

KINETICS OF 3,5-DIACETYL-1,4-DIHYDROLUTIDINE
IN FORMALDEHYDE DETECTION

by

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Abstract

Formaldehyde, a hazardous and toxic substance, can be found in most resin treated durable press fabrics. The current formaldehyde regulations are limited to worker exposure in an industrial setting and the possibility of government regulation of formaldehyde release from textiles is of concern to the textile industry. The most common test of formaldehyde release used by the U.S. textile industry is the AATCC Test Method 112, a colorimetric determination based on the Hantzsch reaction between ammonia, formaldehyde, and acetylacetone. The chromophore formed is 3,5-diacetyl-1,4-dihydrolutidine (DDL). In the AATCC test the ammonia and acetylacetone are in the Nash reagent and the formaldehyde is extracted from the fabric by trapped steam. The formaldehyde in solution and the Nash reagent are mixed and the color developed.

The purpose of this study was to determine if a more effective formulation of the Nash reagent than currently used by industry can be produced. The reaction between the Nash reagent and formaldehyde is first order in formaldehyde, therefore pseudo-first order kinetics was used as the basis of the study. Reagent effectiveness was determined by comparisons and calculations based on the molar extinction coefficient, maximum absorbance, and rate constant. The study was set up in phases to investigate the effect of different ammonia sources, the effects of varying concentrations of the reactant components, the effect of ageing, and the effect of different temperatures on the formation of DDL. In

the final phase the best reformulated reagent was compared to the Nash reagent under the conditions of the AATCC Test Method 112.

Several reformulations were found to be comparable to Nash, but none was found to be more effective in formaldehyde detection. This study has shown some of the complexities of the reaction and that the Nash reagent is not able to obtain 100% conversion of formaldehyde to DDL. Therefore, any test that uses the Nash reagent is underestimating the releasable formaldehyde concentration in the fabric.

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Chapter I

Introduction

Formaldehyde, a common environmental pollutant, is listed as a hazardous and toxic substance by the Occupational Safety and Health Administration (OSHA). This substance has a broad range of physiological effects that include hypersensitivity of the eyes and respiratory tract due to prolonged exposure, and contact dermatitis due to sensitivity to an object containing formaldehyde (O'Quinn & Kennedy, 1965). Other effects are nausea, headache, tiredness, and thirst (Committee on Aldehydes, 1981).

A 1979 study by the Chemical Industry Institute of Toxicology (CIIT) showed that formaldehyde inhalation of 5.6 to 14.3 parts per million (ppm) at an exposure rate of six hours a day, five days a week for 24 months resulted in nasal cancer in rats. This study also showed dose-related changes in the microscopic structure of the tissues of the mucous membrane after exposure at 2, 6, and 15 ppm (Starr, et al., 1985). The results of the CIIT study cannot be extrapolated to define human risk, but many feel these results support the need to monitor, control and investigate human exposure to formaldehyde more thoroughly. People exposed to concentrations of 0.5-1.0 ppm have reported respiratory tract irritation, and in controlled laboratory studies responses were noted at concentrations as low as 0.01 ppm (when combined with other air pollutants) (Committee on Aldehydes, 1981).

High concentrations of formaldehyde pose a threat to exposed individuals, therefore the United States, along with other industrialized nations, has an established occupational standard for formaldehyde exposure. The U.S. occupational standard is an average of 3 ppm over eight hours, while other countries have limits of 1 ppm and as low as 0.4 ppm (Perera & Petito, 1982; Preuss, Daily, & Lehman, 1985).

Industrial workers are the only segment of the population that would be exposed to high concentrations of formaldehyde but other groups may be exposed to levels that could result in a health hazard. It is estimated that 10-20% of the general population may be susceptible to the irritant effects at low concentrations. Some sources that increase the level of formaldehyde in the environment are automobile exhaust, mobile homes, urea-formaldehyde foam insulation (UFFI), particleboard, and plywood (Committee on Aldehydes, 1981). Since the result of prolonged exposure to low concentrations is not known, several European countries have set a standard of an average of 0.1 ppm for residential and recreational interiors (Perea & Petito, 1982).

One of the few countries with consumer-oriented formaldehyde regulations is Japan. The formaldehyde content of household goods is monitored and controlled. It is banned in textiles intended for infants up to 24 months old. For individuals over 24 months old a ceiling is specified on formaldehyde release of 75 ppm or 75 micrograms per gram of fabric (Control Law, 1975).

Since 1980 the formaldehyde issue in the United States has gone full circle. In 1980 the Federal Panel on Formaldehyde reviewed the issue. As a result of the review the Consumer Product Safety Commission (CPSC) banned the use of UFFI, but the Environmental Protection Agency (EPA) and OSHA took no regulatory action to change the current occupational standards or to propose new standards. In March 1981 the EPA designated the substance a priority for regulatory review. In October 1981 the United Auto Workers and other major labor unions petitioned OSHA to set an emergency temporary standard for formaldehyde exposure. In 1982 the EPA concluded that the substance did not pose a significant carcinogenic risk. OSHA concluded that risks at the current exposure limit of 3 ppm were not sufficient to change the standard. In that same year the Formaldehyde Institute filed suit against the CPSC ban on UFFI, and in 1983 the ban was overturned (Ashford, Ryan, & Caldart, 1983). In 1984 the EPA decided to give priority to the issue again and to consider ways to regulate the chemical (Formaldehyde Issue, 1984). In 1987 OSHA set worker exposure to formaldehyde at 1 ppm over an eight hour period. In June 1989, the Amalgamated Clothing and Textile Workers Union (ACTWU) and other labor groups challenged the standard in a lawsuit against OSHA. The labor groups want the standard reduced to 0.5 ppm. The U.S. Court of Appeals for the District of Columbia ordered OSHA to reconsider the standard but took no further action toward lowering the standard (La Russa, 1989).

While the concept of further formaldehyde regulation seems to be in the direction of the industrial setting, the possibility of government regulation of formaldehyde release from textiles is of concern to the textile industry (Madaras, 1980; Ramey, 1981). Durable press (DP) textiles are one source of formaldehyde exposure to humans. Formaldehyde is a common component in resin finishes used to impart DP characteristics to textiles containing cellulosic fibers. DP textiles are not large contributors of the pollutant to the general environment, but are considered to be one of the more controllable sources of formaldehyde. There is interest in DP textiles because of the potential for worker exposure to high concentrations of formaldehyde during processing of the textiles, and for consumer exposure to low concentrations in close proximity to the body over prolonged periods of time.

Since 1975, the textile industry has reduced the formaldehyde content in resin finishes by one-third. The push is for further reductions or discontinued use of formaldehyde in textiles ("Dye, Print, Finish", 1985). In 1985 it was estimated that 85 % of all apparel sold in the United States may have been treated in some way with formaldehyde. As of 1985, there was not a durable formaldehyde-free finish that produced an acceptable product (Frick, 1986), and there have been no recent publications that indicate an acceptable substitute has been found.

There is interest in establishing a nationally, as well as internationally, accepted method of measuring formaldehyde release from

textiles (Ramey, 1981; Vail & Reinhardt, 1981). More countries are becoming aware of the issue and of the potential for regulation of formaldehyde release from textiles.

The most common test for formaldehyde detection in use by the U.S. textile industry is the American Association of Textile Chemist and Colorist (AATCC) Test Method 112 (1988). This test is designed "to determine the amount of formaldehyde released under the conditions of accelerated storage" (AATCC, 1988). Since the development of this test method the formaldehyde levels on DP textiles have been greatly reduced, making accurate detection of the releasable concentration difficult. The Nash reagent is the reagent used in the AATCC test. This reagent reacts with formaldehyde and forms a chromogen, or colored species. The Nash reagent is used because it is fast, simple, not very sensitive to temperature changes, and not hazardous, and it has a sensitive visible wave length range. Even though this reagent is widely used, there are two main concerns with it: 1) the high degree of variability found in interlaboratory studies and 2) of some question as to what the lower limit sensitivity range is. Research on the Nash reagent has dealt with sources of error that would explain the interlaboratory variability but has excluded an extensive study of the reagent formulation and the formation of DDL.

The purpose of this study was to examine the Nash reagent in detail and to determine a more effective reformulation of the reagent. The main objective was to develop a reformulation of the Nash reagent which

will provide greater reagent stability and enhanced sensitivity to formaldehyde detection. The extinction coefficients and kinetics were used to evaluate effectiveness of alternate reagent formulations.

Chapter II

Review of Literature

The topics reviewed are formaldehyde release from durable press textiles, and methods of measuring formaldehyde release from textiles including spectrophotometric determination, gas chromatographic methods and voltammetric methods.

Formaldehyde Release From Durable Press Textiles

In order to obtain durable press (DP) characteristics, the cellulosic component of most fabrics must undergo chemical modification. This is generally achieved by means of a cross-linking agent, or reactant, that forms chemical bonds between cellulose molecules. Most of the effective and efficient reactants utilize the reactivity of formaldehyde (Petersen, 1986). The reactions which crosslink cellulose with these reactants are reversible, and under certain conditions the reactants can break down into compounds from which formaldehyde may be generated (Harper, 1983).

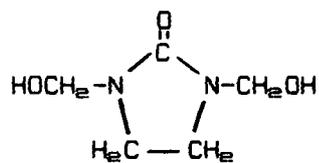
The amount of formaldehyde in DP fabrics is a function of many variables. The variables reviewed include reactant composition, leaving group of the reactant, catalysts, temperature of the cure, additives to the pad bath, concentration of the reactant, afterwash, aftertreatments, and effect of pH in home laundering (Cooke, 1981; Petersen, 1986).

The reactant composition should be such that the molecules will react readily with the hydroxyl groups of cellulose, forming crosslinks

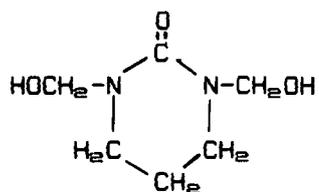
instead of undergoing polymerization. The reactivity of different reactants with cellulose varies widely. There is a direct relationship between this reactivity and the rate of hydrolysis of the reactant from cellulose. The reactants with lower levels of reactivity will have the greatest resistance to hydrolysis (Cooke, 1981).

The most widely used formaldehyde reactant types are cyclic urea-formaldehyde and methylol carbamates (Figure 1) (Cooke, 1981). The leaving group for the reactants is hydrogen. Hydrogen (-H), ethyl (-C₂H₅), and methoxyethyl (-CH₂CH₂OCH₃) are considered to have intermediate reactivities requiring curing temperatures of 130°C-140°C. The leaving group with the lowest reactivity is methyl (-CH₃) with a curing temperature of 150°C (Petersen, 1986).

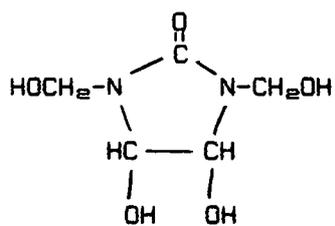
The pH of the pad bath contributes to the reactivity of formaldehyde reactants and cellulose. The reactivity of formaldehyde reactants increases as the environment becomes more acidic. Mineral acids or metal salts, with Lewis or Bronsted acid activity, are used as catalysts for reaction. The strength of the catalysts varies widely. A reactant with low reactivity will increase in crosslinking ability as catalyst strength increases (Cooke, 1981). According to Kullman, Pepperman, and Vail (1978) a fabric treated with an N-methylol reactant (R₂-N-CH₂OH) in combination with a strong catalyst system should result in a highly crosslinked system more resistant to hydrolysis. The problem is that this system could increase the amount of free formaldehyde as well as increase the amount of crosslinking. N-methylol compounds can react in two ways: 1) splitting of the carbon-oxygen bond produces a



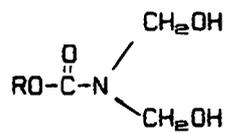
DMEU



DMPU



DMDHEU



Methylol carbamate

Figure 1. Common formaldehyde reactants.

carbonium-immonium ion that can react with a cellulose hydroxyl to form a crosslink; and 2) splitting the nitrogen-carbon bond produces a carbonium-oxonium ion that can react with a cellulose hydroxyl to form a methylene-ether linkage, capable of reacting with water to release free formaldehyde (Petersen, 1970). The nitrogen-carbon dissociation depends on the catalyst and temperature of the pad bath, and it allows free formaldehyde release in the pad bath (Cooke, 1981; Kamath, Weber, Hornby, & Weigman, 1985).

The most effective and efficient formaldehyde reactant used for DP fabrics is dimethyloldihydroxyethyleneurea (DMDHEU). The DMDHEU molecule (Figure 1) is multifunctional, and can bond with cellulose through the N-methylol groups or through the ring hydroxyls (Cooke, 1981; Petersen, 1986; Reinhardt, Andrews, & Harper, 1981). Some possible reactions between DMDHEU and cellulose are shown in Figure 2. Reaction a, that of the two N-methylol group with two hydroxyl groups of cellulose, is the desired reaction for optimum DP characteristics and is the predominant reaction (Petersen, 1986). Reaction c between a ring hydroxyl and cellulose also occurs. Reaction d occurs as a result of free or liberated formaldehyde and is not prevalent in DP fabrics. Cross-linking of the reactant molecules, reaction e, can take place, but is rarely found (Cooke, 1981; Petersen, 1986; Reinhardt, et al., 1981).

Formaldehyde release from fabric is initially the result of unbound formaldehyde in the fabric (Jaco & Hendix, 1982; Reinhardt, et al., 1981). Since a strong catalyst system would increase the initial

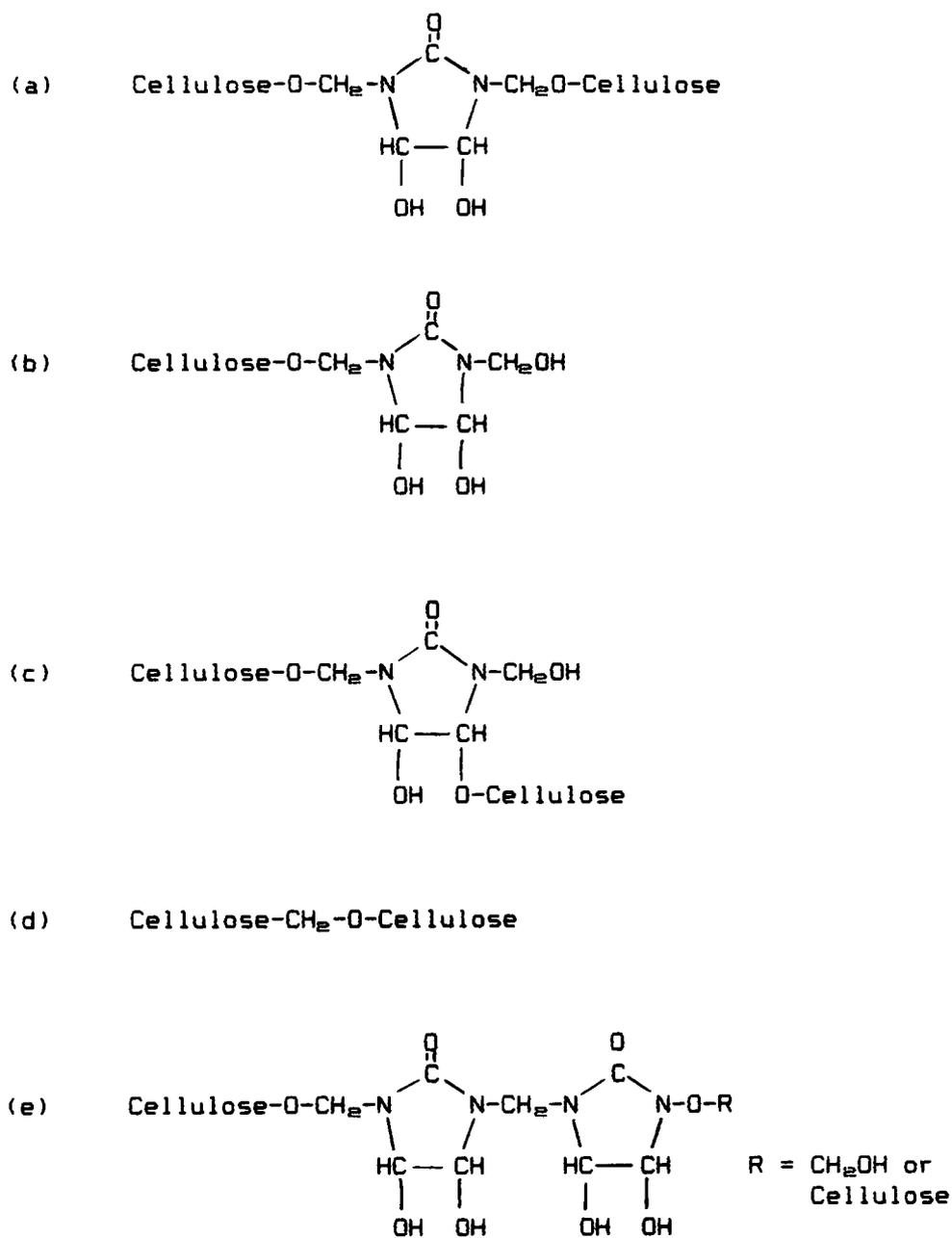


Figure 2. Possible reactions between DMDHEU and cellulose.

formaldehyde release by allowing a higher free formaldehyde content in the pad bath (Kullman, et al., 1978), an afterwash should remove most of the free formaldehyde. However, because an afterwash is not a standard industry process for finishing fabrics, the fabric would reach the consumer with a potentially high formaldehyde content (Reinhardt, et al., 1981). The textile industry has investigated and developed some means of reducing the free formaldehyde content in fabrics.

Formaldehyde scavengers that tie up the formaldehyde, preventing it from depositing in the fabric, have been found to be effective when used in the pad bath or in an aftertreatment. Some scavengers have been able to reduce initial formaldehyde release by 60%, as measured by AATCC Test Method 112. There can be detrimental effects from the use of scavengers, such as odor, discoloration, reduced lightfastness of some dyes, chlorine retention, and decreased curing ability of the reactant (Cashen, 1979; Reinhardt & Daigle, 1984; Perry, Tsou & Lee, 1980).

An alternative method of applying the reactant has been investigated. A foam application of DMDHEU studied by Rowland, Bertoniere and King (1983) did allow for less of the reactant to cover more of the fabric, but the result was not only lower formaldehyde release but also lower durable press ratings.

Formaldehyde release is also the result of hydrolysis of pendant N-methylol groups, as in Figure 2 b, c, and e. The carbon-nitrogen bond is susceptible to hydrolysis in alkaline solutions, such as in home laundering (Reinhardt, et al., 1981). Kamath, Weber, Hornby, and

Weigmann (1985) found that formaldehyde release leveled off under neutral and alkaline conditions, pH 7 and 12 respectively. This indicates that initial formaldehyde release is due to free formaldehyde and pendant N-methylol groups. Once most of the N-methylol groups have been hydrolyzed the rate of formaldehyde release is controlled by the rate of hydrolysis of the ether linkages in the crosslinks. The hydrolysis of the carbon-oxygen bond is very slow in neutral and alkaline solutions (Kamath, et al., 1985).

Methods of Measuring Formaldehyde Release From Textiles

There are numerous test methods for detecting formaldehyde in textiles. The methods reviewed are those considered to be the most widely accepted by the industry and others that have been investigated because of their high sensitivity in detecting low levels of formaldehyde. The test methods include different instrumental analyses to measure the level of releasable formaldehyde. The instrumental techniques discussed are spectrophotometric determination, gas chromatographic methods, and voltammetric methods. The test methods measure formaldehyde released from a textile by vapor extraction, water extraction, or direct extraction within the instrument (Andrews & Reinhardt, 1985). Because of the variety in the extraction techniques, the tests reviewed are used to approximate formaldehyde release from textiles under different conditions. The limitations of each extraction

technique and the quantitative determination will be discussed in each procedure.

Spectrophotometric Determination

The spectrophotometric analysis of formaldehyde is based on the reaction of formaldehyde in the test solution with a specified or suitable reagent to form a dye chromophore that absorbs light at a known wavelength. The wave length of the colored solution is read against a blank solution to compensate for any color that may be present due to impurities in the reagent and liquid medium being used. A blank solution is prepared by the same procedure used for the samples excluding formaldehyde.

The quantitative determinations of the test solutions are based on the Lambert-Beer's law, commonly referred to as Beer's law. Beer's law states that when monochromatic light is passed through an absorbing medium the intensity of the transmitted light (T) is proportional to the concentration of the absorbing molecule and the path length (Swift & Butler, 1972), according to the following relationship.

$$\log T = -ebC \quad \text{where } e = \text{molar absorptivity or extinction}$$

b = path length
C = concentration, moles per liter

Since the absorbance (A) of the incident light follows the relationship

$$A = -\log T = ebC$$

the absorbance of a solution of known concentration can be used to determine the molar extinction of the molecule.

A calibration curve is prepared from a series of solutions containing different known concentrations of formaldehyde. The absorbance of each known solution is determined by reading it against a blank at the predetermined wavelength. The absorbance is then plotted against the formaldehyde concentration. The concentration of an unknown solution can be determined when the absorbance is compared to absorbance readings on a calibration curve.

Spectrophotometric methods of analysis for aldehydes are the most common. This practice is well established, the equipment is common to most textile laboratories, and the operation of equipment and interpretation of results is generally simple.

Formaldehyde Odor in Resin Treated Fabric, Determination of: Sealed Jar Method (AATCC Test Method 112)

The AATCC test method is the most widely accepted test method for the determination of formaldehyde release from textiles by the United States textile industry. The method was accepted as an AATCC test method in 1965, and was revised in 1975, 1978, 1982, and 1984. The revisions have dealt with: the colorimetric reagent used, pararosaniline, or Schiff's, chromotropic acid, and Nash (AATCC Test Method, 1988; Andrews, 1984; Floyd & Yoon, 1981; Nuessle, 1966); sample dilution for exceptionally odoriferous fabrics; the incubation conditions for formaldehyde

extraction, time and temperature (Riccobono, Ring & Roth, 1975); and the reagent-sample ratio. Recent and current research about this procedure has dealt with investigating common sources of error in the test: 1) the relative humidity in the sealed jar during the incubation step (Andrews, 1984), 2) the mechanism of formaldehyde release from the textile (Moran & Vail, 1965; Andrews & Reinhardt, 1986; Roberts & Rossano, 1984; and Vail & Reinhardt, 1981), 3) the environmental conditions in the area where the test is being performed (Andrews & Reinhardt, 1986), 4) the ratio of reagent to sample in the standardization or calibration curve preparation, and 5) the difference in readings due to lab and instrument differences (Andrews, 1984).

This procedure is considered to have the most severe extraction medium, water vapor (Andrews & Reinhardt, 1985; Vail & Reinhardt, 1981). The test is designed to measure formaldehyde release as a result of hot humid conditions that may be encountered during storage, transfer, or handling of the textile (Nuessle, 1966). The amount of formaldehyde released is determined colorimetrically. The detection range of this test method was established to be 300-3500 micrograms of formaldehyde per gram of fabric (AATCC, 1988).

In order to simulate the desired extraction conditions, a one-gram fabric sample is suspended over 50 mL of distilled water in a sealed mason jar. The jars are placed in an oven at 49°C for 20 hours. After the incubation period the jars are removed and cooled to room temperature, at least 30 min. When cool, the fabric samples and

suspension systems are removed from the jars. The jars are then resealed and agitated to thoroughly mix the contained solution and any condensation on the sides of the jar (AATCC, 1988).

The colorimetric analysis is based on the reaction of available formaldehyde in the test solution and Nash reagent. Ten mL of Nash reagent are combined with 1 mL of test solution and incubated in a 58°C water bath for 6 min. After the solution has cooled, the absorbance of the color is determined spectrophotometrically and is used as an indication of the formaldehyde concentration in the system.

The most recent modification to the AATCC test method was the Nash-to-test-solution ratio. The ratio used, the standard 10:1 ratio or the alternative 5:5 ratio, should be selected based on the instrument and approximate formaldehyde concentration. The alternative 5:5 ratio is more appropriate for fabric expected to contain lower formaldehyde levels.

Japanese Law 112-1973

The control law for harmful substances, such as formaldehyde in textiles, went into effect October 1, 1974 in Japan. The regulations regarding formaldehyde covered such textile items as diapers, underwear, sleepwear, and bedding for babies and infants up to two years of age. The tolerance for this classification is that the absorbance of the sample-reagent solution not be larger than 0.05 and is determined by the following formula:

$$(C_{RW} - C_{BR}) - (C_{RW} - C_{BW}) \leq 0.05$$

C_{RW} = reagent-water solution
 C_{BR} = sample-reagent solution
 C_{BW} = sample-water solution

Another classification of textile articles including underwear, sleepwear, gloves, socks, hose, and tights has a limit of 75 ug of formaldehyde per one gram of specimen, or 75 ppm (Control Law, 1975).

Textile specimens for this test are cut into small pieces. Two and a half grams of the fabric are put into a stoppered 200 mL flask, to which is added 100 mL of distilled water. The stoppered flask is put in a water bath at 40°C for one hour and occasional shaking is required. After the incubation period, the flasks are removed from the water bath and cooled to room temperature. When cooled, the sample solution is filtered to remove the fabric pieces. Colorimetric analysis is made on the color that is developed by the reaction between formaldehyde and Nash reagent. Five milliliters of sample and 5 mL of reagent are incubated for 30 min. at 40°C, cooled, and read against a blank of reagent and distilled water (Control Law, 1975).

Reagents

Reagents that have been investigated for spectrophotometric formaldehyde determination include the Nash reagent, pararosaniline, chromotropic acid, and MBTH.

Nash Reagent

The Nash reagent is the colorimetric reagent used for the analysis of formaldehyde in biological materials, textiles, and sugar products

(AATCC, 1988; Czech, 1973; Control, 1975). It is the colorimetric reagent most widely used by the textile industry for the analytical determination of formaldehyde release from fabrics, as specified by the AATCC Test Method 112 and the Japanese Law 112-1973 (AATCC, 1988; Control, 1975). It is selective for free formaldehyde and useful in analyses that specify mild conditions (Sawicki & Carnes, 1968). It is fast, simple, not very sensitive to temperature changes during the color development period, and not hazardous to the analyst, and it has a very sensitive wave length range (Sawicki & Sawicki, 1975; Changes, 1975). This reagent has been used to determine formaldehyde concentration by use of the ultraviolet and the visible spectra (Belman, 1963; Brignell, Eisner & Farrell, 1966; Committee, 1981; Sawicki & Sawicki, 1975). The present study dealt with the use of the reagent in the visible spectrum.

Sulfites can prevent the formation of 3,5-diacetyl-1,4-dihydrolutidine (DDL). Strong oxidizing agents, such as nitrous acid and ozone, can destroy the chromogen by completely breaking down the molecule or by oxidation to the colorless diacetylutidine (Sawicki & Sawicki, 1975).

The main limitation of the Nash reagent is its sensitivity range. Floyd and Yoon (1981) found the reagent to be satisfactory in measuring 200 to 150 $\mu\text{g/g}$ of formaldehyde, but questioned its use for levels below 150 $\mu\text{g/g}$. The reagent has a detection limit of 20 $\mu\text{g/g}$ at 412 nm.

The colorimetric determination of formaldehyde is based on the Hantzsch reaction between ammonia, formaldehyde, and acetylacetone, in a

1:1:2 stoichiometric ratio. The reaction results in the formation of DDL (Figure 3). In Nash's reagent, developed for identifying formaldehyde in biological materials, the DDL formation is controlled by the amount of available formaldehyde; the greater the concentration of formaldehyde in the solution the greater the color intensity (Nash, 1953).

Nash (1953) found the molar extinction coefficient for the initial DDL compound formed in solution to be 8000 at 412 nm; this extinction was based on a reagent-formulation solution containing five times as much acetylacetone as the final reagent formulation. Nash (1953) extracted DDL crystals from the reagent-formulation solution and, using water as the solvent, found an extinction of 7700 at 412 nm. Nash attributed the lower extinction of the crystals in water to incomplete solubility. Nash's analysis also showed DDL to have a melting point of 208°C. Belman (1963) found a melting point ranging from 190°C to 200°C, and was unable to determine a sharp melting point as Nash had done. Belman found the DDL crystals to be completely soluble in ethanol, and was able to obtain a molar extinction coefficient of 8000 in agreement with Nash. The solution Belman used for spectral analysis was diluted with 1 M ammonium acetate.

Nash (1953) worked with solutions containing different molar ratios of ammonium acetate and acetylacetone, adding enough acetic acid to maintain pH 6, and having an initial formaldehyde concentration of 0.0001 M. Ammonium phosphate, molar in ammonia, and 0.01 M acetylacetone were used to measure the relative yields at pH 4

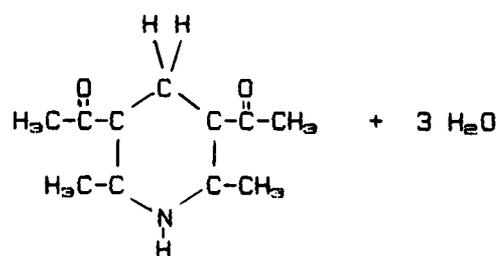


Figure 3. The formation of 3,5-diacetyl-1,4-dihydropyridine

through pH 8. The optimum pH level was pH 6 with a 100% yield.

Ammonium acetate was used in Nash's experiments to investigate the effects of varying concentrations of ammonia and acetylacetone. The reaction conditions were 20°C for 24 hours. The data showed that the concentration of DDL decreased gradually as the ammonium acetate concentration was decreased from 3 M to 0.1 M. Ammonium acetate concentrations below 0.1 M resulted in a rapid loss of efficiency. The concentration of DDL with a 0.033 M concentration of ammonium acetate was 47% to 54% of that with a 0.33 M concentration; the percent varied with the concentration of acetylacetone. The range for the acetylacetone concentration, 0.1 to 0.00033 M, did not have as dramatic an effect on DDL formation. The 0.00033 M concentration produced 75% to 90% of the DDL produced by the 0.1 M concentration. The percentage varied with the concentration of ammonium acetate.

Nash (1953) did not investigate acetylacetone concentrations higher than 0.1 M for two main reasons: 1) by keeping the acetylacetone concentration low, there would be less discoloration in the reagent over time and 2) the absorption of a reagent-water solution (no formaldehyde) would be closer to zero. Nash (1953) concluded the useful range for ammonium acetate to be 1 to 0.1 M and the range for acetylacetone to be 0.1 to 0.001 M. He also determined that DDL can be obtained with only traces of acetylacetone and formaldehyde and an excess of ammonium salt. The most efficient molar ratio determined by Nash (1953) was 2 M ammonium acetate, 0.02 M acetylacetone, and 0.05 M acetic acid.

Given the extremely high concentration of ammonia and acetylacetone in the Nash reagent and the much lower concentration of formaldehyde, the amount of ammonium acetate and acetylacetone consumed by the reaction is negligible compared to the formaldehyde which is totally consumed. Therefore the reaction is considered to be pseudo-first order. Nash found that "the times for 99% completion, calculated from unimolecular plots, follow the Arrhenius relationship closely" (Nash, 1953, p. 418). Based on this information estimates for time and temperature for the reaction were made, such as 40 min. at 37°C and 5 min. at 58°C (Nash, 1953).

The most extensive study of the Nash reagent, after Nash's 1953 report, was by Czech (1973). Czech investigated the reagent in relation to the Association of Analytical Chemists (AOAC) test method for determining the formaldehyde content of sugar products; this test method specified using the acetylacetone reagent (Nash reagent). The purpose of the study was to increase the sensitivity of the Nash reagent. The independent variables for the study were 1) acetylacetone concentration in reagent, 2) sample volume, and 3) acetylacetone volume (Nash reagent volume). The dependent variable was the absorbance reading of each test solution. The reaction conditions, according to the AOAC test method, were 37°C for 30 min. Since the reagent composition was being varied and Nash (1953) had established the importance of maintaining a pH 6, an upper limit of pH 6.5 was set. Sufficient ammonium acetate buffer was added to a base solution to maintain pH 6.5. A base solution of 5.8 M

ammonium acetate and 0.56 M acetic acid was made. To this base solution a varying amount of acetylacetone, 0.15 M to 0.00066 M, was added and each test reagent was diluted to one liter. Each test solution was composed of 2 to 0.15 mL of test reagent and 2 to 3.59 mL of formaldehyde solution. After the incubation period the color was read at 415 nm and the absorbance compared to a standard curve for determination of parts per million of formaldehyde.

Czech's study was based on a simplex optimization in two phases. Phase 1 started with 0.01 M acetylacetone with 0.000167 M formaldehyde, a 60:1 ratio. There were 10 steps, or experiments, in this phase of the simplex with the acetylacetone-formaldehyde ratio ranging from 3:1 to 92:1. Czech (1973) concluded that test reagent 8 was an improvement over Nash's reagent. The test reagent had a 28% increase in absorbance over the original Nash reagent. Calculations based on Czech's data show the molar ratios of the test solution for reagent 8 to be 0.0029 M acetylacetone with 0.000283 M formaldehyde. The extinction coefficient for the initial formulation was 7087, while that for the test reagent 8 was 5340. This indicates that the higher absorbance was simply the result of the increased concentration of formaldehyde. It also shows that there was a 25% decrease in the amount of formaldehyde identified. Based on Czech's calculations from the data for phase 1, test reagent 4, with a 92:1 molar ratio, had the highest extinction coefficient, 7103. This test reagent was able to identify only 0.2% more formaldehyde.

Phase 2 of Czech's study was based on the concentrations used in test reagent 8 and had 11 steps. For this phase of the study Czech (1973) reduced the formaldehyde concentration of the base formaldehyde solution. This phase of the simplex had acetylacetone-formaldehyde ratios ranging from 5:1 to 38:1. The formaldehyde concentrations were in a range that could be more precisely detected with the acetylacetone concentrations used. Based on the absorbance readings, Czech (1973) concluded the superior formulation from phase 2 to be test reagent 15b.

Czech (1973) did not look at the total conversion of formaldehyde. He was assuming that the acetylacetone-formaldehyde ratio did not make any difference to the final outcome. This simplex actually had four variables instead of three. If formaldehyde concentration had been treated as a variable and the extinction coefficient instead of absorbance had been used, the results of this study would have been more precise.

Re-calculations of Czech's data show test reagent 15b to have 0.00235 M acetylacetone with 0.000119 M formaldehyde, with an extinction coefficient of 7031. The superior formulation from phase 2 was actually test reagent 13, with a 38:1 molar ratio and extinction coefficient of 7232.

Pararosaniline

Pararosaniline or p-rosaniline hydrochloride, also known as Schiff's reagent, was the first reagent used in the AATCC test method 112 (AATCC,

1965). The classical Schiff test is neither quantitative nor specific for formaldehyde. This reagent is sensitive to aldehydes and ketones (Trotman & Trotman, 1948). Modifications in the pararosaniline, such as increasing the acidity, helped increase the sensitivity for formaldehyde (Sawicki & Sawicki, 1975; Walker, 1975). In spite of modifications there are still problems with the reagent. Some of the more critical are purity of p-rosaniline, temperature sensitivity during reaction and storage, and reaction time. One of the most critical problems is the wave length range variability of 550 to 585 nm (Sawicki & Sawicki, 1975).

The 1975 revision of AATCC test method 112 specified the use of Nash reagent as the colorimetric indicator. Nash reagent was found to be faster and simpler to handle. It also was found to produce more reliable results because of the decrease in the wave length range variability, 410-415 nm (Changes, 1975).

Chromotropic acid

Chromotropic acid (CTA) has been used extensively in the determination of formaldehyde. Egrive documented the reaction of CTA with formaldehyde and developed a qualitative spot test (MacFadyen, 1945). Boyd and Logan, in 1942, applied the reaction to visual photometry (Altshuller, Miller, & Sleva, 1961). MacFadyen (1945) showed that the extinctions of the developed chromogen followed Beer's law when measured in an appropriate spectrophotometer. The measurements taken at

570 nm made it possible to determine quantitatively the formaldehyde concentrations of reacted solutions.

MacFadyen (1945) dissolved the CTA in water and then diluted it with sulfuric acid. A specified volume of CTA reagent and formaldehyde was mixed and heated in a boiling waterbath for 30 minutes. The acid concentration and heating were thought to be the critical factors in this reaction. CTA in sulfuric acid becomes discolored when heated, and the discoloration increases as acid strength increases. MacFadyen found that at acid concentrations greater than 60% the analytical results were more varied and the formaldehyde measurement accuracy was reduced. The acidity also was found to affect the value of the extinction coefficient; as the concentration of acid drops below 45%, the coefficient increases, then decreases (MacFadyen, 1945). Lee (1956) showed an increase in absorbance as the acid concentration increased to 80% of the final solution, but a decrease in absorbance at higher concentrations. The absorbance of the reaction mixture diluted with concentrated sulfuric acid was 10% higher than that obtained after dilution with water.

Roff (1956) applied the CTA-formaldehyde reaction to the quantitative determination of formaldehyde released from fabrics treated with permanent press finishes. The formaldehyde solution was obtained by hydrolyzing the finishes with 45% sulfuric acid. Aqueous CTA solution, formaldehyde solution, and concentrated sulfuric acid were combined and heated to produce the chromogen. Roff found that the slow degradation

of the cellulose produced interference in the formaldehyde yield, but not more than a 1% difference in the final yield. Again, acid concentration was found to be critical in the reaction. Roff noted that certain water-repellent finishes and cationic softening agents can interfere with color development. Development of full color required strong acid conditions. This method was optimized and found to have a minimal detectable limit of 0.018 $\mu\text{g/mL}$ and a maximum of 3.7 $\mu\text{g/mL}$ (Houle, Long, & Smette, 1970; Roff, 1956; Sawicki & Sawicki, 1975).

Full color development was considered to be dependent on heat as well as acid concentration. West and Sen found that the heat of mixing of the concentrated sulfuric acid, formaldehyde solution, and aqueous CTA (direct addition method) was sufficient to drive the color development to completion (Committee, 1981). Color development peaked at an 85% acid volume (Committee, 1981).

Olansky and Deming (1976) did a simplex optimization of the direct addition method. The absorbance optimum was found with a solution of 56-57% concentrated sulfuric acid, 4-5% aqueous CTA, and 39% aqueous formaldehyde. Preliminary investigations suggested that the peak temperature and duration of heating were affected by the reaction vessel. Styrofoam cups were used to minimize heat absorbed by the reaction vessel.

The disadvantages of CTA as the colorimetric indicator outweigh the advantages. Interferences in the color development can result from the

presence of nitrogen dioxide, alkenes, acetyldehyde, and formaldehyde precursors. There have been several modifications of the reagent and the color developing process to increase its sensitivity for formaldehyde and decrease its sensitivity for the interfering substances. Many of these modifications introduce additional complexities and sources of error, and they require more care in handling (Committee, 1981; Sawicki & Sawicki, 1975). Another concern is the stability of the reagent. It is recommended that fresh reagent be prepared before each use, and at best the reagent is stable for 2 weeks (Andrews & Reinhardt, 1983; Walker, 1975).

MBTH

MBTH (3-methyl-2-benzothiazolinone hydrazone) mainly has been applied to the assay of aliphatic aldehydes and their precursors (Sawicki & Carnes, 1968). It is the reagent most commonly used for the determination of total aliphatic aldehydes in ambient air (Committee, 1981). MBTH has been used to determine formaldehyde content in air, with detection limits of 0.5 to 3 ppm (Sawicki & Sawicki, 1975). The problem with using this reagent for formaldehyde detection is that it is not formaldehyde specific. Interferences in the color development are incurred from acetone, other aliphatic aldehydes and their precursors, and glyoxal (Floyd & Yoon, 1981; Sawicki & Carnes, 1968). The sensitivity for formaldehyde can be increased by an additional step, the addition of an oxidizing reagent (Sawicki & Sawicki, 1975).

Gas Chromatographic Methods

One approach to the determination of formaldehyde release from DP fabrics is more direct than methods that depend on the extraction of the formaldehyde by vapor or water. Headspace gas chromatography (HGC) is based on the determination of formaldehyde in the air around the specimen. A specimen is sealed in a vial and subjected to a treatment. The headspace over the specimen is then evaluated for formaldehyde (Weber, Kamath, & Weigman, 1982).

Gas chromatographic methods using a flame ionization detector (FID) are not capable of the direct determination of low levels of formaldehyde. The formaldehyde must be reduced to methane after it is separated in the column but before it reaches the detector (Schmidt, Antloga & Markelov, 1984). Another problem that must be overcome is the difficulty in quantitatively passing formaldehyde through the column-packing materials (Committee on Aldehydes, 1981).

In a study by Weber, et al., (1982) HGC was applied to the determination of formaldehyde release from textiles. The chromatograph system used included a thermal conductivity (hot wire) detector for water, a methanizer to transform the formaldehyde, and a FID. The fabric specimens were sealed in 20-mL vials under controlled conditions and then incubated. The formaldehyde concentration in the air space of the vial was measured. It was found that the formaldehyde concentration in the vial was controlled by the sorption equilibrium between the fabric and the confined air. At ambient temperatures the formaldehyde

showed an affinity for the fabric. The amount of formaldehyde released into the air space of the vial at ambient temperatures was very small and well below the detection limit of the FID. The incubation temperatures used were 40°C, 65°C, and 100°C. The lower limit of accurate determination of formaldehyde was found to be 10 ppm.

A continuation of this study compared the HGC method with the AATCC test method 112-1978 (Kamath, et al., 1985). The HGC method was found to measure less formaldehyde than the AATCC method, but both tests were capable of distinguishing between releasable and fixed formaldehyde.

A study by Schmidt, et al. (1984) compared formaldehyde samples analyzed by the polarographic, pararosaniline colorimetric method, and HGC. The results of the HGC method were lower by a factor of 40. A detection limit of 0.5 ppm of formaldehyde in water was established, but with reservation.

Discrepancies were found in the appearance of the peak identified as formaldehyde. When the specimen was treated with hydrogen peroxide and sodium bisulfite the peak should have been eliminated, but it was still present. The peak was eliminated after the addition of pararosaniline, which makes the specificity of pararosaniline and the validity of its use in detecting formaldehyde questionable.

Voltammetric Methods

Voltammetry is a form of electrolysis used to investigate the magnitude of the current at an electrode due to a chemical reaction in

the medium in which the electrode is immersed. Polarography is a form of voltammetry in which the working electrode is a dropping mercury electrode (DME) (Ewing, 1985).

Polarography has been applied to formaldehyde detection in biological materials, automobile exhaust, chemical plant streams and raw materials, the workplace environment, and N-methylol resins. This technique measures the reduction of formaldehyde in aqueous solution at the surface of a DME. Because of the various forms formaldehyde takes when in aqueous solution (methylene glycol, oligimers, and monomer) the analysis is pH sensitive. The formation of methylene glycol is favored in acid media. In alkaline media the non-electroactive methylene glycol is dehydrated to electroactive formaldehyde. The formaldehyde can then be reduced to methanol at a dropping mercury electrode. Other aliphatic aldehydes can interfere in the results of this technique if their concentration is greater than that of the formaldehyde (Schmidt, et al., 1984).

In a study by Schmidt, Antloga, and Markelov (1984), the polarographic method was compared to a pararosaniline colorimetric method and a chromatographic method. Based on the results of their study, the authors recommended the polarographic method when evaluating small batches of samples because of the time required in handling and purging, or when the concentration range is unknown. The chromatographic method was found to be unsatisfactory.

In a study by Yoon (1984), square wave voltammetry (SWV) was applied for the detection of formaldehyde in textiles. In this study, the electroactive derivatives of formaldehyde were obtained via hydrazone formation. Yoon compared the results of SWV and colorimetry. The instruments used were a polarographic analyzer with a static mercury drop electrode and a Bausch & Lomb Spectronic 20. For the colorimetric methods, calibration and specimen preparation used were those specified by the AATCC Test Method 112-1988, the Japanese Law 112-1973, and the MBTH (3-methyl-2-benzothiazoline hydrazone) method by Floyd and Yoon (1981). The SWV calibration was for much lower levels of formaldehyde, 0 and 0.02 to 0.60 $\mu\text{g}/\text{mL}$ (corresponding to 1 to 30 $\mu\text{g}/\text{g}$ in the AATCC test). The formaldehyde extraction technique for SWV was the same as in AATCC Test Method 112-1988. Reaction times of 5 to 60 min. were investigated for SWV. The advantage of SWV is the rapid rate at which the entire voltammogram is recorded on a single drop of mercury, eliminating the problem of oscillating current. At 5 min. the reaction was found to be 95% of that obtained at 60 min., therefore the five minute time was determined to be sufficient.

Yoon (1984) found that SWV and the colorimetric methods compared well at higher levels of detection, but that the colorimetric methods became subjective and erratic as the formaldehyde level reached 10 $\mu\text{g}/\text{g}$ and below. The detection limits were found to be 0.30 $\mu\text{g}/\text{mL}$ (15 $\mu\text{g}/\text{g}$ of fabric) for the low-level AATCC method, 0.10 $\mu\text{g}/\text{mL}$ (5 $\mu\text{g}/\text{g}$ of fabric)

for the Japanese method, 0.10 $\mu\text{g}/\text{mL}$ (5 $\mu\text{g}/\text{g}$ of fabric) for the MBTH method, and 0.02 $\mu\text{g}/\text{mL}$ (1 $\mu\text{g}/\text{g}$ of fabric) for the SWV method.

Yoon (1984) concluded that SWV was a more sensitive and precise method of measuring low levels of formaldehyde, but that it would probably not receive general use because of the four-minute purge time before reading each specimen. This method is time consuming when compared to the colorimetric reading time of less than one minute.

Summary

The most effective and efficient durable press (DP) finishes are N-methylol reactants. Formaldehyde release from treated textiles is due to the presence of unbound formaldehyde, pendant N-methylol groups, and the reversibility of the reaction between the reactant and the cellulose molecule.

The most widely used quantitative analysis for formaldehyde release from textiles is the AATCC Test Method 112. Once the available formaldehyde has been extracted from the textile and is in solution, the spectrophotometric analysis is based on the reaction of formaldehyde in the test solution and Nash reagent.

The Nash reagent is preferred because it is selective for formaldehyde and can be used under mild conditions. Formaldehyde detection with Nash reagent is based on the formation of the chromogen 3,5-diacetyl-1,4-dihydrolutidine (DDL). DDL is the result of the Hantzsch reaction between ammonia, formaldehyde, and acetylacetone, in a

1:1:2 ratio. Therefore, the concentration of DDL can be used to estimate the formaldehyde concentration.

The only study, since Nash's (1953) formulation of the reagent, to investigate the composition of the reagent was by Czech (1973). Czech disregarded any change in formaldehyde concentration. This study made the assumption that the acetylacetone-formaldehyde ratio did not have a significant effect on absorbance. This was a false assumption. Nash's study found the most effective ammonia-formaldehyde ratio to be 1:0.1⁻⁴ and the most effective acetylacetone-formaldehyde ratio to be 1:0.1⁻³. Czech's reformulations had acetylacetone-formaldehyde ratios ranging from 5:1 to 38:1. In all of the reagent formulations investigated by Nash and Czech, the ammonia and acetylacetone concentrations were much higher than that for formaldehyde. The formaldehyde concentration was the determining factor for the amount of DDL produced.

Chapter III

Statement of Problem

The most common methods in use in the textile industry for measurement of formaldehyde release from textile products consist of two principal steps. In the first step, the textile product is placed in a closed environment for a specified period of time so that formaldehyde is released from the textile and usually absorbed by a fixed volume of water present in the closed system. In the second step, the formaldehyde concentration in the aqueous solution is measured, usually by colorimetric or spectrophotometric methods (AATCC, 1988; Control, 1975).

The American Association of Textile Chemists and Colorists (AATCC) has developed Test Method 112 for formaldehyde release and analysis (1988). The analytical step is based on the spectrophotometric determination of formaldehyde following color development with acetylacetone (2,4-pentanedione) using a reagent developed by Nash (1953). Because of the simplicity of use and the relative safety of the reagents involved, this method is in wide use in the textile industry.

Even though the AATCC method is widely used, there is a high degree of variability found in interlaboratory studies. Variability of the method can be attributed to many factors, one of which is the Nash reagent itself. The reagent develops a yellow color with time, even when stored in the dark. Many laboratories compensate for the change in

color by running frequent, even daily calibration curves with standard formaldehyde solutions (Andrews, 1984).

The purpose of this study was to examine the Nash reagent in detail; the main objective was to develop a reformulation of the Nash reagent which will provide greater reagent stability, enhanced sensitivity to formaldehyde, and improved reproducibility of quantitatively measured formaldehyde. This will be especially important as finishes with lower levels of releasable formaldehyde are introduced.

Theoretical Framework

To accomplish the reformulation of the Nash reagent, a kinetic study of the chemical reaction leading to the formation of the chromogen was made. The reaction being investigated is the Hantzsch reaction, Figure 4, page 21. In this reaction one molecule of formaldehyde combines with two molecules of acetylacetone and one molecule of ammonia to form the product, 3,5-diacetyl-1,4-dihydrolutidine (DDL). In the AATCC test, this reaction is allowed to proceed for six minutes at 58°C, and the color concentration produced is a direct measure of the formaldehyde present in the test solution.

When the Nash reagent is prepared, 2 moles of ammonium acetate, 0.1 mole of acetic acid and 0.02 mole of acetylacetone are dissolved in distilled or deionized water and the resulting solution is diluted to 1.0 liter in a volumetric flask. When 5 mL of this reagent are mixed

with 5 mL of a test solution containing, for example, 6 µg/mL formaldehyde the resulting concentrations are as follows:

Ammonium Acetate	2.0 M
Acetic Acid	0.05 M
Acetylacetone	0.02 M
Formaldehyde	0.0001 M

If these concentrations are expressed as multipliers of the formaldehyde concentration, the following are obtained:

	(moles/mole of formaldehyde)
Ammonium Acetate	20,000
Acetic Acid	500
Acetylacetone	200

The use of standard Nash reagent in equal volumes with test solutions provides considerable molar excess of all chemicals to the formaldehyde present in the test solution. A formaldehyde concentration of 6 µg/mL corresponds to a fabric with 300 µg/g of releasable formaldehyde, which is considered to be high formaldehyde content by 1988 standards. If all the formaldehyde is converted to DDL, then the concentrations of chemicals in the solution after reaction are as follows:

Ammonium Acetate	1.9999 M
Acetic Acid	0.05 M
Acetylacetone	0.0198 M
Formaldehyde	0.0 M
DDL	0.0001 M

Comparing these values to the initial values shows that the concentrations of the first three chemicals are essentially unchanged over the course of the reaction. Thus, pseudo first-order kinetics can

be used to follow the disappearance of formaldehyde or the appearance of DDL.

In first-order kinetics the following equation is used to represent the relationship between concentration and time:

$$-\ln C/C_0 = kt$$

where C is the concentration at time, t, C₀ is the initial concentration, and k is the rate. In this formula C is any property that is proportional to concentration. In measuring formaldehyde, C is the concentration of formaldehyde and C_{DDL} is the concentration of DDL in the test solution. The concentration of formaldehyde could be expressed as C = (C₀ - C_{DDL}). Substituting this in the equation will give the following:

$$-\ln (C_0 - C_{DDL})/C = kt$$

$$-\ln (1 - C_{DDL}/C_0) = kt$$

According to Beer's Law the concentration of DDL can be expressed as the absorbance (abs) divided by the molar extinction coefficient, abs/e. Therefore the rate of formaldehyde disappearance, or DDL appearance, can be measured by the following equation:

$$-\ln (1 - \text{abs}/eC_0) = kt$$

The rate constant, k, is equal to the slope of the plot

$-\ln (1 - \text{abs}/eC_0)$ versus time. The rate constant (k) and the extinction coefficient (e) will be the bases of the comparison between the reformulations and Nash reagent.

Objectives

The purpose of this study was to examine the Nash reagent in detail; the main objective was to develop a reformulation of the Nash reagent which will provide greater reagent stability, enhanced sensitivity to formaldehyde, and improved reproducibility of quantitatively measured formaldehyde. The study was set up in seven phases with the objective(s) for each phase as follows:

1. To determine the molar extinction, ϵ , for DDL using the original and two alternate reagent formulations; and to determine if the absorbance of DDL is pH sensitive.
2. To determine the effect of the counter ion and reagent pH on DDL formation.
3. To determine the effect of the ammonia concentration on DDL formation while holding the acetylacetone concentration constant and maintaining a 2 M concentration of the acetate ion.
4. To determine the effect of varying the acetylacetone concentration, while holding all else constant, and to determine the effect of aging.
5. To determine the best reformulations from Phases 2, 3, and 4.
6. To determine the effect of temperature on DDL formation with standard Nash and with the reformulated reagents from Phase 5.
7. To determine the effectiveness of the reagents from Phase 6 when performing the AATCC Test Method 112.

Limitations

The following limitations were established for the purpose of this study:

1. There were be two ammonia sources.
2. Time allowed for DDL formation was 30 min. because the test procedures that use Nash reagent have development times of 30 min. or less.
3. The formaldehyde concentration was 0.0002 M because this amount is representative of the lower levels of extractable formaldehyde on textiles.
4. The proportion of reagent to formaldehyde solution was 1:1 because this is the ratio recommended for low formaldehyde detection.

Assumptions

The following assumptions were made for the purpose of this study:

1. That the spectrophotometer was accurate and precise.
2. That the reagent grade formaldehyde solution maintained a 37% concentration and that no notable amount of formaldehyde polymerized out of solution.
3. That the reaction being investigated is first order in formaldehyde.

Chapter IV

Methodology

This chapter covers operational definitions, formaldehyde solutions, absorbance readings, kinetic measurements, and experimental procedures.

The purpose of this study was to examine the Nash reagent in detail; the main objective was to develop a reformulation of the Nash reagent which will provide greater reagent stability, enhanced sensitivity to formaldehyde, and improved reproducibility of quantitatively measured formaldehyde.

Reagent effectiveness was determined by comparisons and calculations based on the molar extinction coefficient and the maximum extinction coefficient. The study was set up in seven phases to investigate the extinction of DDL crystals, the effect of different ammonia sources, the effects of varying the concentrations of ammonia and acetylacetone, the effect of ageing, and the effect of different temperatures on the formation of 3,5-diacetyl-1,4-dihydrolutidine (DDL).

Operational Definitions

1. Absorbance (A) - is defined as

$$A = -\log T = eCb$$

where T is the percent incident light transmitted by the solution, and e, C, and b are as indicated on page 14 (Swift & Butler, 1972).

2. Activation energy (E_a) - the minimum amount of energy required for a species to react (Chang, 1981).
3. Molar extinction coefficient (e) - the absorbance x concentration (moles/liter) x path length (centimeters). "To the extent Beer's law is obeyed by a particular substance e is a constant for that substance" (Swift & Butler, 1972, p. 683). For this study e_1 was used to symbolize the molar extinction coefficient found in Phase 1. The path length for this study was 1 and therefore dropped from the equation.
4. Reaction rate - "the number of moles of a substance formed or destroyed per unit time" (Lewis, 1974, p. 4). For this study the reaction rate was based on the concentration of DDL formed.
5. Rate constant (k) - a proportionality constant between the concentration of a substance formed, DDL, and time. The determination of the rate constant was limited to the linear portion of each kinetic run.

Formaldehyde Solutions

A stock solution of approximately 1500 µg/mL of formaldehyde was prepared by diluting 3.8 mL of reagent grade formaldehyde (37%) to one liter with distilled water. The concentration of the stock solution was determined according to AATCC test method 112, section 12.6 (AATCC, 1988). Formaldehyde solutions for the experiments were prepared from the stock solution.

Reagents

1. 1 M sodium sulfite
2. 0.1% thymolphthalein indicator in ethanol
3. 0.02 N nitric acid.

Procedure:

1. Pipet 50 mL of 1 M sodium sulfite into an Erlenmeyer flask.
2. Add 2 drops of thymolphthalein indicator.
3. Add a few drops of acid until blue color disappears.
4. Add 10 mL of the stock formaldehyde solution.
5. Titrate the solution with the 0.02 N acid until color disappears.

Record the volume of 0.02 N acid used.

Calculations: $\mu\text{g/mL formaldehyde} = (\text{mL of acid used}) \times$
 $(0.02) \times (30,030) / (10 \text{ mL of sample}).$

Absorbance Readings

According to Beer's law, the absorbance of a solution is directly proportional to the concentration of the absorbing molecules in the solution. In this study the absorbing molecule was DDL, which was the molecule formed from the reaction of ammonia, acetylacetone, and formaldehyde. The DDL absorbance was used to indicate the concentration of formaldehyde in the solution.

A standard curve was prepared for each reagent formulation as needed. The formaldehyde concentrations for the curve were approximately 0.00015 M, 0.00020 M, 0.00025 M, and 0.00030 M. A 1:1 ratio of reagent to formaldehyde solution was used. The base line was set with the solvent or reagent being used in each particular experiment.

A zero absorbance was established with distilled water in place of formaldehyde. Color was developed in a circulating water bath at 58°C for 6 min., or as stated in the procedure for each experiment. The absorbance readings for this study were measured on a Bauch & Lomb 2000 spectrophotometer.

Kinetic Measurements

The kinetic data for this study were obtained by measurement of the increases in the absorbance of the solution as the concentration of DDL increased over time. Since the formation of DDL follows pseudo first-order kinetics, the rate of DDL formation can be easily calculated from the absorbance readings versus time.

The kinetic measurements were done in a constant temperature cell in the spectrophotometer. All kinetic runs were replicated three times. The reference and sample cell holders were miniature circulating water baths and maintained temperatures between room temperature and 58°C, depending on what temperature was specified in the experimental procedure. The temperature in each cell holder was checked after three kinetic runs by using cuvettes filled with water and a thermometer. The temperature of the thermal pump was adjusted to accommodate any changes in ambient temperature. The reagents, formaldehyde solution and distilled water were preheated to the test temperature before being introduced into the cuvette. The reagent and sample aliquots were injected into the sample cuvette simultaneously and took approximately 3 seconds to mix. The instrument was programmed to take absorbance readings every 20 seconds. The reference and sample cuvettes remained in the instrument over the time period of the readings.

Experimental Procedures

The experimental procedures for this study were executed in seven phases. This section includes the objectives, laboratory procedures, and calculations for each phase.

Phase 1

Objectives:

1. To determine if the same crystal (DDL) is formed by three different ammonia sources by comparison of molar extinctions and absorbance scans.
2. To determine the average molar extinction coefficient (ϵ_1) for the DDL crystal.
3. To determine if the absorbance of DDL is pH sensitive.

Procedure:

1. Crystals were prepared for each reagent formulation being investigated. Ammonia sources were ammonium acetate, ammonium sulfate, and ammonium phosphate. Nash's (1953) crystals were made with 1 mole (M) ammonium acetate, 0.2 M acetylacetone, and 0.1 M formaldehyde. The crystal formulations shown below are molar in ammonia, although the molarity of the counter ion was not maintained at the same level.

Crystal Formulations

Composition	Crystal Batch		
	1-0	1-1	1-2
Ammonium acetate, $\text{NH}_4\text{OOCCH}_3$	1 M		
Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$		0.5 M	
Ammonium phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$			1 M
Acetylacetone, $\text{CH}_3\text{COCH}_2\text{COCH}_3$	0.2 M	0.2 M	0.2 M
Formaldehyde, CH_2O	0.1 M	0.1 M	0.1 M

2. Recrystallizations were done by the use of ethanol for each group of crystals to ensure purity. The crystals were dissolved in ethanol, then diluted with distilled water to drop out crystals. After each recrystallization the absorbance was recorded. The final solution used was 5% ethanol. Recrystallizations were repeated until a consistent extinction coefficient was obtained. The extinction coefficients were compared for each crystal batch. The average extinction coefficient of the three crystal batches referred to as e_1 was determined.
3. The pH sensitivity of the extinction was checked by the absorbance of the crystals dissolved in various buffers, pH 1, pH 4, pH 6, and pH 10. The buffers were purchased from Fisher Scientific.

<u>pH</u>	<u>Buffer composition</u>
1	potassium chloride, hydrochloric acid
4	potassium biphthalate
6	potassium phosphate monobasic, sodium hydroxide
10	potassium carbonate, potassium borate, potassium hydroxide

Calculations:

1. e was calculated for each crystal group.
$$e = \text{absorbance} / \text{molar concentration of DDL}$$
2. A Duncan Multiple Range Test was used to compare the extinction coefficients of each set crystal by the number of recrystallization each set crystal had undergone.
3. e_1 was calculated based on the results of the Duncan Multiple Range Test.
4. e was calculated for each buffer and compared to e_1 .

Phase 2

Objective: To determine the effect of the counter ion and reagent pH on DDL formation.

Procedure:

1. Reagents were mixed and refrigerated for 12 hours before

use. The reagent formulations were 2 molar in ammonia, however the molarity of the counter ion was not maintained at the same level.

Reagent Formulations

Composition	Reagent code		
	2-0	2-1	2-2
Ammonium acetate, $\text{NH}_4\text{OOCCH}_3$	2 M		
Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$		1 M	
Ammonium phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$			2 M
Acetic acid, CH_3COOH	0.05 M	0.05 M	0.05 M
Acetylacetone, $\text{CH}_3\text{COCH}_2\text{COCH}_3$	0.02 M	0.02 M	0.02 M

2. After 12 hours a 0.0002 M formaldehyde solution was prepared.
3. The pH for each reagent formulation was determined at room temperature.
4. The pH of some of the standard reagent, 2-0, was adjusted with acetic acid to 6.05.
5. Kinetic runs were done at 58°C, using a 1:1 reagent-formaldehyde ratio.

Calculations:

1. e was calculated for each formulation and compared with e_1 .
2. A plot of $-\ln(1-\text{abs}/e_1C_0)$ versus time was made.
3. The rate constant (k) was calculated for each reagent formulation.

Phase 3

Objective: To determine the effect of the ammonia concentration on DDL formation while holding the acetylacetone concentration constant and maintaining a 2 M concentration of the acetate ion (OAc^-).

Procedure:

1. Reagents were mixed and refrigerated for 12 hours before use. The amounts given for each reagent formulation in the following table are molar.

Reagent Formulations

Composition	Reagent code						
	3-0	3-1	3-2	3-3	3-4	3-5	3-6
Ammonium acetate	2	0.02	0.05	0.10	0.25	0.50	1.0
Sodium acetate		1.98	1.95	1.90	1.75	1.50	1.0
Acetic acid	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Acetylacetone	0.02	0.02	0.02	0.02	0.02	0.02	0.02
$\text{NH}_4 : \text{CH}_2\text{O}$	10,000	100	250	500	1,250	2,500	5,000

2. After 12 hours, a 0.0002 M formaldehyde solution was mixed.
3. The pH of the reagent formulations was checked.
4. Kinetic runs for each reagent mixture were done at 58°C.

Calculations:

1. A plot of $-\ln(1 - \text{abs}/e_1C_0)$ versus time was made. The rate constant (k) of each reagent formulation was determined.

2. A plot of $\log k$ versus $\log [\text{NH}_4]$ was made and the k 's were compared.

Phase 4

Objective:

1. To determine the effect of varying the acetylacetone concentration, while holding all else constant.
2. To determine the effect of aging on the superior reagent formulations.

Procedure:

1. Reagents were mixed according to the table below, and were refrigerated for 12 hours before use; all amounts are molar.

Reagent Formulations

Reagent code	4-0	4-1	4-2	4-3	4-4
Ammonium acetate, $\text{NH}_4\text{OOCCH}_3$	2 M	2 M	2 M	2 M	2 M
Acetic acid, CH_3COOH	0.05 M	0.05 M	0.05 M	0.05 M	0.05 M
Acetylacetone, $\text{CH}_3\text{COCH}_2\text{COCH}_3$	0.02 M	0.04 M	0.01 M	0.005 M	0.002 M
AcAc : CH_2O	100	200	50	25	10

2. The pH of the reagent formulations was checked.
3. Kinetic runs for each were done at 58°C .

Calculations:

1. A plot of $-\ln(1-\text{abs}/e_1C_0)$ was made. The rate constant, k , was determined for each reagent.
2. A plot of $\log k$ versus $\log [\text{AcAc}]$ was done and the k 's compared.

Effect of aging: The reformulated reagent which gave good efficiency in color development was compared with the standard reagent approximated every seven days over a period of 30 days. The reagents were refrigerated. The maximum absorbance of each reagent was used for the comparison.

Phase 5

Objective: To determine the best reformulations from Phases 2 and 3, and to combine these with the best reformulation from Phase 4.

Procedure: The reformulations were evaluated according to the following: maximum absorbance, followed Beer's law, had the least variation, and which were the most stable over time. Details on the selection of the superior reformulations are given in the Results and Discussion chapter. The reformulations are given in the procedure for Phase 6.

Phase 6

Objective: To determine the effect of temperature on DDL formation with standard Nash and with the reformulated reagents from Phase 5.

Procedure:

1. Reagents were prepared and refrigerated for 12 hours before use.

Reagent Formulations

<u>Reagent code</u>	<u>6-0</u>	<u>6-1</u>	<u>6-2</u>
Ammonium acetate, $\text{NH}_4\text{OOCCH}_3$	2 M	2 M	1 M
Sodium acetate, CH_3COONa			1 M
Acetic acid, CH_3COOH	0.05 M	0.05 M	0.05 M
Acetylacetone, $\text{CH}_3\text{COCH}_2\text{COCH}_3$	0.02 M	0.04 M	0.04 M

2. A 0.0002 M formaldehyde solution was prepared.
3. Kinetic runs for each reagent were done at 58°C, 50°C, 42°C, and 35°C.

Calculations:

1. A plot of $-\ln(1-\text{abs}/e_1C_0)$ versus time was made and k was determined for each reagent tested.
2. For each reagent an Arrhenius plot of $\ln k$ versus $1/t$, was done.
3. The activation energy, E_a , was calculated for each reagent.

$$E_a = -\text{slope} (1.986 \text{ cal K}^{-1}\text{mol}^{-1})$$

Phase 7

Objective: To determine the effectiveness of the reagents from Phase 6 when performing the AATCC Test Method 112.

Procedure:

AATCC Test Method 112 was performed (AATCC, 1988).

1. Reagents were prepared, and then refrigerated for 12 hours.

Reagent Formulations

Composition	Reagent code	
	7-0	7-1
Ammonium acetate, $\text{NH}_4\text{OOCCH}_3$	2 M	2 M
Acetic acid, CH_3COOH	0.05 M	0.05 M
Acetylacetone, $\text{CH}_3\text{COCH}_2\text{COCH}_3$	0.02 M	0.04 M

2. From the stock formaldehyde solution, solutions of different but known formaldehyde concentrations were prepared for the standard curve. The concentrations were approximately 0.00015 M, 0.00020 M, 0.00025 M, and 0.00030 M.
3. Specimen preparation was as stated in the test method. Three specimens from six different sections of one permanent press sheet were evaluated for formaldehyde release.
4. A 1:1 ratio of reagent to formaldehyde solution was used. Color development of the known and test solutions was done in a shaking water bath.
5. Absorbance readings were taken at room temperature.

Calculations:

1. The calculations were those specified in the test method performed. Calculations included standard curve preparation and mg/g on weight of fabric specimen.

$$\begin{array}{l} \text{mg/g CH}_2\text{O on wt of} \\ \text{fabric specimen} \end{array} = \frac{[(\mu\text{g/mL}) \text{CH}_2\text{O in sol} \times 50]}{(\text{wt of fabric specimen in g})}$$

Chapter V

Results and Discussion

The results of the experimental work are presented according to the phases specified in the experimental procedures.

Phase 1

The objectives of this phase were to determine if the same crystal is formed by the different ammonia sources investigated, to determine the average molar extinction coefficient (ϵ_1) for the 3,5-diacetyl-1,4-dihydrolutidine crystal (DDL) and to determine if DDL is pH sensitive.

Three ammonia sources were investigated in the formation of DDL. The ammonia sources were ammonium acetate, ammonium sulfate, and ammonium phosphate. The crystal DDL is formed by ammonia, acetylacetone, and formaldehyde. The three batches of DDL were obtained by the formulations in Phase 1. The formulations were one molar in ammonia; the molarity of the counter ion was not maintained at equal levels. The extinction coefficient and absorbance peak were used to establish uniformity in crystal structure. The extinction coefficients (ϵ) were calculated according to Beer's Law.

$$\epsilon = A/(bC)$$

The absorbance (A) was measured on a Bausch & Lomb Spectronic 2000 spectrophotometer. The path length (b) was one centimeter and the

concentration (C) was stated in moles per liter of the DDL crystals in the solution.

The three crystal batches were recrystallized until a consistent extinction coefficient was obtained. It was necessary to use a 5% ethanol solution to dissolve the crystals. An absorbance scan in the visible range showed no absorbance for the ethanol solution when read against distilled water. It was therefore assumed that the 5% ethanol had no effect on the absorbance readings of the crystals.

A Duncan Multiple Range test was used to compare the means of the extinction coefficients for each formulation at each recrystallization. The results of the test are shown in Table 1. The average of the extinction coefficients in group A was calculated and used as e_1 , 8086. The peak wavelengths were also analyzed. The Duncan test indicated a significant difference between the peak wavelengths for each crystal batch. This statistical significance is not of practical significance because of the very small difference between the means and the capability of the equipment with wavelength accuracy of ± 1 nm. The average peak wavelengths ranged from 411.6 to 412.3 nm, with an average of 411.95 nm. This range falls within the accuracy of the equipment, 410.95 to 412.95 nm. The examples of a typical scan for each crystal batch can be found in the Appendix. The peak for each scan was broad and appears to cover more than one nanometer.

Table 1

Duncan Multiple Range Test on Extinction Coefficients in Phase 1

e	Batch	Recrystallization	Results*
8167	0	2	A
8132	0	6	A
8120	2	5	A
8067	2	6	A B
8064	2	4	A B
8046	1	1	A B C
8046	1	3	A B C
8046	0	5	A B C
7988	1	5	B C
7984	1	4	B C
7967	2	2	B C
7935	1	2	C D
7839	0	1	D E
7746	0	4	E F
7691	2	3	F
7566	2	1	G
7386	0	3	H

* e's with the same letter are not significantly different. Each e represents the average of three extinction coefficients.

The wavelength used for the kinetic runs was based on the wavelengths for the extinction coefficients used to determine ϵ , and was found to be 412 nm.

The pH sensitivity of DDL was investigated by dissolving the crystals in ethanol and then diluting with the appropriate buffer solution, the end solution not to exceed 5% ethanol. Table 2 shows the pH effect on the extinction coefficient. A Duncan Multiple Range test indicates no significant difference between pH 6 and 10. There was a significant difference between pH levels 1 and 4, and between pH levels 4 and 6. The extinction coefficient of the solution increased as the pH increased until it started to level off at pH 6.

A Duncan test indicates a significant difference in the peak wavelengths between pH levels 1, 4, 6, and 10. Again, this statistical significance is not significant because the average peak wavelengths fall within the ± 1 nm accuracy range of the instrument. The peak wavelengths ranged from 411.39 nm to 414.32 nm, with an average of 412.65 nm. The accuracy range for the spectrophotometer for these readings was 411.65 to 413.68. The peak wavelengths fall within this range or are extremely close.

Phase 2

The objective of this phase was to determine the effect of the counter ion and reagent pH on DDL formation.

Table 2

Duncan Multiple Range Test on pH Effect on the Extinction Coefficient

pH	e	Results*
1	3627	A
4	7225	B
6	7910	C
10	8022	C

* e's with the same letter are not significantly different. Each e represents the average of three extinction coefficients.

Three reagents were mixed according to step 1 in Phase 2 of the experimental procedures. The three ammonia sources were ammonium acetate, ammonium sulfate, and ammonium phosphate. The reagent formulations were two moles in ammonia; the molarity of the counter ion was not maintained at the same level. The pH, the rate constant (k), and the maximum amount of CH_2O detected were obtained for each reagent. The results are shown in Table 3.

The pH of the three reagents ranged from 6.01 to 6.86. The percent of maximum conversion ranged from 93% to 48%. In Phase 1 the pH was found to affect the extinction, but this effect leveled off at pH 6. The difference in extinction of these reagents cannot be totally attributed to the difference in pH. For comparison purposes the pH of standard Nash, containing ammonium acetate, was adjusted to 6.05. The change in pH lowered the rate by 16% and the maximum absorbance by 7.5%. Therefore pH does affect the extinction but can not explain the discrepancy between the Nash reagent with a total conversion of 94%, the ammonium sulfate reagent with a total conversion of 48%, and the ammonium phosphate reagent with a total conversion of 58%. The acetate ion appears to facilitate the formation of DDL.

Phase 3

The objective of this phase was to determine the effect of the ammonia concentration on DDL formation while holding the concentration

Table 3

Effect of Counter Ion on DDL Formation

Ammonia Source	Counter Ion Molarity	pH	k* ($\times 10^3$)	% Conversion to DDL (max abs/0.8086)
Ammonium Acetate	2	6.86	15.78	94
Ammonium Sulfate	1	6.10	1.51	48
Ammonium Phosphate	2	6.01	1.90	58
Ammonium Acetate (pH adjusted)	2	6.05	13.22	87

* Each k is equal to the average of three kinetic runs.

of the other ingredients constant and maintaining a 2 M concentration of the acetate ion.

In order to determine the effect of the ammonia concentration, the ammonia concentration was varied while the acetylacetone and formaldehyde concentrations were held constant, and sodium acetate was added to maintain a two molar concentration of acetate. The reagents were mixed according to step 1 of Phase 3 in the experimental procedures. The pH of each reagent formulation was checked in order to maintain consistency with the pH of standard Nash. Initial analysis of the data for Phase 3 indicated that the reaction under investigation was more complex than anticipated. Plots of absorbance versus time indicated that the ammonia concentration not only affected the reaction rate but also affected the amount of product. Figure 4 indicates that the amount of product is kinetically limited. At low ammonia concentrations the formation of DDL is slowed and there appears to be a competing reaction for the formaldehyde. At higher ammonia concentrations the formation of DDL is faster and consumes the formaldehyde faster than the competing reaction, resulting in a higher possible absorbance. To account for the limiting value of DDL formed the formula

$$-\ln(1-\text{abs}/e_1C_0) = kt$$

was changed for all subsequent kinetic calculations to the following

$$\ln(A_\infty - A_t) = \ln(A_\infty - A_0) - kt$$

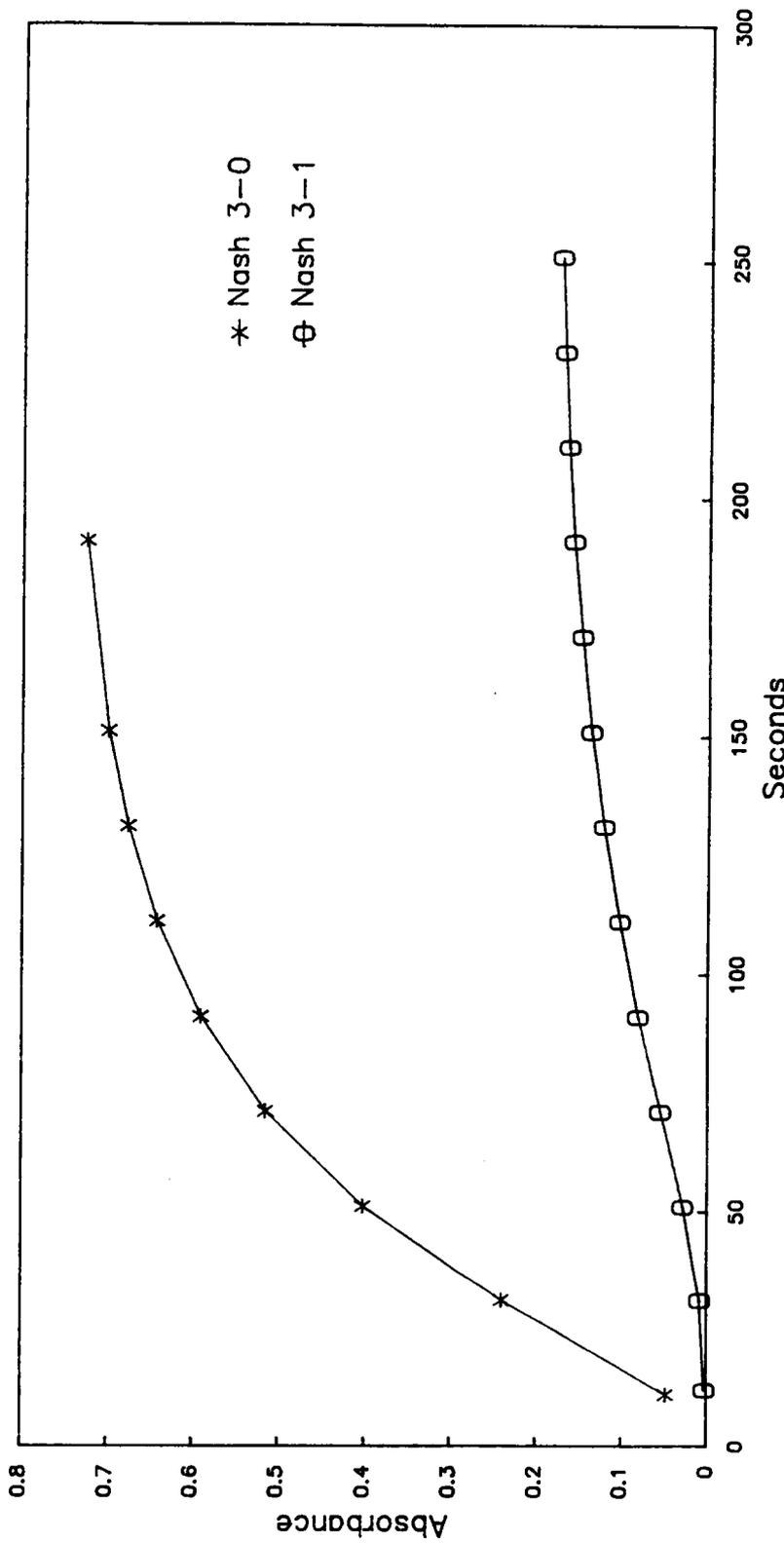


Figure 4. A plot of absorbance versus time for Nash 3-0 and Nash 3-1

where A_{∞} is the experimental absorbance at the maximum value, A_t is the absorbance at time t , and A_0 is the initial absorbance at time zero. A plot of $\ln(A_{\infty}-A_t)$ versus t will have a slope of $-k$. A plot of k versus concentration will indicate the reaction order.

The results for Phase 3 are shown in Table 4. The pH of each reagent formulation was within the ± 0.1 range of the pH of standard Nash, therefore no adjustment in pH was made. It is assumed that any variation in the rate of DDL formation was not due to a difference in pH. Figure 5 shows the relationship of the rate of DDL formation to the ammonia concentration, up to 2 M. DDL formation accelerates with increased ammonia concentrations until a concentration of 0.5 moles is reached, then the reaction becomes independent of ammonia concentration. The average slope of the line that includes molarities of 0.02, 0.05, 0.01, 0.25, and 0.5 is 0.92, indicating first order behavior in low ammonia concentrations.

Phase 4

The objective of this phase was to determine the effect of the acetylacetone concentration on DDL formation while holding all else constant. The reagents were mixed according to step 1 of Phase 4 in the experimental procedures. The pH of each reagent formulation was checked in order to maintain consistency with the pH of standard Nash. For analysis the data for standard Nash included the results for standard Nash from Phase 2 and Phase 3.

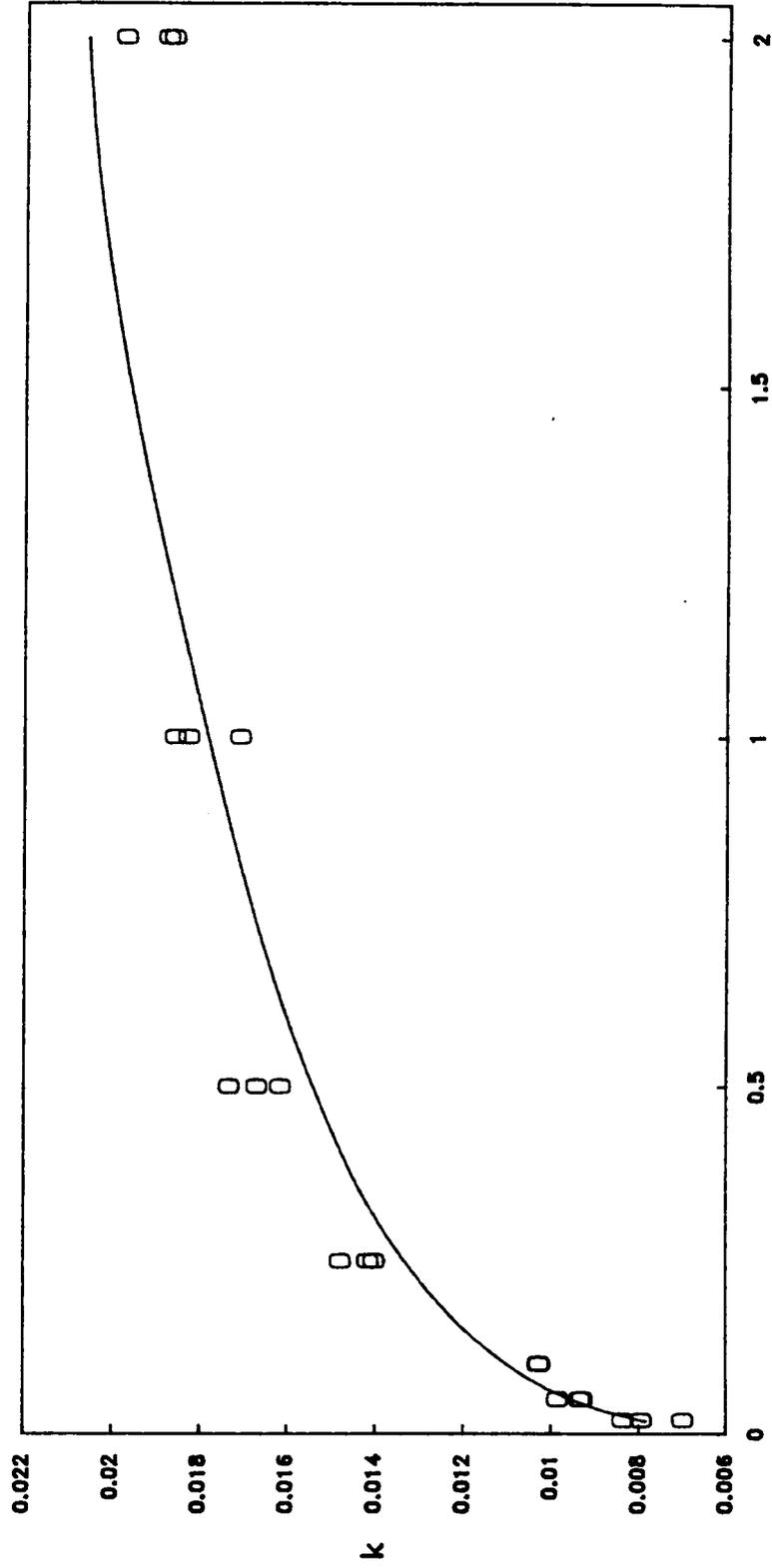


Figure 5. A plot of k versus ammonia concentration

Table 4

Effect of Ammonia Concentration on DDL Formation

Ammonia Molar Conc.	pH	k* ($\times 10^2$)
2	6.80	1.9087
1	6.79	1.7989
0.5	6.80	1.6746
0.25	6.79	1.4326
0.10	6.79	1.0279
0.05	6.77	0.9502
0.02	6.75	0.7777

* Each k is equal to the average of three kinetic runs.

The results of Phase 4 are shown in Table 5. The pH of the reagent formulations was within the ± 0.1 limit of the pH of standard Nash. It was therefore assumed that any variation in the rate of DDL formation was not due to a difference in pH. Figure 6 shows the relationship of the acetylacetone concentration on the initial rate of DDL formation. As shown, the initial rate of DDL formation increases as the concentration of acetylacetone increases. The average slope of the line covering concentrations of 0.002 M, 0.005 M, and 0.01 M is 0.98. This indicates that the first order behavior over lower concentrations. At acetylacetone concentrations above of 0.01M the reaction rate seemed to be independent of the concentration.

Reagents 4-0, standard Nash, and 4-1, having 0.04 molar concentration of acetylacetone, were tested over a period of 30 days. The reagents were mixed, in duplicate, and refrigerated over the 30-day period. Since the reaction rates of the two reagents were similar, the maximum absorbance was used for comparative purposes. Table 6 shows the results of this comparison. Reagents 4-0a and 4-0b, standard Nash, had the highest and lowest average absorbance, respectively. Reagent 4-1b had the least amount of variation in absorbance, while 4-1a had the highest amount of variation in absorbance. In comparison to e₁, 8086, standard Nash, reagent 4-0, identified 88% to 93% of the formaldehyde present. Reagent 4-1 identified 89% to 93% of the formaldehyde present. Overall, reagent formulations 4-0 and 4-1 seem to have similar results.

Table 5

Effect of Acetylacetone Concentration on DDL Formation

Acetylacetone Molar Conc.	pH	k* ($\times 10^2$)
0.04	6.79	2.1700
0.02	6.87	1.5527
0.01	6.75	1.3826
0.005	6.78	0.8397
0.002	6.76	0.3112

* Each k is equal to the average of 3 kinetic runs.

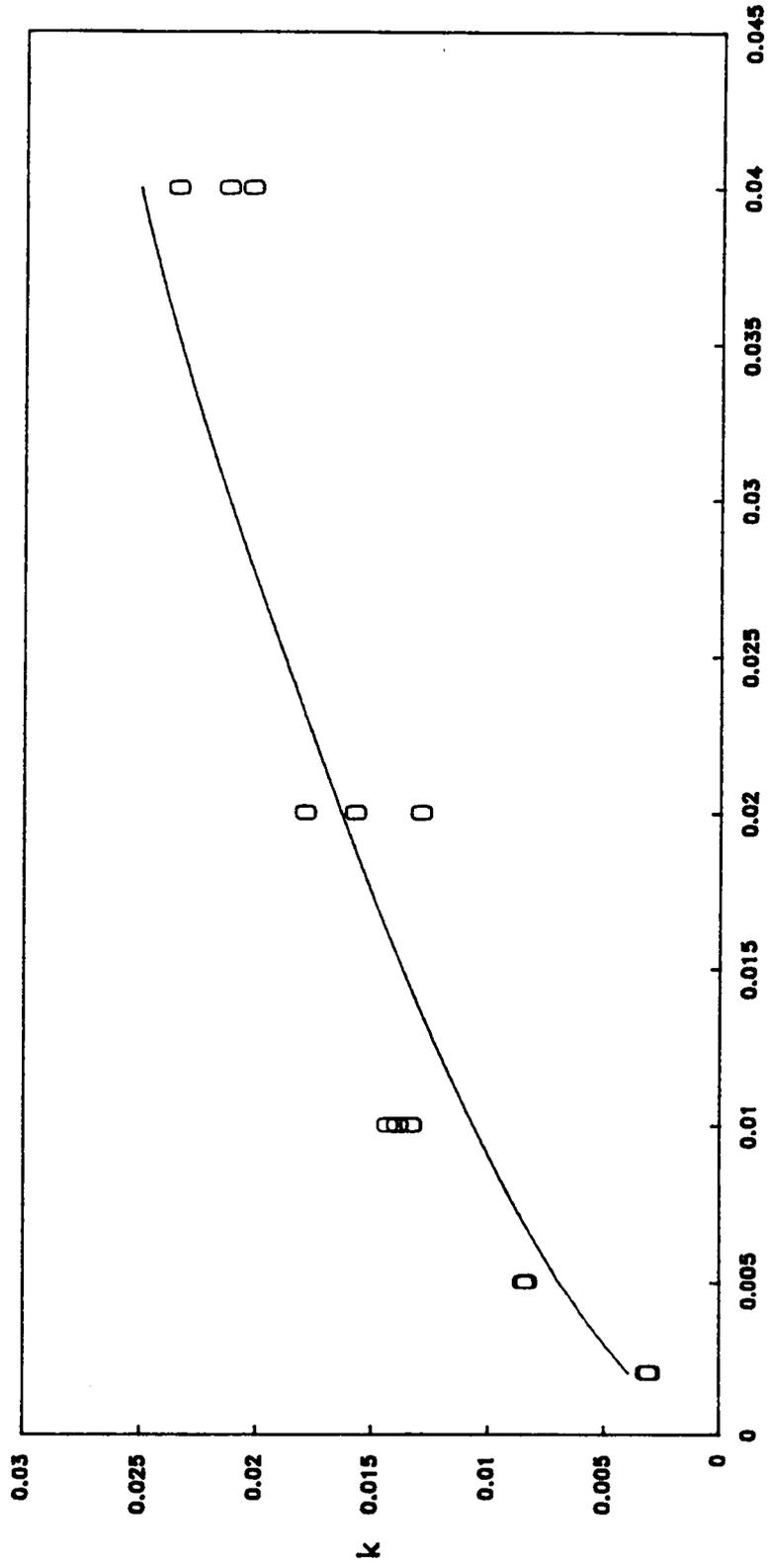


Figure 6. A plot of k versus acetylacetone concentration

Table 6
Comparison of Reagents 4-0 and 4-1 Over Time

age (days)	maximum absorbance			
	4-0a	4-0b	4-1a	4-1b
1	.728	.727	.724	.725
	.736	.735	.736	.741
	.739	.717	.731	.737
9	.723	.725	.707	.711
	.737	.731	.730	.731
	.713	.722	.710	.724
16	.702	.703	.736	.706
	.724	.714	.731	.692
	.724	.713	.721	.713
22	.734	.720	.720	.714
	.739	.726	.714	.728
	.731	.724	.723	.730
30	.715	.714	.722	.719
	.730	.709	.725	.730
	.723	.714	.727	.708
mean	.727	.720	.724	.721
standard deviation	.042	.0052	.0067	.0098

Phase 5

The objective of Phase 5 was to determine the best reformulations from Phases 2 and 3, and to combine these with the best reformulation from Phase 4.

In Phase 2 ammonium acetate was found to be the best ammonia source. Ammonium acetate is the ammonia source for standard Nash. In Phase 3 the concentration of ammonium acetate was investigated. The effectiveness of the concentration of ammonium acetate started to level off at 0.5 M. The concentration with the highest rate constant was 2 M, reagent 3-0. The next highest rate constant was from the 1 molar formulation, reagent 3-6. In Phase 4 the effectiveness of the acetylacetone concentration leveled off at 0.02 M. The rate constant for reagent 4-1, with a 0.04 M concentration, was slightly higher than that of standard Nash. Reagent 4-1 was also found to be effective over the period of 30 days.

Three reagent formulations were selected for the next phase of the study. The first was the standard Nash formulation, the second was reagent 4-1, which differed from the standard Nash only in the doubled concentration of acetylacetone, and the third reagent was a combination of reagents 4-1 and 3-6, the acetylacetone concentration was doubled and the ammonia concentration reduced by one half.

Phase 6

The objective of Phase 6 was to determine the effect of temperature on DDL formation with standard Nash and with the reformulated reagent from phase 5.

Figure 7 shows the effect of temperature on DDL formation for the three reagents tested in Phase 6. As the temperature was increased from 35°C to 58°C the rate of DDL formation increased. The activation energy, E_a , for each reagent formulation was calculated (Table 7). The activation energy values of the three reagent formulations were similar, approximately 18 kcal K⁻¹ mol⁻¹. Therefore, each reagent formulation required approximately the same amount of energy for the formation of DDL.

Phase 7

The objective of this phase was to determine the effectiveness of the reagents from Phase 6 when performing the AATCC Test Method 112 (1988). Due to miscalculations by the author, reagent formulation 6-2 was dropped from the study. This is not expected to have had a major impact on the study because of the similarities between the reaction rates and activation energies of the reagent formulations investigated in Phase 6.

The results for Phase 7 are shown in Table 8. According to the AATCC test, reagents 7-0 and 7-1 identified the same amount of formaldehyde. The standard deviation of the individual means shows little difference in the reagents.

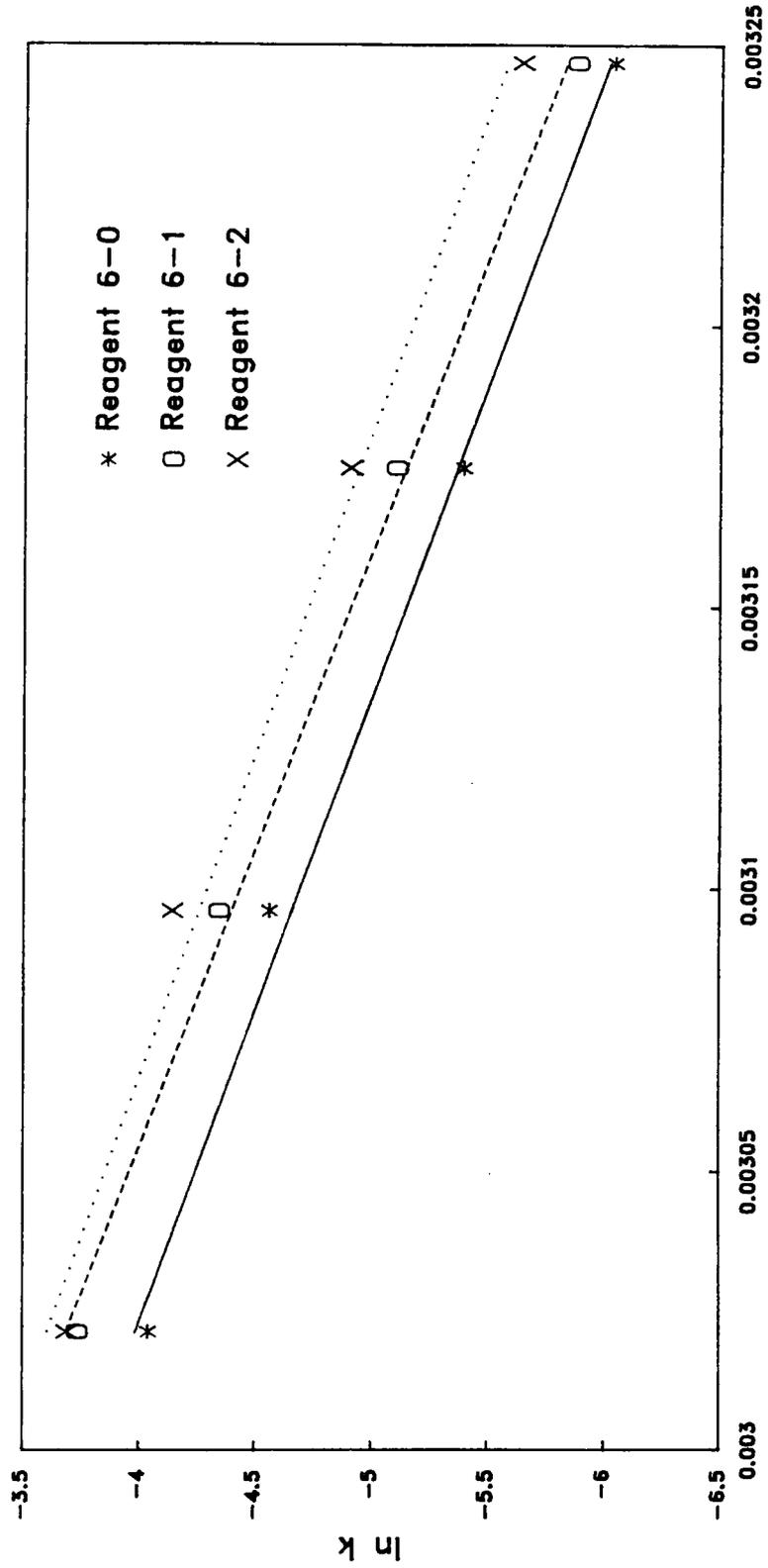


Figure 7. Arrhenius plot, for reagents in Phase 6.

Table 7

Activation Energies (E_a) for Phase 6

<u>Reagent</u>	<u>E_a</u>
6-0	17.9 kcal K ⁻¹ mol ⁻¹
6-1	18.9 kcal K ⁻¹ mol ⁻¹
6-2	17.4 kcal K ⁻¹ mol ⁻¹

Table 8
Results of AATCC Test Method 112

	<u>Reagents</u>	
	<u>7-0</u>	<u>7-1</u>
slope $\times 10^{\text{E}}$	793.78	799.68
Intercept $\times 10^{\text{E}}$	-2.44	-0.65
<u>specimen</u>	<u>mg/g*</u>	
	<u>7-0</u>	<u>7-1</u>
1	110	111
2	116	114
3	124	123
4	115	114
5	114	113
6	106	109
grand mean	114	114
standard deviation	6.08	4.82
average of the standard deviation of the individual means	1.15	1.36

*mg/g = average formaldehyde concentration on weight of fabric specimen

The standard deviation of the grand mean for reagent 7-1 is less than that of standard Nash, indicating that reagent 7-1 might give more consistent readings with specimens of varying formaldehyde concentrations.

Chapter VI

Conclusions and Summary

The purpose of this study was to examine the Nash reagent in detail; the main objective was to develop a reformulation of the Nash reagent which will provide greater reagent stability, enhanced sensitivity to formaldehyde, and improved reproducibility of quantitatively measured formaldehyde. Standard Nash contains 2 moles of ammonium acetate, 0.02 moles of acetylacetone, and 0.05 moles of acetic acid. Ammonia, acetylacetone and formaldehyde form the chromogen 3,5-diacetyl-1,4-dihydrolutidine, referred to as DDL in this study. This reaction is first order in formaldehyde. In standard Nash the ammonia and acetylacetone concentrations are in great excess over a possible formaldehyde concentration. Therefore, the amount of DDL formed is dependent on the formaldehyde in the solution and can be used as a direct indication of the formaldehyde concentration. In order to develop a more effective reagent the ammonia source, ammonia concentration and acetylacetone concentration were investigated by pseudo-first order kinetics. The effect of temperature on DDL formation was also studied.

In the first phase of the study the formation of the molecule from three ammonia sources was investigated and the extinction coefficient of DDL was determined. The ammonia sources were ammonium acetate, ammonium sulfate, and ammonium phosphate. The verification of molecular identity

was based on the absorbance scans for the crystals formed with each ammonia source. The peak wavelength and the extinction coefficient were determined for each crystal formulation. A Duncan Multiple Range Test on the extinction coefficients indicated no significant difference between the three crystal formulations. The significant difference between the peak wavelengths was of no practical significance because the peak readings were within the accuracy, ± 1 nm, of the spectrophotometer. The molar extinction coefficient for DDL was determined to be 8086 and the peak wavelength was 412 nm. This is essentially the same as that found by Nash (1953); the molar extinction from Nash's study was 8000 at 412 nm. The extinction of DDL was found to be affected by the pH of the solution. This effect leveled off at pH 6. Since pH 6 is the approximate pH of the reagent formulations that were investigated, the pH of the formulations was checked but no adjustments were made.

In Phase 2 the effect of the counter ion and reagent pH was investigated. The ammonia sources were ammonium acetate, ammonium sulfate, and ammonium phosphate. The pH levels of the three reagents were 6.86, 6.10, and 6.01, respectively. Since the pH of each formulation was within the range set, ± 1 , no adjustments were made. The percent of formaldehyde converted to DDL in each reagent formulation varied from 93 %, ammonium acetate formulation, to 48 %, the ammonium sulfate formulation. The pH of standard Nash, the ammonium acetate

formulation, was lowered from 6.86 to 6.05 to verify if the difference in conversion was due to the pH difference. The lowered pH only accounted for a three-percent reduction in formaldehyde conversion. The counter ion does have an effect on DDL formation, and the acetate ion creates the most desirable environment for the reaction.

In the third phase of the study the objective was to determine the effect of the ammonia concentration on DDL formation. The ammonia source was ammonium acetate. The concentration of ammonia for standard Nash was reduced to six different molar levels. The rate constants, k , were determined for each concentration. The plot of $\ln k$ versus $\ln[\text{NH}_4]$ showed the formation of DDL to be first order over the molar concentration of 0.02 to 0.5. The reaction rate was not affected by ammonia concentrations above 0.5. Nash (1953) found the useful range for ammonium acetate to be 0.1 M to 1 M.

The objective of the fourth phase was to determine the effect of the acetylacetone concentration on DDL formation while holding all else constant. The formation of DDL was found to be first order over the acetylacetone concentrations of 0.002 M to 0.01 M. The rate of DDL formation leveled off at 0.02 M of acetylacetone. Nash (1953) indicated the useful range for acetylacetone to be 0.001 M to 0.01 M. In spite of this Nash determined the most efficient molar ratios for the reagent to be 2 M ammonium acetate and 0.02 M acetylacetone. The present study

found the useful range for the ammonium acetate and acetylacetone concentrations to be higher than originally stated by Nash (1953).

Standard Nash, 4-0, and the reagent formulation with the 0.04 molar concentration of acetylacetone, 4-1, were tested approximately every seven days over a 30-day period. The average conversion of formaldehyde to DDL for each reagent formulation over the 30-day period was 91%. At one day old the mean conversion was 92%; by day 30 the mean conversion dropped to 89%, only a three-percent loss in effectiveness. There was some fluctuation in the extinction coefficients over the 30-day period. There was a drop in the extinction at day 16, an increase at day 22 and a drop at day 30. Each reagent had an average standard deviation of 129. It was concluded that aging had the same effect on each reagent and that each was effective in formaldehyde detection over the 30-day period.

The reagent formulations determined to be the most effective in formaldehyde detection were standard Nash, reagent 3-6, which had half the ammonia concentration of standard Nash, and reagent 4-1, which had twice the acetylacetone concentration of standard Nash. In the sixth phase of the study standard Nash, reagent 4-1, and a combination of reagents 3-6 and 4-1 were compared to determine the effect of temperature on DDL formation. The reagents were found to follow the Arrhenius relationship, i.e., as the temperature increased the reaction rate increased. The activation energy was approximately the same for

the three reagent formulations, $16 \text{ kcal K}^{-1}\text{mol}^{-1}$. Therefore, each formulation requires the same amount of energy in the formation of DDL.

In the final phase of the study the test used to detect extractable formaldehyde from textiles, AATCC Test Method 112 (1988), was performed. Six specimens from a white polyester and cotton sheet were evaluated by standard Nash and reagent formulation 4-1. Each reagent identified an average of 114 mg/g of formaldehyde on the sheet, the average standard deviation of the means for standard Nash was 1.15 and for 4-1 it was 1.36.

In conclusion, no reagent reformulation in this study was found to be more efficient than standard Nash in the detection of formaldehyde. Several of the reformulations were found to be comparable to standard Nash. Overall, this study has shown that the Nash reagent is not able to obtain the 100% conversion of formaldehyde to DDL as stated by Nash (1953).

Some implications for further research would be to clarify the role of the acetate ion in DDL formation and to determine if formaldehyde concentration affects the rate of DDL formation; that is, does formaldehyde concentration affect the rate of the competing reaction?

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Appendix

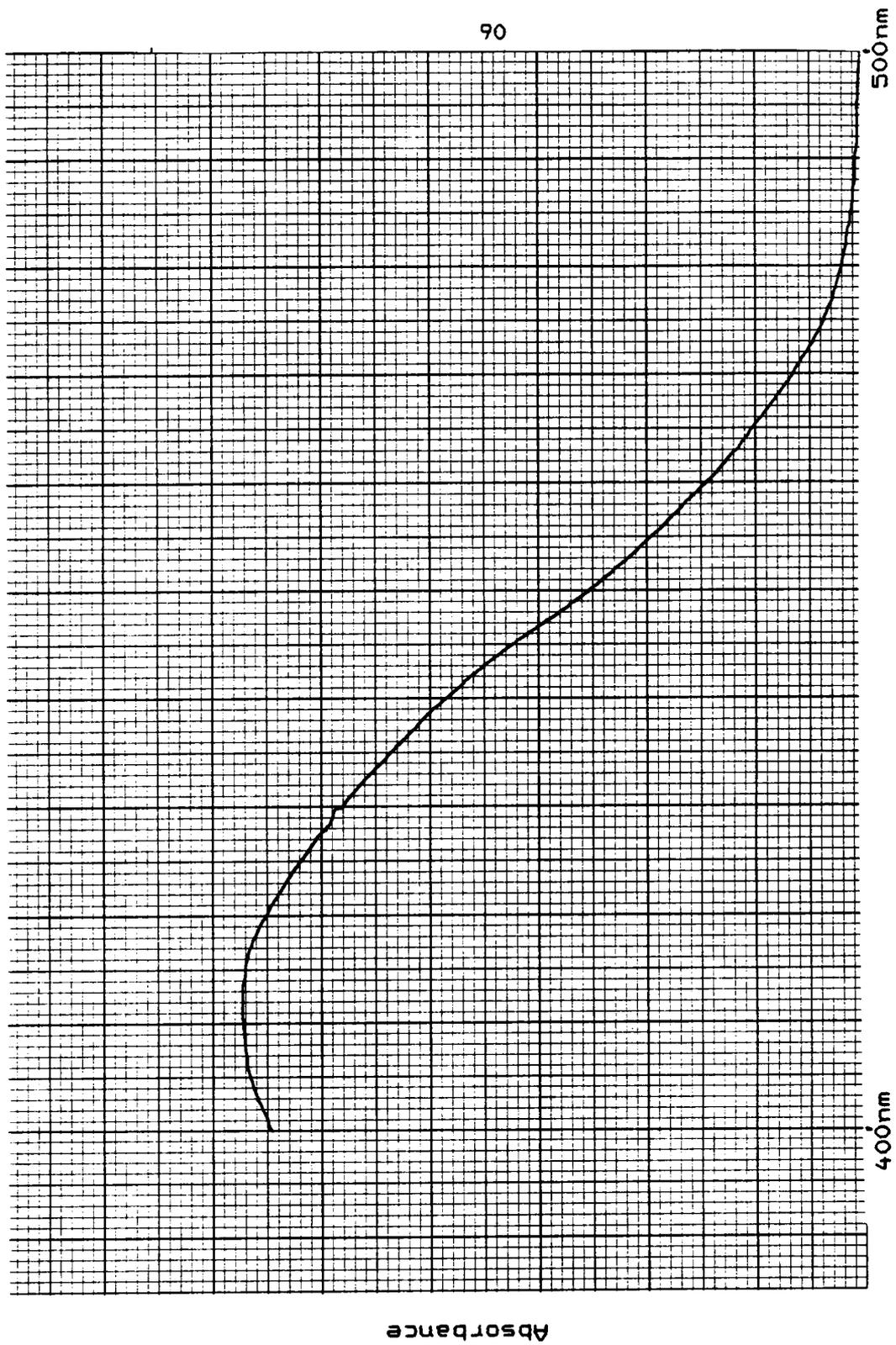


Figure 8. Absorbance scan for DDL crystals made with ammonium acetate.

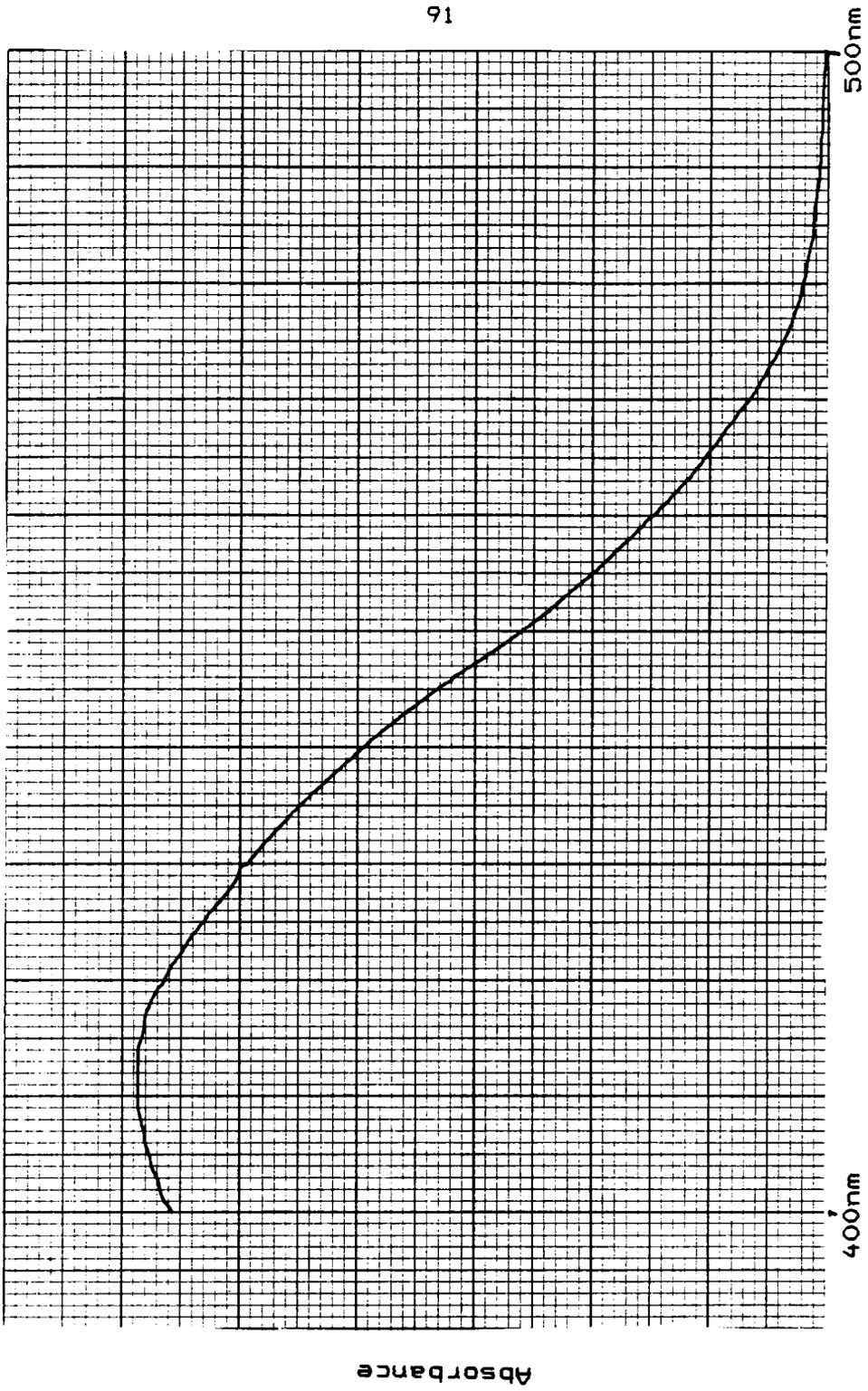


Figure 9. Absorbance scan for DDL crystals made with ammonium phosphate.

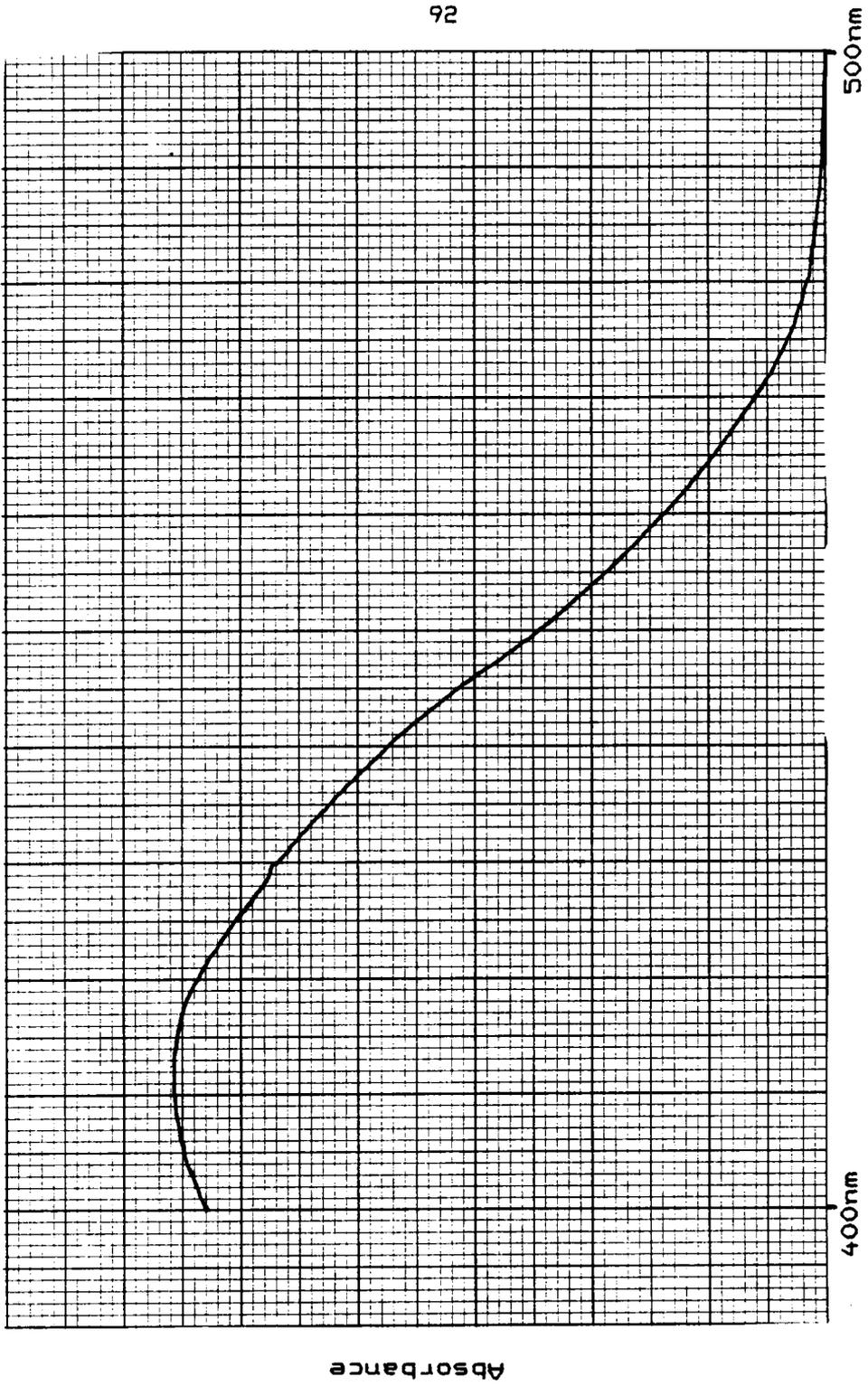


Figure 10. Absorbance scan for DDL crystals made with ammonium sulfate.

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