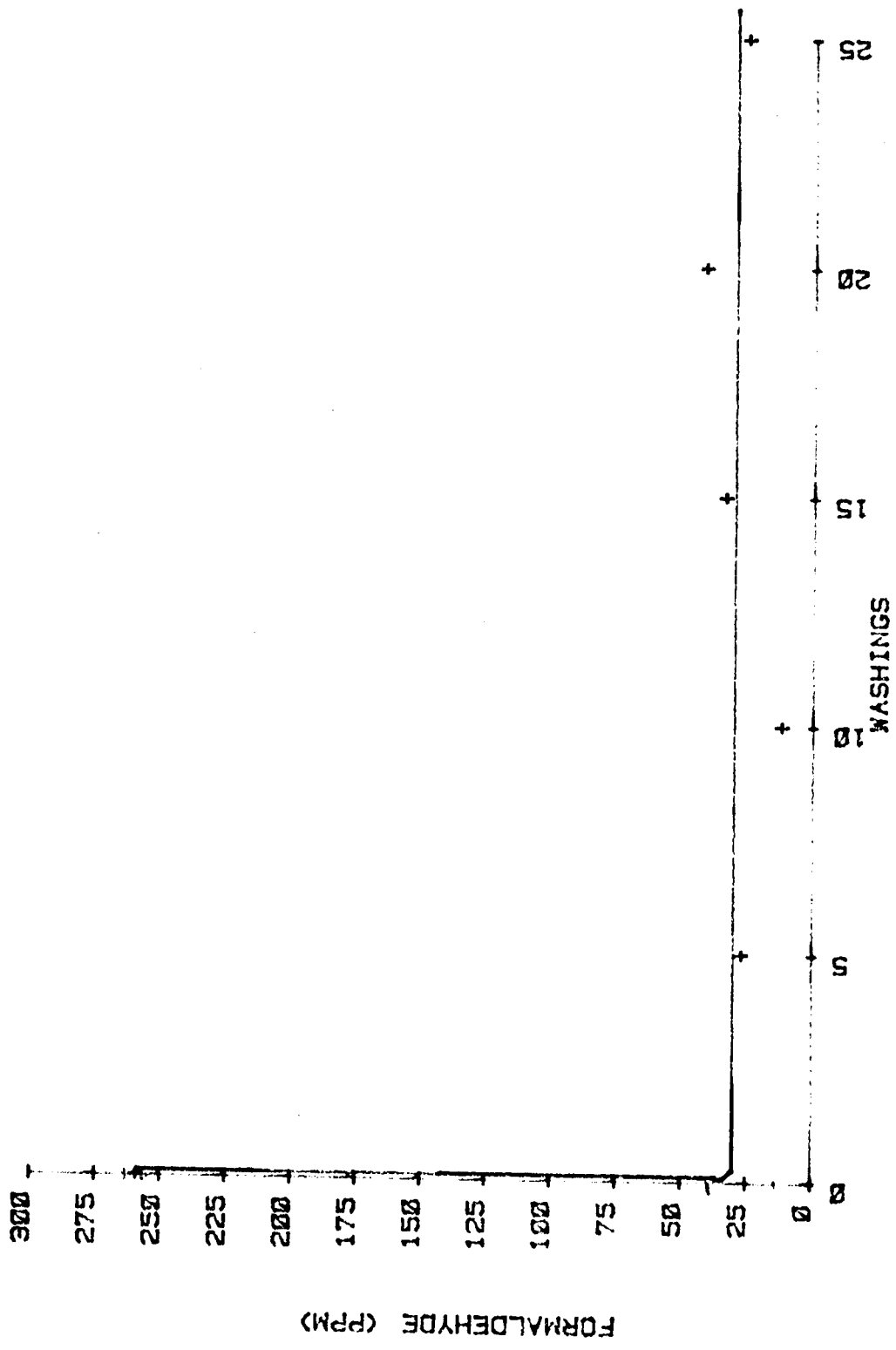


Figure 5. Formaldehyde extracted from 60% cotton/40% polyester shirts (acetylacetone analysis).

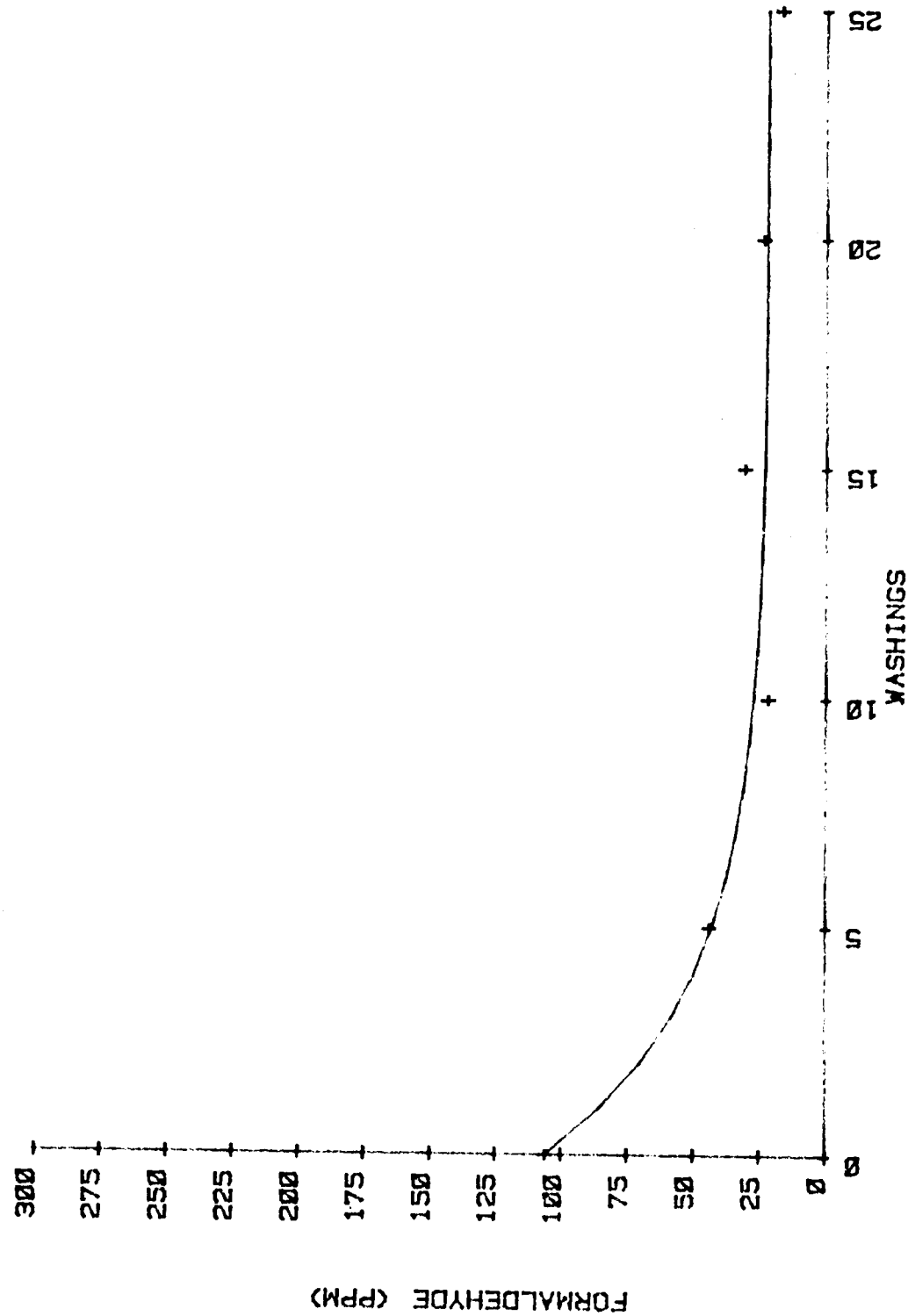


Figure 6. Formaldehyde extracted from 65% polyester/35% cotton shirts (acetylacetone analysis).

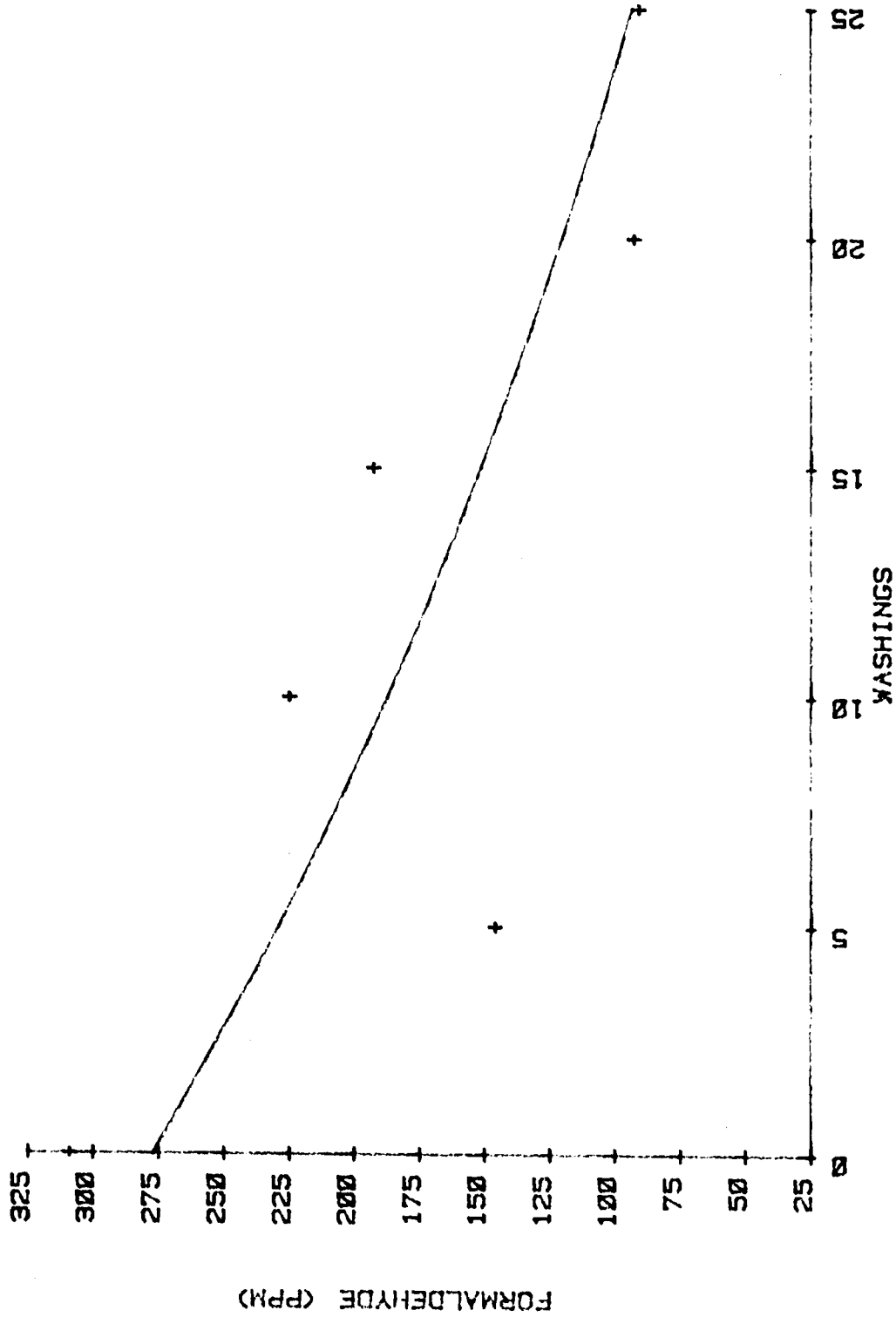


Figure 7. Formaldehyde extracted from 100% cotton shirts (chromotropic acid analysis).

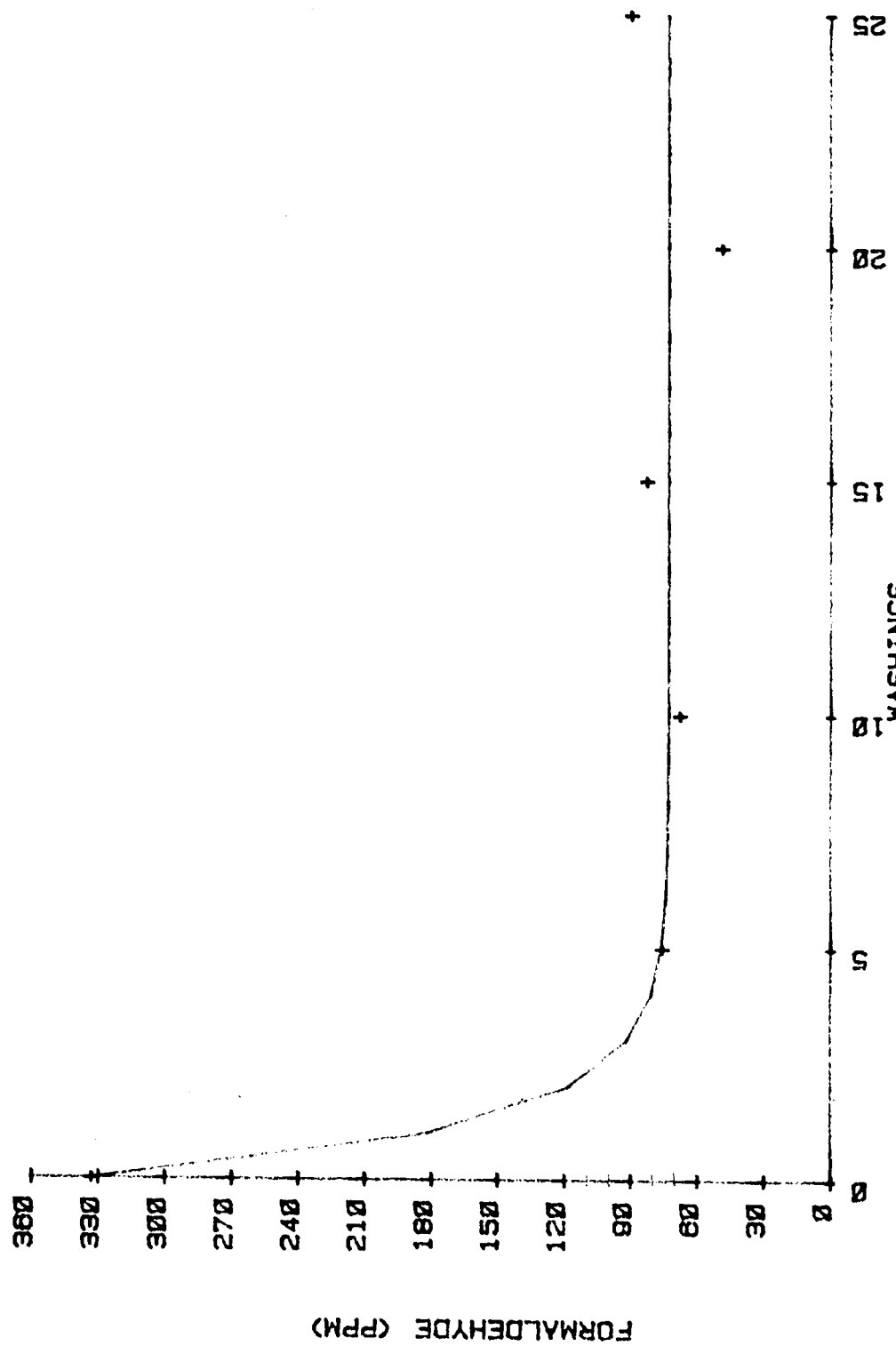


Figure 8. Formaldehyde extracted from 60% cotton/40% polyester shirts (chromotropic acid analysis).

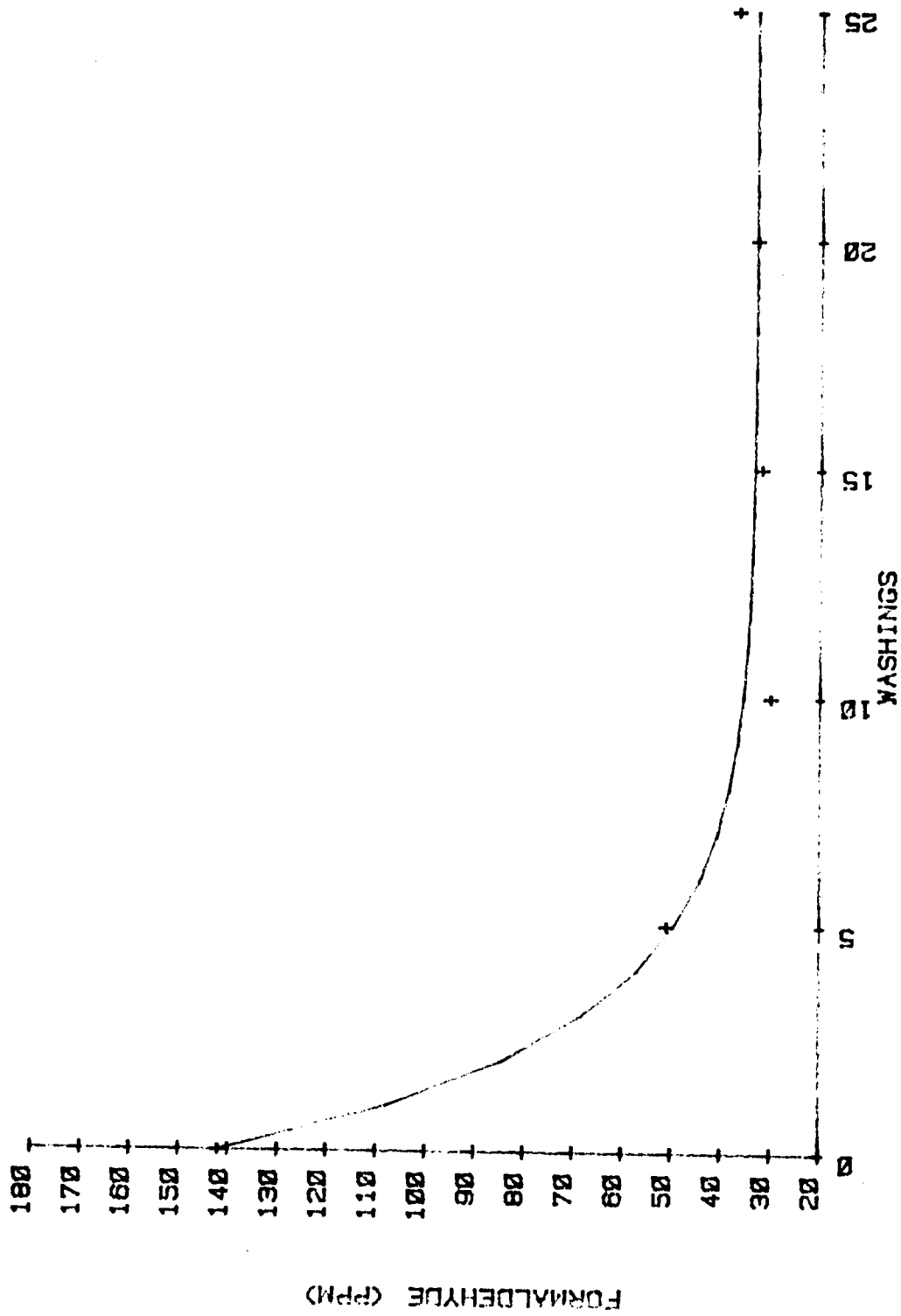


Figure 9. Formaldehyde extracted from 65% polyester/35% cotton shirts (chromotropic acid analysis).

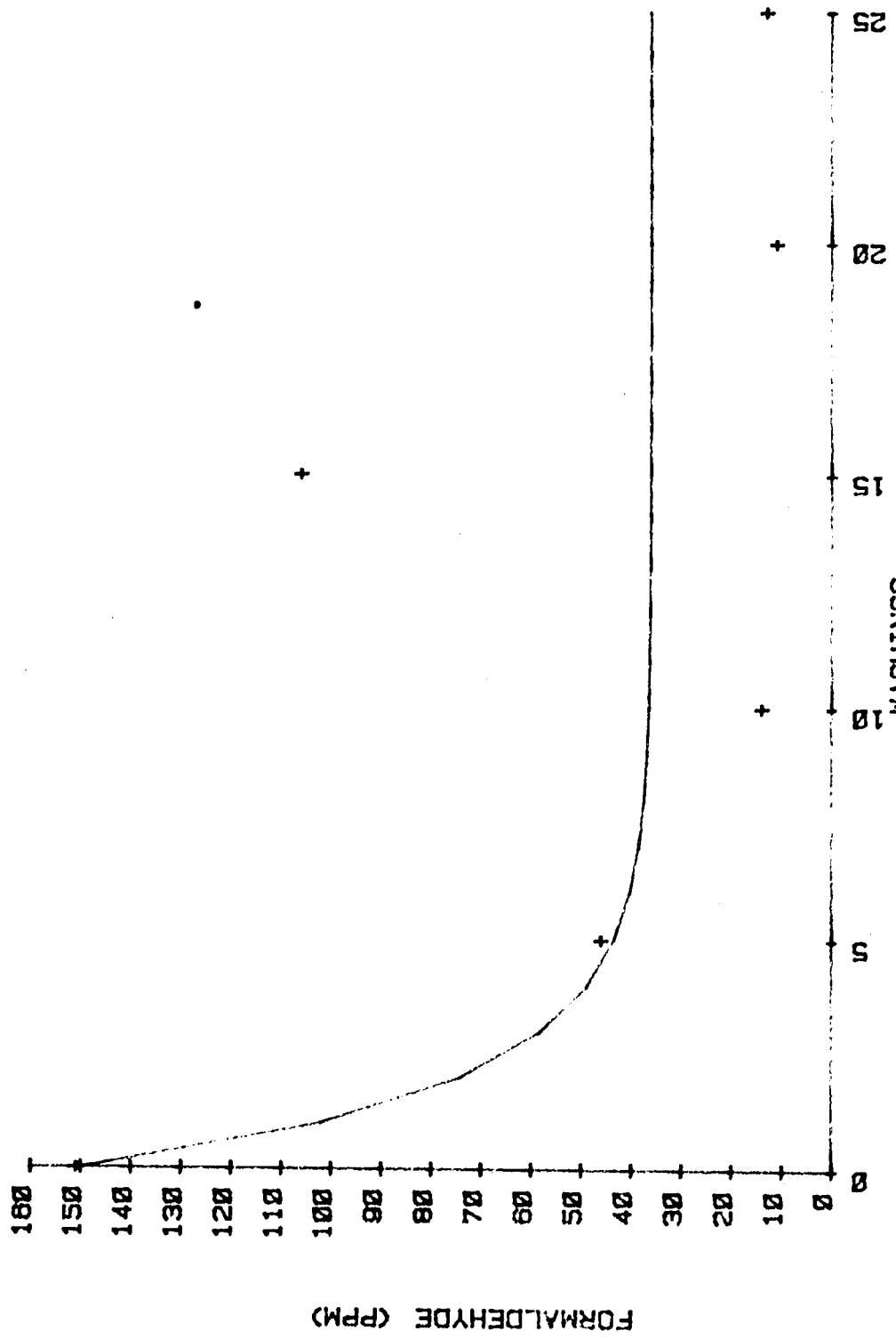


Figure 10. Formaldehyde released from 100% cotton shirts (acetylacetone analysis).

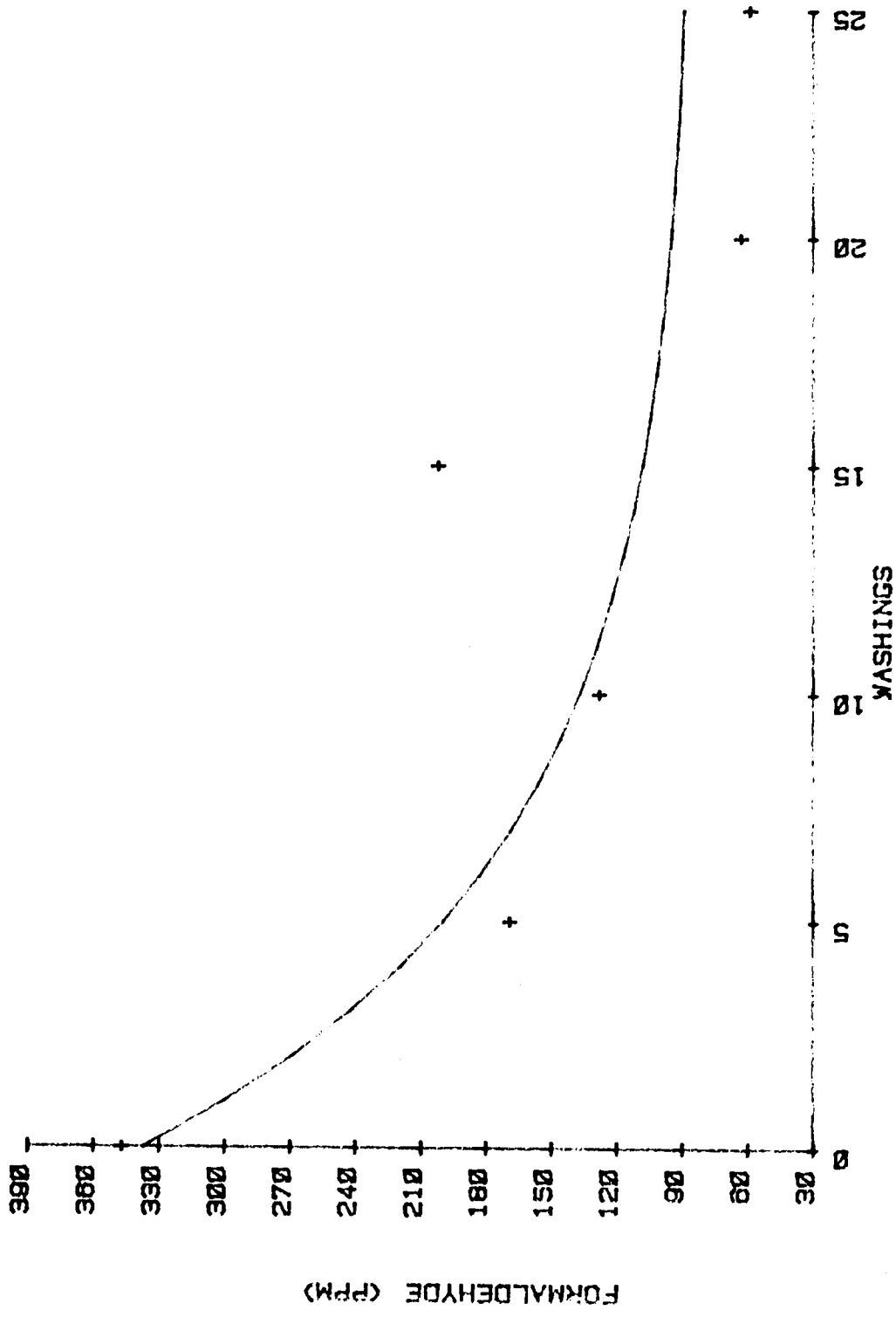


Figure 11. Formaldehyde released from 60% cotton/40% polyester shirts (acetylacetone analysis).

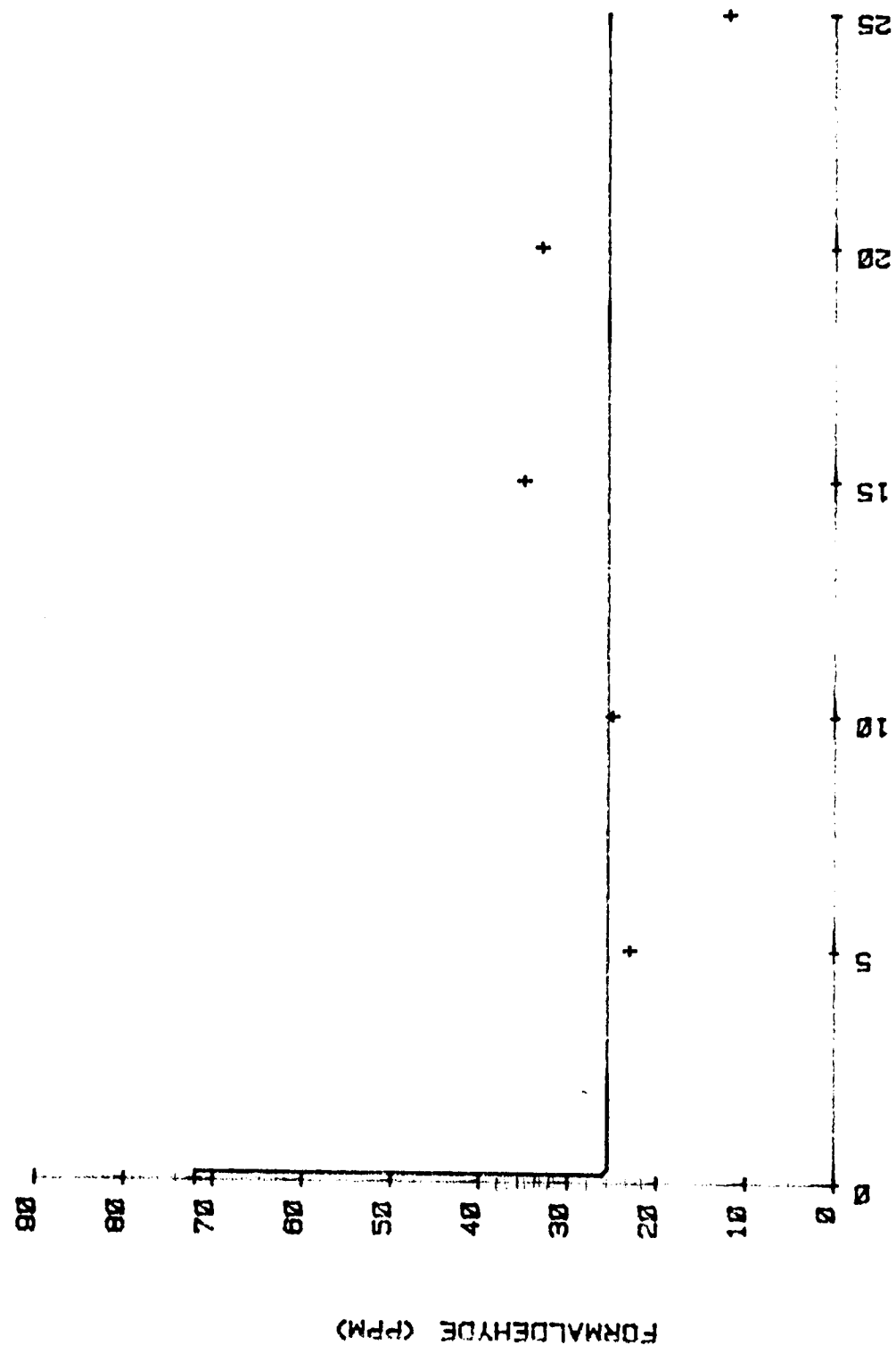


Figure 12. Formaldehyde released from 65% polyester/35% cotton shirts (acetylacetone analysis).

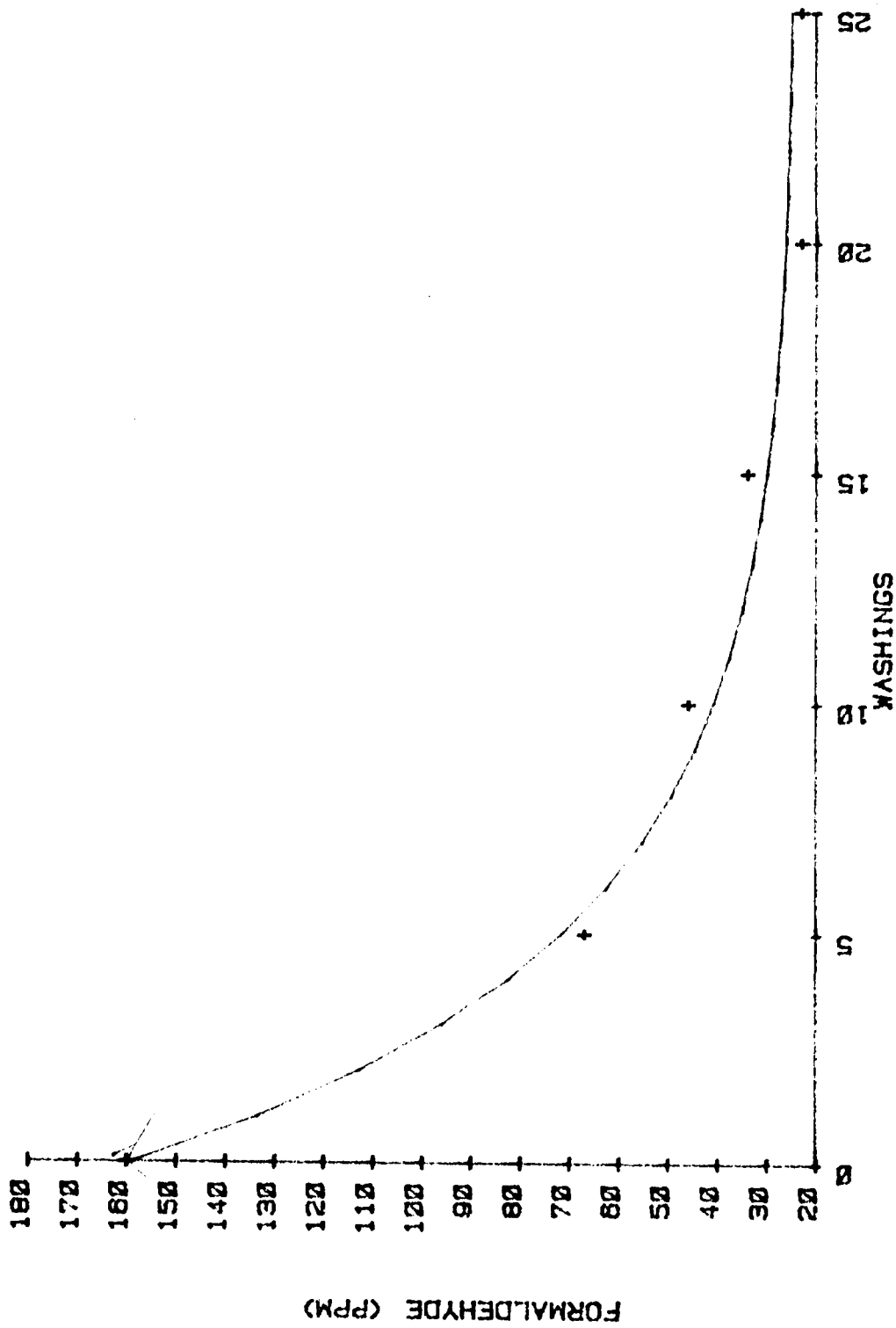


Figure 13. Formaldehyde released from 100% cotton shirts (chromotropic acid analysis).

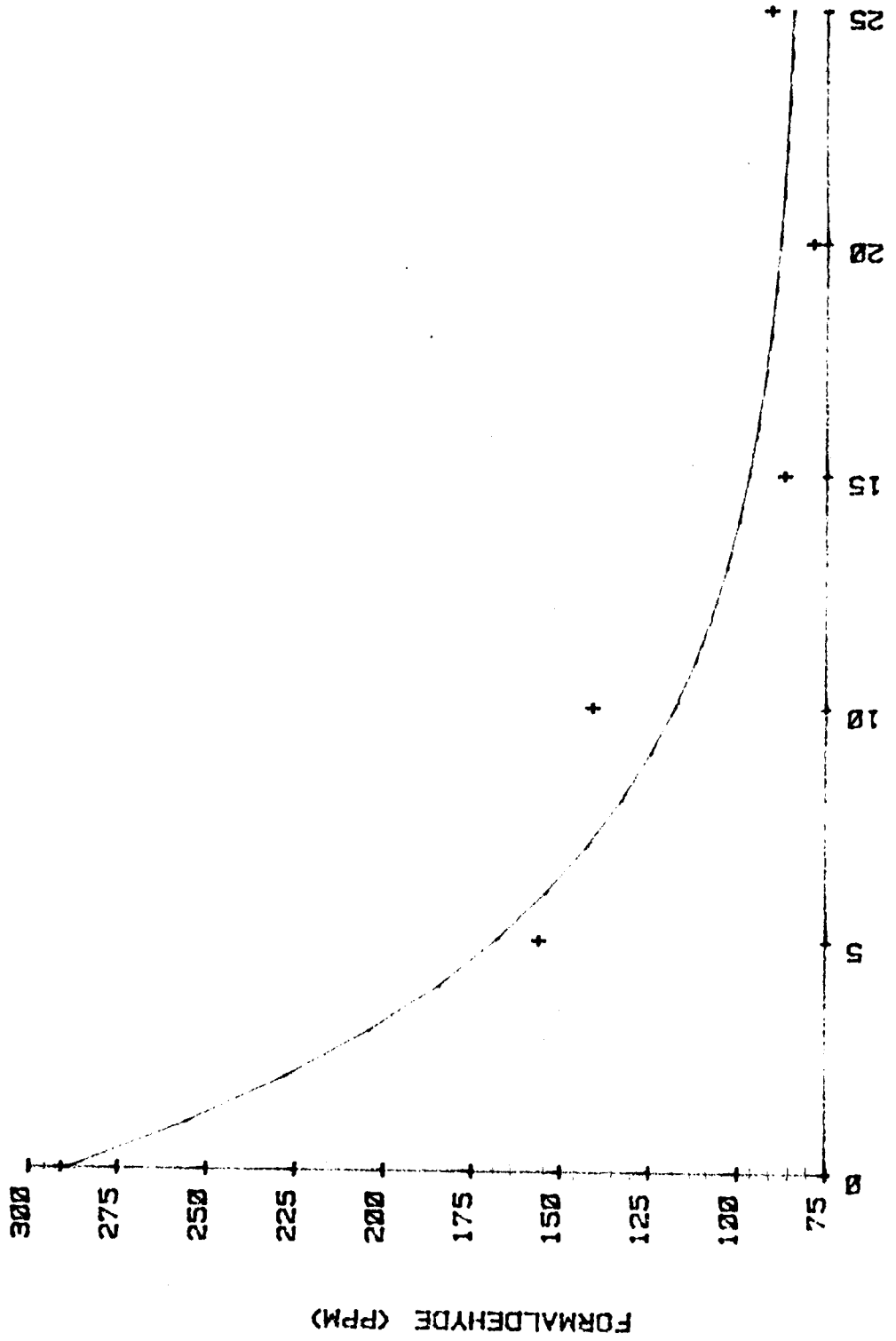


Figure 14. Formaldehyde released from 60% cotton/40% polyester shirts (chromotropic acid analysis).

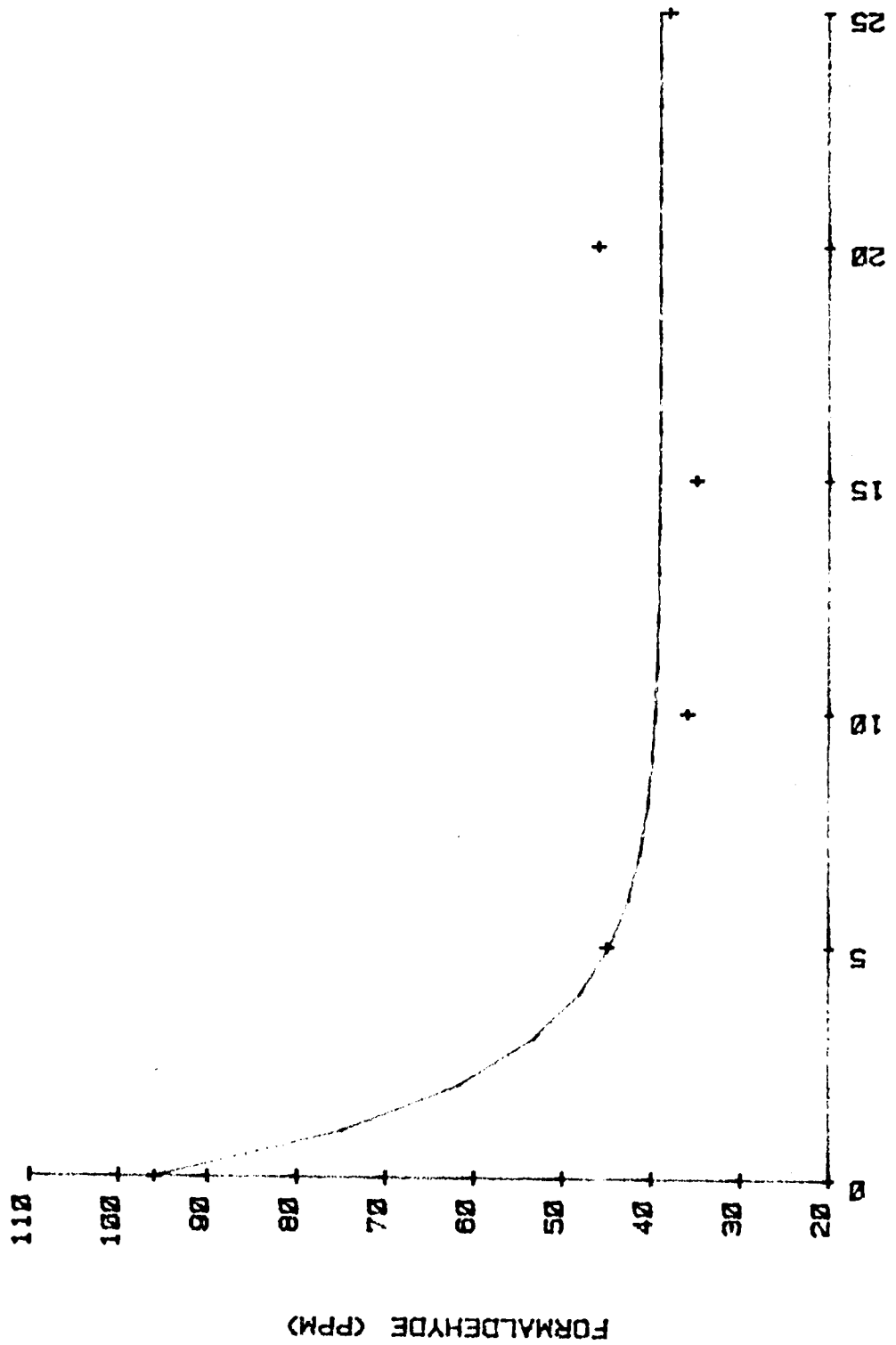


Figure 15. Formaldehyde released from 65% polyester/35% cotton shirts (chromotropic acid analysis).

The more gradual slope for total formaldehyde is probably due to accessibility of formaldehyde in the fiber. The milder conditions of the release or extraction procedures will only hydrolyze the more accessible crosslinks, whereas the digestion in 12N acid is theoretically hydrolyzing most of the crosslinks. If laundering is removing some of the formaldehyde in the most accessible regions of the fiber, this would be seen most dramatically in the release and extraction tests.

The exponential model values indicate that the amount of formaldehyde extracted or released from the shirting fabrics will be reduced by laundering. In the case of the 60% cotton/40% polyester shirts, laundering even one time would reduce the formaldehyde release to at or below the voluntary Japanese standard of 300 ppm. One exception was the regression curve for the Japanese extraction of the 100% cotton shirting fabric. By both AA and CTA analysis, this fabric showed a very gradual reduction in formaldehyde with laundering, similar to the graph for total formaldehyde. In both cases, too, the limiting A value was negative, suggesting that a sufficient number of launderings would eventually reduce the extractable formaldehyde to zero. These are the fabrics finished by the Sanfor-Set liquid ammonia process. Under such treatment, the ammonia molecules enter the cotton fibers, opening up the structure, and then are completely removed (30). After removal of the ammonia, the augmented structure remains. Such a structure would allow for deeper penetration of the extraction liquid and increased access to crosslinks. From the results of the present study, the accessibility in the AATCC sealed jar test is more limited.

Physical Properties

Wrinkle recovery angles were measured for each fabric after each laundering interval (Table 4). Linear regression analysis revealed a correlation (at the 0.10 level) between laundering and wrinkle recovery angle (warp + filling) for the 100% cotton and the 60% cotton/40% polyester shirts (Table 5). The 65% polyester/35% cotton fabric showed a slightly less significant correlation with washing. With a smaller cotton content, this fabric is less dependent on crosslinking resin for its durable press characteristics. From the slopes of the regression lines, it is evident that washing had a greater effect on the wrinkle recovery of the 60% cotton shirts than on the others.

Tearing strength of the shirting fabrics was evaluated at 0 and 25 launderings (Table 4). The data indicate a higher tearing strength for the fabrics with the greater polyester content. According to literature, crosslinking resins reduce the tearing strength of fabrics (34, 37, 76, 77). Consequently, if significant amounts of crosslinks were removed by washing, tearing strength should increase. However in this case, the tearing strength decreased between 0 and 25 washings. So any effects from resin removal were offset by loss of strength from repeated launderings. The largest decrease in tearing strength was in the 60% cotton/40% polyester shirts.

Comparison of Test Methods

From the figures for formaldehyde release (Table 2, page 38) it is evident that the several test procedures differ in determining evolution

Table 4. Physical properties of shirting fabrics

Fabric and wash interval	Wrinkle recovery Angle (°) (Warp + fill)	Tearing force (g)	
		Warp	Fill
100% cotton			
0	255	368	291
5	243	—	—
10	250	—	—
15	244	—	—
20	242	—	—
25	245	275	240
60% cotton/40% polyester			
0	290	426	307
5	270	—	—
10	264	—	—
15	265	—	—
20	265	—	—
25	269	195	118
65% polyester/35% cotton			
0	295	582	365
5	298	—	—
10	284	—	—
15	291	—	—
20	294	—	—
25	284	358	262

Table 5. Linear regression values for wrinkle recovery angle (standard error of estimation)

Fabric	Intercept	Slope	F value
100% cotton	251 (2)	-0.3257 (0.1604)	4.12*
60% cotton/40% polyester	279 (4)	-0.6495 (0.2232)	8.47*
65% polyester/35% cotton	295 (3)	-0.3238 (0.1900)	2.90

*Significant at 0.10 level.

of formaldehyde from durable press fabrics. The AATCC release test has generally been considered harsher than the Japanese extraction test because of the higher temperature and longer time (8, 82).

An analysis of variance procedure was used to determine differences among the two release methods and the two analysis methods for the 0 and 25 wash intervals (Tables 6-8). Release method was a significant factor (at the 0.05 level) for the 65% polyester/35% cotton fabric at 0 washings. After 25 washings, when the level of release was much lower, the method of release was significant for the other two fabrics. From this analysis, it would appear that in unwashed fabrics, the two release procedures would predict approximately the same level of formaldehyde evolution, except where that level of evolution is very low. Examination of the mean values for release (Table 2, page 38) fails to show any consistent trend of one method releasing more formaldehyde than the other. What is of interest is that comparison of coefficients of variation indicates generally more variable results for the Japanese test (Table 9).

Reference to the analysis of variance tables reveals greater differences between the procedures for analytical determination of formaldehyde than between the two release methods. The factor of analysis was significant for all fabrics except the unwashed 60% cotton/ 40% polyester. This means that analysis of the same liquors by AA or by CTA is giving anomalous results.

Difference in the two analysis procedures might arise because of the precision of the two methods of color development and absorbance measurement. When the recommended procedure for the development of

Table 6. Analysis of variance for test methods on 100% cotton shirts

Source	Sum of squares	df	F value
0 washings			
Model	103038.00	3	59.18*
Release	1776.33	1	3.06
Analysis	54136.33	1	93.28*
Resease × analysis	47125.33	1	81.20*
Error	4542.6	8	
Total	107680.67	11	
25 washings			
Model	13397.58	3	45.73*
Release	2914.08	1	29.84*
Analysis	6486.75	1	66.42*
Release × analysis	3996.75	1	40.92*
Error	781.33	8	
Total	14178.92	11	

*Significant at 0.10 level.

Table 7. Analysis of variance for test methods on 60% cotton/ 40% polyester shirts

Source	Sum of squares	df	F value
0 washings			
Model	14426.25	3	2.97
Release	1564.08	1	0.97
Analysis	252.08	1	0.16
Release × analysis	12610.08	1	7.79*
Error	12944.67	8	
Total	27370.92	11	
25 washings			
Model	8612.33	3	93.87*
Release	867.00	1	28.35*
Analysis	6912.00	1	226.01*
Release × analysis	833.33	1	27.33*
Error	244.67	8	
Total	8857.00	11	

*Significant at 0.10 level.

Table 8. Analysis of variance for test methods on 65% polyester/ 35% cotton shirts

Source	Sum of squares	df	F value
0 washings			
Model	7548.33	3	4.06*
Release	4800.00	1	7.75*
Analysis	2640.33	1	4.26*
Release × analysis	108.00	1	0.17
Error	4955.33	8	
Total	12503.67	11	
25 washings			
Model	1584.67	3	10.85*
Release	16.33	1	0.34
Analysis	1541.33	1	31.67*
Release × analysis	27.00	1	0.55
Error	389.33	8	
Total	1974.00	11	

*Significant at 0.10 level.

Table 9. Coefficients of variation for formaldehyde analyses

Fabric and wash interval	Standard deviations (ppm)			
	Japanese AA*	Japanese CTA**	AATCC AA*	AATCC CTA**
100% cotton				
0	0.86	0.06	0.07	0.03
5	0.80	0.09	0.48	0.03
10	0.58	0.18	1.07	0.15
15	0.54	0.09	0.07	0.03
20	0.18	0.68	0.18	0.04
25	1.13	0.19	0.31	0.04
60% cotton/40% polyester				
0	0.12	0.08	0.19	0.08
5	1.22	0.39	0.15	0.06
10	1.25	0.09	0.04	0.01
15	0.47	0.05	0.06	0.02
20	0.12	0.20	0.14	0.03
25	0.23	0.06	0.05	0.01
65% polyester/35% cotton				
0	0.30	0.26	0.04	0.02
5	0.30	0.31	0.13	0.11
10	0.82	0.04	0.48	0.08
15	0.13	0.06	0.11	0.09
20	0.63	0.21	0.61	0.22
25	0.76	0.05	0.25	0.05

*Acetylacetone analysis.

**Chromotropic acid analysis.

color with AA is used, the absorbance values are very low at the low concentrations encountered in this study. The absorbance values are in fact below 0.1, i.e., in the range of maximum error (86). CTA analysis of the same solutions, however, yielded absorbance values above 0.2, in the range of minimum error. If the coefficients of variation for the several analyses are examined, the precision of the CTA method is generally greater (Table 9). This conclusion is understandable as the CTA method used was the result of an optimization experiment (61).

Considering the interaction of release method and analysis, the most precise and consistent results are those from the AATCC test analyzed by the CTA method.

Determination of Temperature Coefficients

In order to further examine the differences between the Japanese and AATCC procedures and to determine the physical or chemical nature of the processes involved in each test, a temperature coefficient was determined for the 100% cotton fabric. The Japanese test and the AATCC test were performed at three different tempe-atures. As previous analyses had revealed the CTA method to be more precise, this was the procedure employed for formaldehyde determination of the extraction or release liquors. Plots of reciprocal temperature versus the logarithm of the rate constant (k) are presented in Figure 16 (Japanese test) and Figure 17 (AATCC test). The slope was used to calculate the energy change according to the equation:

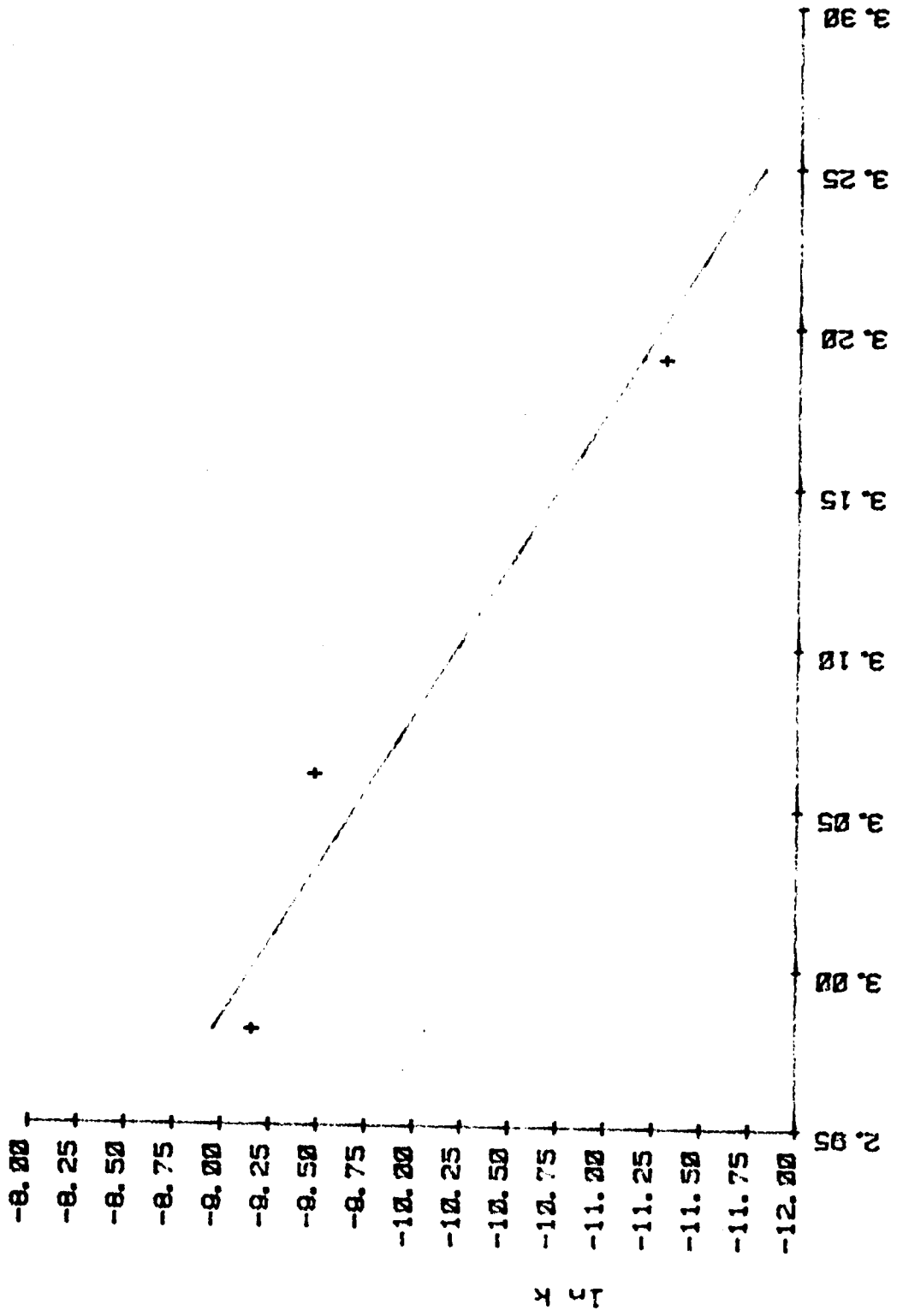


Figure 16. Temperature coefficient for Japanese test.

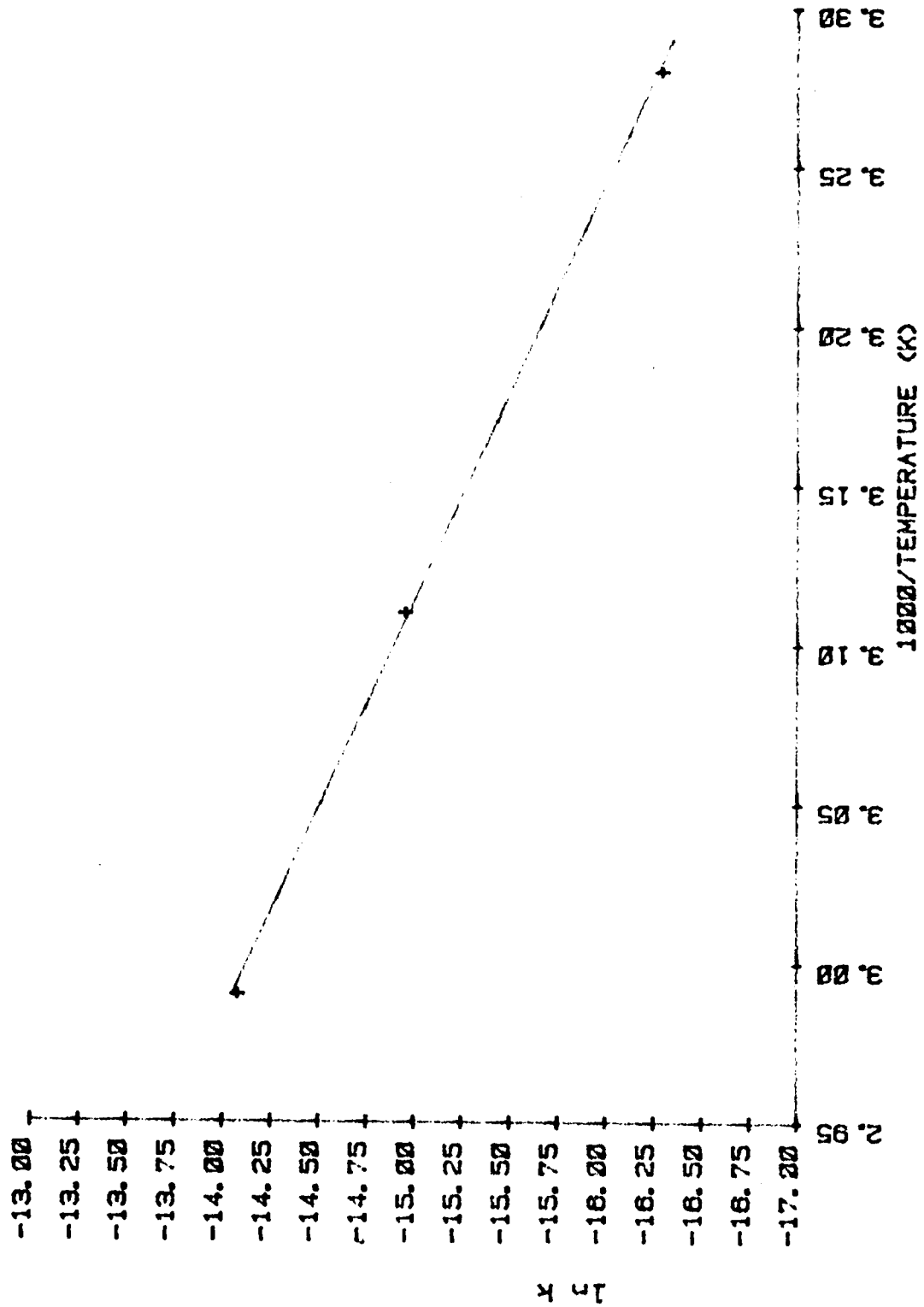


Figure 17. Temperature coefficient for AATCC test.

$$\ln k = - \frac{E_a}{R} \left(\frac{1}{T}\right) + C$$

where

R = gas constant,

T = temperature in °K, and

C = intercept.

The regression equation values for each test are presented in Table 10. The calculated E_a for the AATCC test was 15.2 kcal; the E_a for the Japanese test was 21.0 kcal.

It would appear from the magnitude of the calculated activation energies that, in each case, a chemical reaction is taking place. It is not likely that only a physical removal of adsorbed free formaldehyde is operative. Such judgment is confirmed by the negative results for free formaldehyde mentioned earlier.

Table 10. Temperature coefficients for formaldehyde evolution from 100% cotton fabric (standard error of estimation)

Test	Temperature coefficient (slope)	Frequency factor (intercept)	F value
Japanese	-10558 (2673)	22.50 (8.23)	15.61
AATCC	-7638 (175)	8.77 (0.54)	1896.77*

*Significant at 0.10 level.

CHAPTER 5

SUMMARY AND CONCLUSIONS

This study proposed to address the inchoate problem of formaldehyde in durable press consumer products. Two areas worthy of investigation were the determination of formaldehyde levels in consumer products in the market, and a comparison of existing test methods used to assess the extent of the problem of formaldehyde in textiles.

Men's dress shirts, as representative of durable press products on the market today, were purchased and analyzed for formaldehyde content and release, initially and after selected laundering intervals. Three different shirting fabrics were tested: 100% cotton with a Sanfor-Set finish; 60% cotton/40% polyester with a durable press finish; and 65% polyester/35% cotton with a durable press finish.

The shirts with 60% cotton content contained and released the greatest amount of formaldehyde. Although the 100% cotton fabric had a higher cotton content, the fabric finish was a combination of liquid ammonia mercerization and durable press resin. Consequently the formaldehyde content of these shirts was less than that of the 60% cotton/40% polyester. The 100% cotton fabric, however, contained and released slightly more formaldehyde than the 65% polyester/35% cotton fabric.

Formaldehyde in the shirting fabrics was determined in several forms; as free or adsorbed formaldehyde; as formaldehyde in methylol groups ($>CH_2OH$); and as total formaldehyde which includes the above groups as well as formaldehyde in methylene ether crosslinks. Analytical

determinations showed the shirting fabrics to contain little or no free or methylol formaldehyde. Total formaldehyde in the fabrics ranged from 4,000 to 13,000 ppm.

Very little of the total formaldehyde was released in tests designed to evolve hydrolyzable formaldehyde from durable press fabrics. The two standard tests for formaldehyde evolution, the Japanese test and the AATCC test, were performed to assess the effect of laundering on formaldehyde release. Results indicate that the greatest amount of formaldehyde was released from unwashed fabrics. Thereafter, with continued washing, the shirts quickly reached a limiting value for formaldehyde release which was unaffected by further washing. In the case of each shirting fabric, this value was well below the Japanese voluntary standard of 300 ppm in durable press shirts for consumer use. This leads to the conclusion that laundering, either by the manufacturer or by the consumer, would greatly lower the degree of risk from formaldehyde in textile products. It should be remembered also that the two test methods represent conditions much harsher than would be encountered in ordinary consumer use of the products, and therefore the limiting levels for formaldehyde release are not an absolutely accurate estimate of any hazard. If these tests are used to assess consumer risk, there is a large safety factor built in.

The two test methods, as well as two different colorimetric procedures for formaldehyde determination, were compared. Neither the Japanese nor the AATCC test could be said to consistently evolve more formaldehyde in these typical consumer products. There were significant

differences between the two only at low levels of release. However, there did appear to be differences between the two procedures for determination of formaldehyde (acetylacetone and chromotropic acid). The latter method, CTA, proved to be more precise, perhaps because absorbance values for this reagent were in the range of minimum error.

Further comparison between the Japanese and AATCC tests was made by determining temperature coefficients, and derivatively activation energies for each procedure. The ΔE for the Japanese test was 21.0 kcal, and for the AATCC test was 15.8 kcal. These values indicate that in the case of each test a chemical reaction is taking place, viz., hydrolysis of the ether crosslinks.

The results of this study indicate that the CTA determination should prove of more utility in assessing formaldehyde release from fabrics. Further work is needed on the procedures for formaldehyde release. It would be of interest to vary the times and temperatures involved in the Japanese and AATCC tests to establish a procedure which more adequately reflects consumer use conditions. Andrews (6) has proposed, also, maintenance of a lower relative humidity in the AATCC test.

Dr. Robert Barker (14) has suggested that any imminent regulation will concern free formaldehyde in consumer products, rather than liberated or bound formaldehyde. In such a case, more accurate methods for determination of free formaldehyde will be necessary. In this study no free formaldehyde could be detected in typical consumer products. Does this mean that these products are free from risk? Clearly the

matching of test method to perceived risk to the public should precede promulgation of standards for formaldehyde levels in such consumer textiles.

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VITA

Billie Jean Walters was born in Bunkie, Louisiana, on September 6, 1944. She graduated from Fortier High School, New Orleans, Louisiana, in 1962. She attended Newcomb College of Tulane University, New Orleans, and graduated, cum laude, in June 1966, receiving a Bachelor of Arts degree in Applied Music. She taught piano in New Orleans from 1966 to 1968.

In June 1974, she entered The University of Tennessee, Knoxville, as a graduate student in the Textiles and Clothing Department, College of Home Economics; and in January 1975, she received a research assistantship from the U.S.D.A., A.R.S., Textiles and Clothing Laboratory. She received a Master of Science degree in June 1976. In March 1977 she entered the interdisciplinary doctoral program in Home Economics at The University of Tennessee, Knoxville, and in September 1977 received a teaching assistantship. In September 1978 she received a research assistantship from the U.S.D.A., A.R.S., Textiles and Clothing Laboratory. She received a Doctor of Philosophy degree in June 1981.

She is a member of the American Association of Textile Chemists and Colorists, the American Home Economics Association, Phi Kappa Phi, Phi Bhta Kappa, and Omicron Nu.