THE EFFECT OF A DILUTE UREA SOLUTION, AN ACID SIMULATED PERSPIRATION SOLUTION, AND DISTILLED WATER ON A POLYURETHANE COATED FABRIC

by

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CHAPTER I

INTRODUCTION

Invention of the diisocyanate polyaddition process thirty years ago led to the formation of urethane polymers which are widely applicable to the synthesis of new products. The urethane polymers have had considerable commercial importance, particularly in rigid and flexible foams. Recently, the urethanes have become very important in plastics application and fabric coating (1). Because of many favorable properties, the polyurethanes have become popular for thin coatings, where low weight with comparable resistance to wear can be produced. With most other high molecular weight substances it is not possible to make coatings as thin as this that will wear as well (1).

Although polyurethane coated fabrics were almost unknown ten years ago, there has been a rapid growth in their development and production in the last five or six years (2). In addition to the desirable properties that polyurethane products possess, the increasing costs of natural leather and polyvinyl chloride, also used for leather-like fabrics, have spurred the strong growth of polyurethane leathers at the present time (3).

In 1973, the global consumption of all artificial leather was 23 million square meters per month. Europe consumed 15 million square meters per month, the United States consumed 4 million square meters per month, and the Asian countries consumed 3.2 million square meters per month (4). These figures include artificial leathers other than those based on polyurethane and indicate that consumers were willing to accept and purchase articles made of a leather substitute (4).

According to predictions based on current trends, the uses and applications of polyurethanes will continue to grow. Currently, the most growth is occurring in the areas of thin films. Sweeting (5) has said that the growth in polyurethane thin films will occur in belts, hoses, and abrasion liners for industry, and upholstery and synthetic leathers for consumers.

At the present time, there are many varieties and qualities of polyurethane upholstery fabrics and synthetic leathers on the market. . Basically, the product is tough, durable, and lends itself well to various design media. Unfortunately, these polyurethane synthetic leathers are sometimes hydrolytically unstable and perspiration degradation has been reported as a major problem (6, 7, 8, 9).

Although the term "hydrolysis" will be used many times in this thesis, it has not been accepted by this researcher and others, that polyurethane coated fabrics are hydrolytically unstable. While perspiration damage has occurred, it has not been established as fact that hydrolysis is the reaction taking place. However, many people accept it as fact, and reference to hydrolysis in this thesis will be based on their published articles, and are not necesarily the beliefs of this researcher. The urethane polymers are very complicated structures, and there is still a great deal of question as to how these films are hydrolyzed, if indeed hydrolysis is the reaction taking place. Very little investigation has been made into these problems.

Several methods for testing hydrolytic damage to the polyurethane synthetic leathers have been proposed by the Shoe and Allied Trades Research Association (SATRA). The tests are very time consuming and involve equipment that furniture and apparel manufacturers would not usually have. The evaluation techniques are difficult and often require expensive equipment. For these reasons, manufacturers using polyurethane synthetic leathers, rarely undertake their own testing for hydrolytic or perspiration damage. While many polyurethane synthetic leathers are stable, the manufacturers have often suffered losses from the types that were damaged by hydrolysis or perspiration. These manufacturers have become reluctant to buy polyurethane leathers. at all. Since they do not have the testing facilities, they lack the protection against unknowingly buying the urethane leathers with poor resistance to perspiration or hydrolysis.

Furniture manufacturers need an easy-to-perform test that can be accomplished in a relatively short time, to use prior to their styling and purchasing decisions. With a new method of evaluation, they will have a greater degree of protection, and therefore should be more willing to again consider the polyurethane synthetic leathers.

Before developing a new test method, investigation must be made of the effects of various solutions, temperatures, and methods of treatment on the urethane leathers. While it was hoped that the end product of this research would be a feasible test for perspiration damage on polyurethane synthetic leathers, it has become evident that considerable groundwork is needed before a test can be developed. Therefore, the objectives for this study will be:

1. To determine the feasibility of using the Glass Plate Method and the LaunderOmeter^R Method in testing the degradation of polyurethane synthetic leathers.

2. To investigate two soak times, two temperatures, and two solutions in relation to the Glass Plate Method.

3. To investigate the effect of two solutions and distilled water, the time-temperature relationship, and the pH change of these solutions when treating polyurethane synthetic leathers by the LaunderOmeter^R Method.

4. To evaluate the effects of the test solutions on the durability of polyurethane synthetic leathers by means of surface and . flex abrasion.

LaunderOmeter^R--Registered Trademark of the Atlas Electric Devices Company.

CHAPTER II

SURVEY OF RELATED LITERATURE

History of Polyurethane Coated Fabrics

The first use of coated fabrics was recorded by the Egyptians; they used natural gums and resins as preservatives for their mummy wrappings (10). In the 19th century, linseed oil was used as a coating to make oilcloth and a type of linoleum. Similarly, rubber latexes were used to coat rainwear. The development of cellulose nitrate in the late 1800's led to increased research and development in synthetic coatings for fabrics. The search for improved coatings continued, and during World War II the Germans developed improved plastic and film forming compositions (10, 11). More work has been done since World War II in the United States and Europe, and today there is a variety of coatings available that meet the quality requirements for car and home upholstery and other artificial leather applications (10). Polyurethane coated fabrics are one of the more recent developments to emerge from the research to find better and less expensive substitutes for leather.

Although the urethane coated fabrics are relatively new, the history of the urethane polymer began in 1849 with the synthesis of the first aliphatic isocyanate group by Wurtz. This discovery was made in the laboratories of the German company Bayer (11, 12). Isocyanate, or diisocyanate, is the basic starting product for the polyurethane polymer. Very little commercial use was made of this discovery until well into the 20th century. In 1937, Bayer made the first commercial investigation into the uses of the diisocyanates, and it was at this time that they disclosed the development of the diisocyanate polyaddition process (1, 12), which was widely applicable to the synthesis of new products.

It was in 1950-52, that developments leading to the production of the polyurethane elastomers and flexible foams were made (1). Bayer formed a joint venture with Monsanto, which they named Mobay, to commercialize these products in the United States (13). Spurred on by German discoveries, scientists in the United States began to see the wide applications and commercial importance of these diisocyanate-based products. German technology was the catalyst for polyurethane developments made in laboratories in the United States. Soon, however, American urethane development became important in its own right as new and cheaper resins for use in a broad range of polyurethane products were synthesized (1).

In these early stages, the main product was a polyurethane foam to be used as a substitute for the rubber latex foams. The urethane foams could be produced at half the density, had high surface resistance, and resisted chemical attack by oils, chlorinated solvents, water, and detergents. They were pliable, resilient, and had excellent air permeability (13). These properties attracted attention to the polymer and the resulting research led to the development of many new uses for polyurethanes.

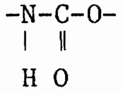
By 1960, Mobay was not the sole producer of isocyanates and polyurethanes. Other large companies, such as Allied Chemical, E. I. du Pont de Nemours and Co., the Curtiss Wright Corporation, and Union Carbide had entered the field (13). As competition grew, new uses were found for the urethane polymer. It is now produced as a fiber in addition to being used for upholstery cushioning, carpet backing, and soft and rigid foams for furniture. Polyurethane coatings are used in clothing, fancy leathers, shoe uppers, tents, inflatable boats, and other end uses (1, 14). Doyle (15) has stated that "A polyurethane polymer can be formulated for more end uses than any known polymer today."

The first polyurethane coated fabrics were introduced in the European market in 1960; they were imported into the United States from Italy and Spain in 1962 (2). Light weight, breatheable, soft, and luxurious, with an almost sensuous feel, they had great consumer appeal. But, complaints of delamination, chipping, popping, coating defects, lack of adhesion, lack of color stability, and poor resistance to hydrolysis soon ruined the initial appeal (2). It became evident that new and improved resins needed to be developed to correct the problems of the original polyurethane synthetic leathers. These new resins corrected most of the early faults of the urethane leathers; they improved the performance while maintaining the aesthetic properties. However, some polyurethane synthetic leathers are still subject to hydrolysis, and it has been found that many are subject to perspiration damage and bacteriological damage (8, 9, 16, 17).

Chemistry of Polyurethanes

Although "polyurethane" is the commercial name of the polymer and is often used in scientific writing, the correct chemical name of the polymer is "polyurethan." The ending "ane" is not in accordance with the accepted chemical nomenclature (12). The spelling used in this paper will be in accordance with common usage, "polyurethane."

The basic structure of polyurethane involves a diisocyanate backbone with repeating urethane groups (15).



$$-\underset{H}{\underset{|}{N}}-\underset{O}{\underset{\|}{C}}-O-$$

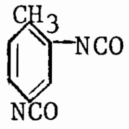
Urethane linkage, or group.

The Encyclopedia of Polymer Science and Technology (12) stated that "A polyurethane does not actually have to contain primarily urethane groups, but is a polymer which contains a significant number of urethane groups, regardless of what the rest of the molecule may be."

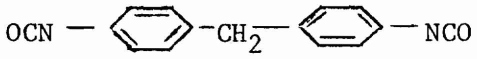
Different structures are accomplished by the addition of a variety of groups: ureas, esters, ethers, amines, biurets, allophanates, and of course, the hydrocarbons. The number, variation, and repeatability of these other groups along with the urethane groups depend upon which active H-bearing material, or materials are reacted with the diisocyanate to form a polymer.

The manner in which these groups are combined and where and how much they branch, will determine the major physical properties of the finished polymer. But no matter what form the material is in--elastomer, hard coating, or a foam--it is called a "urethane" by the industry.

The production of polyurethane depends on the reactivity of the isocyanate groups (-NCO). The most used isocyanates are: tolylene diisocyanate (TDI), methylene-bis-(4-phenylisocyanate) (MDI), and hexamethylene diisocyanate (HDI).



(TDI)



(MDI)

$$OCN\text{-}(CH_2)_6\text{-}NCO$$

(HDI) (2)

The basic diisocyanate reaction involves reacting a diisocyanate with a diol to form a substituted urethane structure (2).

$$\underset{\text{diol}}{n\ HO\text{-}R\text{-}OH} + \underset{\text{diisocyanate}}{n\ OCN\text{-}R'\text{-}NCO} \longrightarrow$$

$$\underset{\text{polyurethane}}{HO\text{-}R\text{-}(O\text{-}CO\text{-}NH\text{-}R'\text{-}NH\text{-}CO\text{-}O\text{-}R)_{n-1}\text{-}OCO\text{-}NH\text{-}R'\text{-}NCO} \qquad (2,\ 5)$$

This is accomplished by addition polymerization in the rearrangement of the molecules (15).

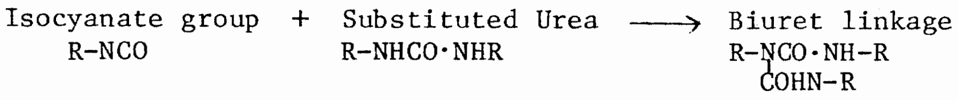
The isocyanate group can undergo reactions with a wide variety of hydrogen donors. Several combinations and linkages shown below, will serve to illustrate the many possible end products.

Isocyanate group + Primary alcohol ⟶ Urethane linkage
R-NCO R-OH R-NHCO·O-R

Isocyanate group + Primary amine ⟶ Urea linkage
R-NCO $R\text{-}NH_2$ R-NHCO·NHR

Isocyanate group + Urethane ⟶ Allophanate linkage
R-NCO R-NHCO·OR

$$R\text{-}\underset{\substack{| \\ COHN\text{-}R}}{N}CO\cdot OR$$



$$\underset{\text{R-NCO}}{\text{Isocyanate group}} + \underset{\text{R-NHCO·NHR}}{\text{Substituted Urea}} \longrightarrow \underset{\text{R-}\underset{\text{COHN-R}}{\text{N}}\text{CO·NH-R}}{\text{Biuret linkage}}$$

(18)

These are just linkages in the polymer chains. The -R- radical can be many compounds and is generally a polymeric group itself. Most often the -R- radical is a polyester or polyether.

It is helpful to think of the polyurethane polymer in terms of hard and soft segments. The hard segments are the isocyanate-derived linkages--and the soft segments are the -R- radicals. The hard segments, the urethane and urea groups, have a great influence upon elasticity and thermal behavior. Second order transition, temperature, modulus, and resistance to hydrolysis are largely a function of the soft segments (1).

In a polymer with a greater ratio of hard to soft segments, one with a high concentration of closely and regularly spaced urethane groups in each chain, the resulting product will be a hard, rigid plastic with non-elastomeric physical properties (15).

When the polymer is made with approximately the same amount of diol and diisocyanate, these groups will react to give a polymer of high molecular weight and will eliminate significant reactive terminal group effects (2). In this case, branching and crosslinking are cut down, but the intermolecular forces between the urea and urethane groups are sufficiently strong to behave like actual crosslinks. These forces are usually called "hydrogen bonds", but strong dipole moments of the urea structures and van der Waal forces are also factors (2).

For the soft and flexible polyurethane products the -R- radical is usually polymeric, and polyester or ether in structure. Sometimes, a combination of diols is used with some containing small -R- radicals and some containing polymeric -R- radicals. In this process, it is possible to regulate the incorporation of diols into the polymer chains to produce random or block polymer structures (5).

In the production of complex polyurethanes, a pre-polymer is prepared first. This will be the major component of the polymer, and is composed of a linear, hydroxy-terminated polyester or polyether that has been reacted with an excess of a diisocyanate. The original molecular weight of the polyester or ether group is usually between 500-6,000. This reaction is normally run with a two-to-one isocyanate/hydroxyl molar ratio. The resulting pre-polymer has isocyanate end groups and can be thought of as a macro-diisocyanate. In the second step, this macro-diisocyanate is reacted in substantially stoichiometric quantities with a diol or a diamine to produce a high molecular weight polyurethane. Generally, the second step of the reaction is carried out in the presence of a solvent, resulting in a solution of the polyurethane (19).

If the original isocyanate or hydroxyl-containing compound has a functionality greater than two, crosslinking and extensive branching can take place. If a branched structure is desired, the reaction is carried out in bulk rather than in a solvent, due to the insolubility of the network in solvents. The molecular weight of the final network can be infinitely large, theoretically (18).

Process of Manufacture

Most polyurethane synthetic leathers are produced using the transfer coating process where the urethane film is transferred from a release paper to a fabric substrate. A picture is taken of the grain of the leather which will be simulated. Engraved embossing rolls are then made to produce the release paper with this embossed grain. From a large bolt, the release paper is fed through rollers where a thin coating of urethane in solution is accurately applied with a doctor blade. The release paper, plus the top skin, proceeds through a series of dryers where the maximum temperature may reach 205^oC, depending on the solvent used. This procedure substantially removes the solvent from the urethane top skin. A urethane adhesive is next applied to the back of the top skin, and the substrate, for example, a highly napped woven fabric, is pressed into the adhesive. This composite structure, paper/top skin/adhesive/substrate, proceeds through several drying zones where the maximum temperature again may reach 205^oC depending on the adhesive solvent used. The release paper is then stripped off, rewound for future use, and the product is taken up at a winding station (19, 20).

The base color of the synthetic leather is achieved by the addition of pigments to the urethane for the top layer and/or adhesive layer. After the release paper has been stripped off, the synthetic leather is often rotogravure printed or sprayed with a darker color to give a more realistic leather look. This simulates the grain and color gradations of natural leather. New printing techniques, such as photogravure and paper transfer printing are being investigated by the manufacturers of synthetic leathers for their feasibility (21).

Characteristics and Properties

Since many of the polyurethane coated fabrics are formulated for synthetic leathers, it would be desirable for the product to be similar to natural leather. Leather is a random, three-dimensional array of collagen fibers, tanned by one or more of a variety of treatments to preserve the protein. The collagen fibers are large and coarse on the flesh surface and decrease in size toward the grain. In the grain, the fibers are microscopically fine, and tend to be parallel to the surface. Leather is noted for its strength, flexibility, and its ability to absorb and transmit moisture (6).

Ideally, an artificial leather would possess a similar, all fibrous structure, with superior strength, flexibility, and hydrophilic properties. Allewelt and Bauer (13) said that a coated material should be "soft, breatheable, odorless, and able to withstand both washing and drycleaning." In practice, this has not been totally achieved. Several synthetic leathers have been produced which contain varying degrees of the original leather properties. Some of the most successful artificial leathers are those made of polyurethane. The Business Research Division of the Journal of Coated Fibrous Materials (20) stated that ". . . of the many coatings commercially used, urethanes have superior performance, unparalleled versatility, and the most desirable price to performance ratio."

To be accepted by industrial and private consumers, a coated article must fulfill several functions. The aesthetic, technical, and economical demands on a product differ according to the present market and to the end-use (1, 22). For apparel products, heat and moisture balances, water vapor permeability, easy care, heat resistance, and low temperature flexibility are important (23). On the other hand, upholstery manufacturers want a coated fabric to have fastness to hydrolysis, abrasion resistance, and scuff and snag resistance. Shoe uppers require a fabric with good mechanical properties such as impact, snag, and abrasion resistance (1, 24). Requirements are not as rigid for novelty items which will receive little wear. Polyurethane synthetic leather can meet most of the above requirements for coated fabrics.

The urethane linkages give the polyurethane coated fabrics an inherent mechanical strength and high abrasion resistance (2). A wide variety of products and properties is achieved by the alteration of the -R- radicals in the starting products. Various effects can also be achieved by different production methods. Polyurethane synthetic leathers vary from country to country, as major processing differences exist between the United States, Europe, and the Asian countries (4).

Properly formulated, urethane films are chemically resistant to esters, aliphatic and aromatic hydrocarbons, and most chlorinated hydrocarbons. They are not harmed by vegetable, animal, and mineral oils, or fats and neutral salt solutions. Polyurethane films are also resistant to the lower aliphatic alcohols, water, and alkaline solutions including soap and ammonia solutions (5).

As a class, the urethanes are tough and flexible (3, 25). A number of valuable properties can be combined in a single coating. Very thin coatings can be produced with comparable resistance to wear. Polyurethane coatings possess a certain degree of water vapor and air permeability which can be varied over a wide range (10, 20).

Depending on the desired end use, polyurethane coated fabrics can be made to resist flex cracking, and to have high tear strength, good adhesion, resiliency, resistance to spots and soils, lightfastness, heat resistance, dimensional stability, electrical properties, resistance to oxygen aging, and resistance to hydrolysis (1, 5, 8, 13, 23). They are soft, breatheable, and odorless (13). In contrast to polyvinylchloride synthetic leathers, urethanes do not need to be formulated with plasticizers, which often give polymer coatings an oily feel as migration occurs (2).

Degradation and Hydrolysis

The major forms of degradation affecting polyurethane synthetic leathers are hydrolysis, microbiological attack, and ultraviolet light damage (6, 16, 17). Perspiration damage, often considered a form of hydrolytic damage, is also a major problem (9). Most of these forms of degradation can be controlled by altering the starting products.

The amount of resistance to hydrolysis is an important criterion when considering coated fabrics (1), and many polyurethane synthetic leathers have shown poor hydrolytic stability in the past (7). However, some types of wear damage, formally thought to be hydrolysis, have been found to be due to defects in the coating process (8).

The polyurethane synthetic leathers are usually polyester or polyether based. The polyester based urethanes have a more skin-like hand and the polyether based urethanes are more rubber-like (26). Those products with polyester bases are considered to have the best combination of properties overall, but those with polyethers have better hydrolytic stability (27). Urethane and ester linkages, both are susceptible to hydrolysis, but the ester linkages found in the polyester groups are more easily hydrolyzed (9). Some ester-type polyurethanes are decomposed by prolonged contact with water, dilute acids, or moist heat, which causes swelling and slow hydrolysis (18).

Since these polyester based films are susceptible to hydrolysis, they should not be used in environments of excessive humidity or high temperature. However, since the degradation may take up to three years to be noted, these films might be successfully used for articles intended to have short lives, such as clothing, as opposed to use in upholstery where a longer wear life is desirable (2).

The resistance to hydrolysis can be increased in the polyester urethanes by lengthening the carbon chain between the ester linkages, or by using glycols containing secondary hydroxyls (27). By increasing the hydrophobic nature of the higher molecular weight hydroxy compounds and by increasing the quantity of diisocyanate chain extenders, a polyester urethane can be made more resistant to hydrolysis. Even with these improvements, the polyether based urethanes have better resistance to hydrolysis (6). In addition to the differences found between the polyester and ether based urethanes, it has been found that aromatic polyurethanes usually have better stability to hydrolysis than do the aliphatic polyurethanes (28).

Hydrolysis causes a breakdown in the polymer chain and a deterioration in the properties (8). The breakdown occurs as the film becomes brittle, followed by cracks from flexing (9). The rate of hydrolysis is increased considerably by the presence of certain catalysts. Impurities introduced during manufacture can catalyze hydrolysis as can certain components of human perspiration (6, 8, 9).

There is a marked difference in the rate of hydrolysis or saponification, depending on the pH value. The alkaline pH range saponification takes place as follows:

$$\underset{\text{ester}}{R - COOR'} + -OH \rightleftharpoons \underset{\text{anion}}{RCOO^-} + \underset{\text{alcohol}}{R'OH}$$

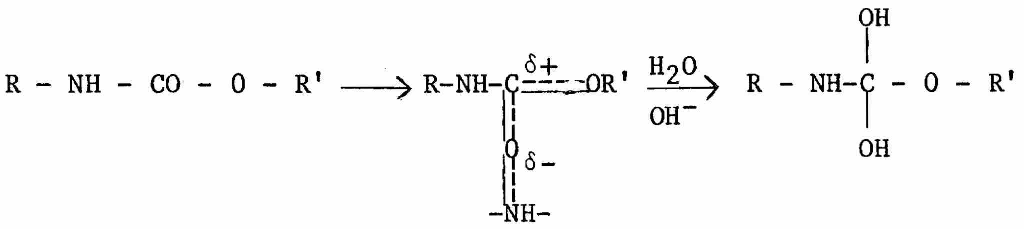
The amount of alcohol is directly proportional to the concentration of the OH^- ions (26).

In the acid range, the reaction is as follows:

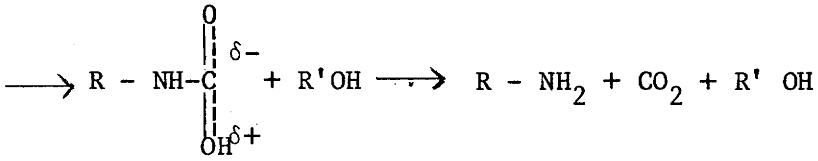
$$R - COOR' + H_2O \rightleftharpoons RCOOH + R'OH$$

The amount of alcohol is directly proportional to the concentration of H^+ ions. Hydrolytic effects are least in the neutral range and more severe in the alkaline state (26).

The main theory concerning hydrolysis states that the polyurethane undergoes a nucleophilic attack if the nitrogen in the urethane link is already involved in an inter- or intra-chain hydrogen bond (9).

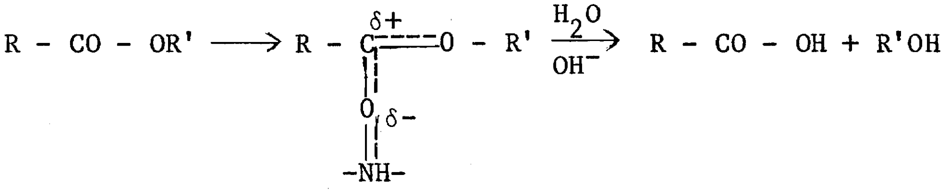


$$R - NH - CO - O - R' \longrightarrow R\text{-}NH\text{-}\underset{\underset{\underset{\text{-NH-}}{\vdots}}{O\,\delta-}}{\overset{\delta+}{C}}\text{-}\,\text{-}OR' \xrightarrow[OH^-]{H_2O} R - NH\text{-}\underset{OH}{\overset{OH}{C}} - O - R'$$



$$\longrightarrow R - NH-\overset{\overset{O}{\|}\ \delta-}{\underset{\underset{OH^{\delta+}}{\|}}{C}} + R'OH \longrightarrow R - NH_2 + CO_2 + R'\ OH$$

The hydrolysis of an ester link is postulated to proceed as follows:



$$R - CO - OR' \longrightarrow R - \overset{\delta+}{\underset{\underset{\underset{-NH-}{\|}}{O\ \delta-}}{\underset{\|}{C}}}{=\!=\!=}O - R' \xrightarrow[OH^-]{H_2O} R - CO - OH + R'OH$$

This is in agreement with the explanation for the hydrolysis rate dependence on pH. Catalysts for nucleophilic reactions accelerate the degradation rate. As mentioned above, various substances in human perspiration are capable of catalyzing the hydrolysis of the polyester based urethane (8).

In the polyurethane synthetic leather, the adhesive or tie coat has been found to be more susceptible to hydrolysis (9). This can cause the film to delaminate before cracking and degradation appear on the surface. Because of the differences in hydrolytic resistance between the two coats, the film is usually taken separately for hydrolytic tests. Film samples are usually hydrolyzed in steam at 80-120°C for 15-32 hours (6, 9). They are then tested for loss in tensile strength and are checked for flex damage using the SATRA CM-28 test method developed in Great Britain (1, 6, 8, 28).

Another method of hydrolysis involves treating samples in 95 percent relative humidity for 14 days at 70°C. After this treatment, films designated for clothing should retain 10-20 percent of film strength, and those to be used for upholstery should retain 70 percent of film strength (1).

Damage by Perspiration

In their investigation of the resistance to hydrolysis of polyurethane synthetic leathers, researchers at SATRA found that the rate of hydrolysis increased in the presence of urea, a component of perspiration (8). This has led to increased studies on the effects of perspiration on these materials.

It was shown earlier, that there was a difference in the rate of hydrolysis depending on the pH value (26). Hole and Abbot found that hydrolysis of polyurethane top skins in distilled water did not correlate with findings in actual wear trials (9). They thought that the small quantity of acid formed by hydrolysis would not readily alter the pH. But, the chemistry of polyurethanes is very complicated, and reactions can be easily influenced by components present in perspiration, even in extremely low concentrations (26). These components can act as catalysts in the process of hydrolysis (8). The skin exudants found to be most degrading were urea, ammonia, and oleic acid (6).

The effect of perspiration on polyurethane leather was first investigated as it pertained to shoe uppers. Hydrolysis usually occurs under heat and moisture, and the foot skin temperatures can range from $15^{o}C$ in the morning to about $36^{o}C$ in the late afternoon and evening (6). In addition to the environment of moisture and heat, perspired upon areas can be infested with micro-organisms which can degrade the polymer (1, 16, 17).

In the past, testing for damage by perspiration has been difficult. It is almost impossible to collect large amounts of perspiration for laboratory quality control work. As a result, synthetic perspiration solutions have been developed to simulate the action of a normalized perspiration on the product being tested.

In 1905, perspiration was first considered as a variable in the fading of dyes. The test involved steeping the sample in dilute acid (29). There was much debate, however, as to whether perspiration was acid or alkaline. In the late 1920's, the Society of Dyers and Colourists undertook elaborate and extensive experiments to collect and analyze perspiration. The nitrogen content in the form of ammonia, urea, and amino acids was determined and the pH was found to be slightly acid (29). But it has also been found that normal perspiration can turn alkaline due to bacteriological decomposition (26). Alkaline perspiration can also be found in persons suffering from certain diseases or with extremely poor hygiene (30).

The first perspiration tests involved two solutions; one acid, based on lactic acid, and the other alkaline based on ammonium carbonate. These were saline solutions with disodium phosphate added and were developed by the American Association of Textile Chemists and Colorists (AATCC) (29). The International Organization for Standardization identified some of the amino acids in perspiration and found that a small amount of histidine monohydrochloride could simulate the action of these amino acids most reliably. AATCC amended their test to include .25g/l histidine monohydrochloride, and the textile organizations in other countries added .50g/l. This seemed to increase the reliability of the test, which became AATCC Method 15, Colorfastness to Perspiration. However, the alkaline solution portion is still questioned by some researchers, and it has been recommended by the RA-52 committee of AATCC that this portion of the perspiration test be dropped (29, 30).

Other perspiration tests were developed by different industry groups. Table 1 shows the formulations for several of the most often used simulated perspiration solutions.

The AATCC Method 15 is used to measure a fabric's colorfastness to perspiration. This test has not been reported as being used on leather-like materials, nor has it been used for degradative purposes. It involves soaking a test piece in a simulated perspiration solution for 30 minutes and then placing the sample between glass plates at a pressure of 10 pounds and heating at 38^{o}C for six hours (31).

The test specified by the American Society for Testing and Materials (ASTM) is designed for chrome tanned white shoe uppers made from natural leather. It involves treating a test sample in a controlled condition of 23 ± 1^{o}C and 50 ± 4 percent relative humidity for 48 hours after soaking in the solution in Table 1 under ASTM (32). A test for perspiration damage of glove leathers uses the same conditions and formulation for simulated perspiration, but is only treated for four hours, and is rated by visual observation and feel after removal from the oven and air drying. Percent shrinkage is determined (33). A test similar to this is also done on chrome tanned leather (34).

The SATRA CM-28 test involves flexing a sample after a laboratory hydrolysis treatment with the urea solution (8). Tests are also done

TABLE 1

FORMULATIONS SIMULATING
HUMAN PERSPIRATION

	AATCC-15		ASTM	SATRA
	Acid	Alkaline	D-2322-64T	CM-28
Sodium chloride	10g.	10g.		
Lactic acid	1g.			
Sodium lactate[a]			86g.	
Disodium phosphate anhydrous	1g.	1g.	.165g.[b]	
Ammonia carbonate		4g.		
Urea			1.67g.	1.2g.
Histidine monohydrochloride	.25g.	.25g.		
Distilled water[c]				
pH	4	8	7.5	Not Spec.

[a] 60 percent sodium lactate in water.

[b] $Na_2HPO_4 \cdot 12\ H_2O$

[c] Amount needed to make one liter of total solution.

by soaking the top skin and then exposing the moist test piece to 80-100 percent relative humidity at 28-30°C for 14 hours and then testing for loss in tensile strength (6).

CHAPTER III

EXPERIMENTAL AND TEST PROCEDURES

Description of Test Fabric

This study involved observing the effects of various chemical solutions on a 389.82g/m^2 (11.53oz/yd^2) white polyurethane synthetic leather. The polyurethane top skin was approximately .01cm (4mils) thick and the total structure was .09cm (34 mils) thick. The fabric substrate was 100 percent cotton, woven in a very steep twill, and could be called a gabardine fabric.

The urethane top skin was produced by reacting a combination of diols with adipic acid to give a polyester glycol of molecular weight about 2,000. The polyester glycol was then reacted with the saturated equivalent of MDI, which is an aliphatic diisocyanate. This resulting prepolymer was reacted with an excess of diamine to give the urethane polymer.

It has been stated by the supplier of this polymer (19) that the resulting product has been shown in market use not to have good hydrolytic stability. The extra hydrogen atoms in the aliphatic diisocyanate cause the polyurethane skin to be more subject to nucleophilic attack.

Glass Plate Method

This researcher has found no evidence to indicate that the AATCC perspiration test has been used to show degradative effects on synthetic leathers. The Glass Plate Method was developed, using certain procedures and concepts from AATCC Method 15, to enable the composite polyurethane synthetic leather to be treated and evaluated for the effects of the test solutions.

Experimental Procedure

Test Solutions:

Two solutions were chosen. The acid solution specified by the AATCC Method 15 was used with a substitution of .50g/1 for .25g/1 histidine monohydrochloride. The alkaline solution specified by AATCC Method 15 was not used as it has been shown to give unreliable results (30). A dilute urea solution was also chosen. The concentration of 1.2g/1 urea, specified by SATRA was doubled and used in this study.

Modified AATCC Acid Solution

10 g.	Sodium chloride
1 g.	Lactic acid
1 g.	Disodium phosphate
.50 g.	Histidine monohydrochloride

Distilled water to make 1 liter

Modified SATRA Urea Solution

2.4 g. Urea

Distilled water to make 1 liter

500 ml. was used to treat each sample.

From this point on, the Modified AATCC Acid Solution will be termed "Acid", and the Modified SATRA Urea Solution will be termed "Urea".

Time of Soak:

A 30 minute soak time was compared to a 12 hour time of soak. The AATCC perspiration test specifies a 30 minute soak. Many hydrolysis tests use soak times or high humidity treatments of 12 hours or greater. The samples were soaked from the urethane skin side by making a tray-effect with the sample. This was accomplished by clipping the edges with paper clips to form a tray. After soaking, excess moisture was blotted from the samples with a terry cloth towel.

Temperature:

After the samples were soaked in the test solutions for the specified time, they were placed between glass plates (43 cm X 31 cm) and heated for six hours in an air circulating oven. From the AATCC perspiration test, the temperature of $38^{o}C$ was chosen. For contrast, a temperature of $100^{o}C$ was also used. After heating, the samples were air dried if necessary.

Sample:

Samples were cut to be 43 cm X 31 cm. Eight samples were necessary to evaluate the variables stated above.

Test Procedure

Surface abrasion was used to indicate degradation of the urethane skin and was evaluated using the Taber Abraser^{R}. Emery wheels rotated over the structure in a circular pattern. For this study, an H-22 wheel with a head weight of 500 g. per wheel was used, which

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Taber Abraser^{R}--Registered Trademark of Taber Instrument Corporation.

is the grade and weight recommended respectively for synthetic leathers. The wheels were refaced after each sample, or after 250 cycles, whichever was greater (35).

Each sample was 13.5 cm X 13.5 cm and a small hole was cut in the center. The sample was mounted onto the platform of the Taber Abraser^R, secured, and allowed to be abraded by the emery wheels. The sample was checked for skin breaks frequently. An actual break in the skin, rather than an enlarged pore, was the endpoint desired.

Flex abrasion results were also obtained to determine whether these solutions changed the flex life by degrading the urethane top skin. The Bally Flexometer^R was the instrument employed. Five 4½ cm. X 7cm. samples were cut from the treated area. These samples were flexed with a moving crease until a crack in the urethane skin occurred.

LaunderOmeter^R Method

Most hydrolytic tests recognized for use on natural and synthetic leathers involve soaking in a solution or treating a soaked material with high humidity so that the material stays in contact with the solution throughout the treatment time. The LaunderOmeter^R lends itself well to this concept in treating polyurethane synthetic leathers.

In the LaunderOmeter^R, an enclosed system can be rotated in a constant temperature bath. Several different systems can be run as long as the temperature requirement is the same. The urethane leathers can be treated in an unrestricted form (36).

Bally Flexometer^R--Registered Trademark of Bally CTU.

Experimental Procedure

Test Solutions:

This method was performed using the acid solution and the urea solution described above, and distilled water.

Sample Size:

Samples were pre-cut 13.5 cm X 13.5 cm for use on the Taber Abraser^R. Three samples were taken at each level of treatment and three replications were made.

Time and Temperature Treatment:

From preliminary experimentation, it was found that a 12 hour treatment at all temperatures produced samples too degraded to test by surface abrasion. A six hour treatment gave poor results for 72°C and 95°C. A two hour test time produced acceptable samples at 72°C but not at 95°C. The two hour test time at 72°C was chosen for the procedure.

Protection of Sample:

It was found in preliminary investigation that samples tended to protect each other when more than one was placed in a LaunderOmeter^R cup. Therefore, it was decided that the three samples for each treatment be taken separately in individual cups.

Abrasion against the side of the LaunderOmeter^R cup was also noticed. This was alleviated somewhat by enclosing each sample in a 28.65g/m^2 (1 oz/yd^2) 100 percent cotton cheesecloth bag. This was adopted for the procedure as the synthetic leather backing was also cotton.

LaunderOmeter^R Procedure:

1. The samples were cut 13.5 cm X 13.5 cm and enclosed in cotton cheesecloth bags.

2. The solutions were made prior to each run according to formulations given above. pH measurements were taken of the acid solution, urea solution and the distilled water.

3. One sample and 500 ml of solution were put into a size 2 LaunderOmeter^R cup. The filled cups were placed in the warming tray of the LaunderOmeter^R for five minutes where water from the constant temperature bath warmed the system. The cups were sealed and placed in the LaunderOmeter^R.

4. The cups were rotated at 72°C for two hours.

5. The cups were removed. Solution from each cup was saved for a pH measurement. The samples were removed from the cup and the cotton cheesecloth bags were cut away. Samples were laid flat on a metal drying rack.

Test Procedures

The samples treated by the LaunderOmeter^R Method were evaluated by the Taber Abraser^R as above in the Glass Plate Method. If wrinkles or abrasion at points of contact with the cup had occurred, these points were not rated.

The pH for each solution, including distilled water, was measured before and after the treatment in the LaunderOmeter^R.

CHAPTER IV

RESULTS AND DISCUSSION

Data and Interpretations for the Glass Plate Method

Data for the following were obtained according to the procedures described in Chapter III. Cycles needed to show the first skin break were recorded using the Taber Abraser^R. Flex life was determined using the Bally Flexometer^R. The following paragraphs describe observations which could not be formally analyzed.

Soak Process:

This researcher was not able to treat the top skin alone without treating the fabric backing. The urethane skin is naturally porous enough to allow air and moisture to pass through, and the test fabric had additional pinholes, which were defects in the manufacturing process. This allowed the test solutions to completely soak through the test fabric after 30 minutes.

Oven Treatment:

When treated at 100^{o}C between glass plates, the samples' grain-like surface tended to deform slightly to a slick, shiny surface. Samples had to be peeled off of the glass plates. Often the sample would show inconsistent slick and grainy areas. Several of these areas would often be exhibited on the same sample cut for the surface abrasion test (Figure 1).

Evaluation of Degradation:

Both test procedures chosen entailed very subjective evaluations on the part of the operator. Since the pinholes were already breaks in the top skin, the operator had to be careful to look for another break and not just an enlargement of a pinhole.

On abrading with the Taber Abraser^R, the white sample picked up emery dust from the wheels after each refacing. The dark ring on the test area made evaluation difficult. Any wrinkle or bubbling of the sample on the platform caused erroneous results. These areas had to be discarded, limiting the test area on the sample.

The rate of the Bally Flexometer^R was about 100 flexes per minute. At this speed it was difficult to see the break when it first occurred. But, since this test gave results in the range of 10,000-50,000, the error involved in missing the exact end-point by 100 flexes was low.

Data Interpretation:

Due to the many technical difficulties encountered in this method, the results obtained were not reproducible. The method was not replicated since it was shown during the first run to be inadequate in many respects. It can be seen in the following tables (Tables 2, 3 4, and 5) that increasing the temperature to 100^{o}C usually increased the average abrasion resistance of the film, regardless of which treatment had been chosen. It was found that the heat and the weight of the glass plate slightly deformed and flattened the grain structure of the surface. The smoother surface abraded less easily. This

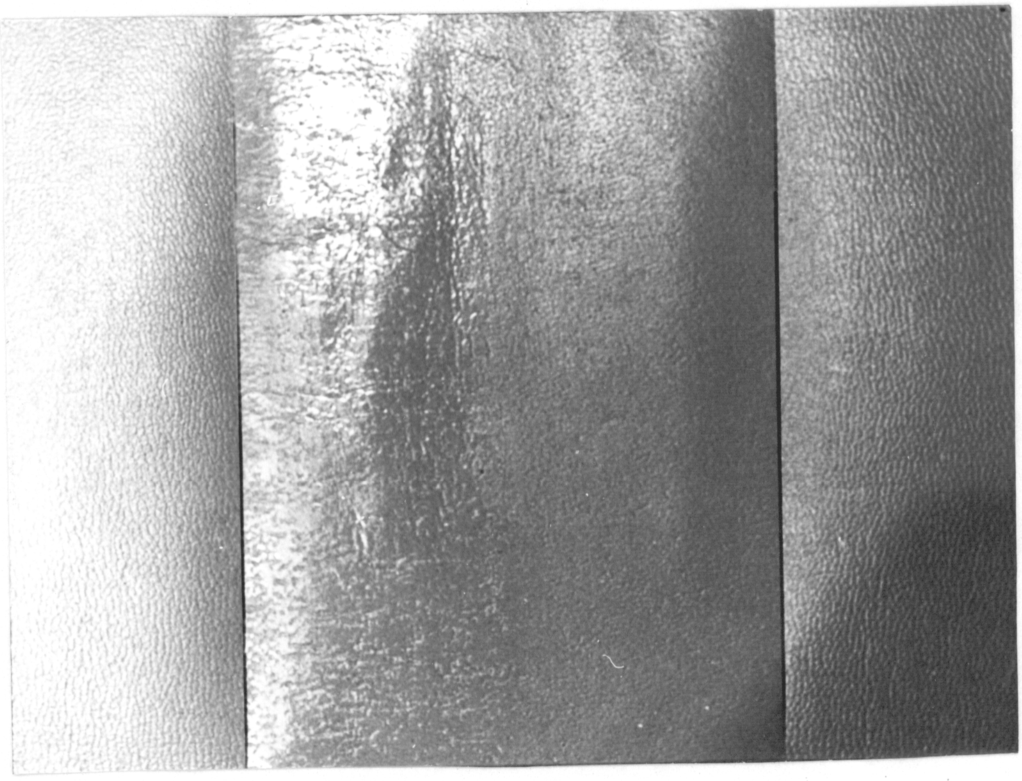


Figure 1. Control with sample after being heated between glass plates at 95°C.

TABLE 2

ABRASION RESULTS REPORTED IN CYCLES FOR SAMPLES TREATED WITH UREA SOLUTION

Soak Times	30 min.		12 hours		Untreated Control
Temperatures	38°C	100°C	38°C	100°C	
Sample 1	163[a]	265	275	181	564
2	240	219	459	166	624
3	282	273	518	184	562
4	153	218	195	242	...
5	132	227	221	213	...
Average	194.0	240.4	333.6	197.2	583.3

[a] Number of cycles to first film break.

TABLE 3

ABRASION RESULTS REPORTED IN CYCLES FOR SAMPLES TREATED WITH ACID SOLUTION

Soak Times	30 min.		12 hours		Untreated Control
Temperatures	38°C	100°C	38°C	100°C	
Sample 1	119[a]	205	133	211	564
2	111	226	93	223	624
3	159	139	137	244	562
4	174	211	153	176	...
5	110	281	116	374	...
Average	134.6	212.4	126.4	245.6	583.3

[a] Number of cycles to first film break.

TABLE 4

FLEX-LIFE OF SAMPLES TREATED WITH UREA SOLUTION

Soak Times	30 min.		12 hours	
Temperatures	38°C	100°C	38°C	100°C
Sample 1	30,500[a]	72,000	74,000	30,200
2	31,200	28,200	27,600	26,500
3	51,000	73,000	52,000	28,200
4	53,000	29,400	17,000	18,700
5	28,000	17,300	45,500	16,600
Average	38,740	49,980	43,220	24,040

[a] Number of flexes until first film break.

TABLE 5

FLEX-LIFE OF SAMPLES TREATED WITH ACID SOLUTION

Soak Times	30 min.		12 hours	
Temperatures	38°C	100°C	38°C	100°C
Sample 1	16,500[a]	43,100	26,600	53,000
2	15,800	18,000	15,900	73,000
3	14,800	18,000	16,600	51,400
4	14,600	17,900	16,700	17,600
5	15,000	16,800	14,400	17,800
Average	15,340	22,760	18,040	42,560

[a] Number of flexes until first film break.

property disguised any effect of the treatments on urethane film degradation.

Although great variation occurred in the results, the averages from the two tests agreed in direction; all averages increased with increasing temperature except the values obtained from the sample soaked with urea for 12 hours and heated at 100°C. On comparing the two test solutions, it appeared that the samples treated with the urea solution had more abrasion resistance, except in the case, again, with those samples soaked in urea for 12 hours and heated at 100°C. Experimental error may have been involved in the treating of that sample.

Data and Interpretations for the LaunderOmeter^R Method

The following observations and data were obtained according to the procedures outlined in Chapter III. The pH measurements were taken for each solution before and after each run. The pre-cut samples were tested for abrasion resistance on the Taber Abraser^R. The paragraphs preceding the data describe observations which could not be formally analyzed.

Protection of Sample:

The rotation of the LaunderOmeter^R caused considerable motion of the sample in the LaunderOmeter^R cup. The weight of the soaked sample caused it to crumple down upon itself. As the LaunderOmeter^R rotated, the distorted sample rubbed against the sides of the cup, often causing very abraded areas at the points of abrasion. Cotton cheesecloth bags were designed to stop this abrasion. Although the results for abrasion resistance were higher, with less variance between samples (Table 6) the added soaked weight of the cheesecloth caused even more wrinkling which limited the available areas for testing.

pH of Solution:

A change in pH was found to occur in the urea solution and the distilled water after contact with the urethane synthetic leather. The change started quickly, so the pH had to be taken on solutions before being put into the cup with the samples. The pH change of the acid solution was negligible. Higher temperatures increased the rate of change (Table 7).

Time and Temperature:

During preliminary investigation, a time of six hours and a temperature of 95°C was chosen. Although the samples were too degraded to test by surface abrasion, the effects of the three test solutions was very evident (Figure 2, 3, 4). The water and acid solution treatment almost totally decomposed the film. This researcher wished to use surface abrasion as an indication of film degradation, so a lower temperature and a shorter time were chosen. At a temperature of 38°C and a two hour test time, the degradation was so slight that this combination was discarded. Initial investigation showed that treatment at 72°C for six hours gave results too drastic (Figure 5, 6, 7), but a test at 72°C for two hours gave a valid sample where only a slight amount of degradation could be observed visually (Table 8).

TABLE 6

ABRASION RESULTS REPORTED IN CYCLES OF SAMPLES PROTECTED VS. NO PROTECTION

Solution	Two Hour Test, 72°C	
	With Bags	Without Bags
Urea	175[a]	162
	133	85
	Average 154.0	Average 123.5
Water	94	65
	90	71
	Average 92.0	Average 68.0
	62	48
	73	91
	Average 67.5	Average 69.5

[a] Number of cycles until first film break.

TABLE 7

pH MEASUREMENTS AT 3 TEMPERATURES

Solution	Two Hour Test Time					
	38°C		72°C		95°C	
	Before	After	Before	After	Before	After
Urea	5.50	6.70	5.75	7.01	5.50	8.45
Water	5.80	6.80	5.80	6.91	5.70	7.30
Acid	4.05	4.30	3.95	3.98	4.00	4.30

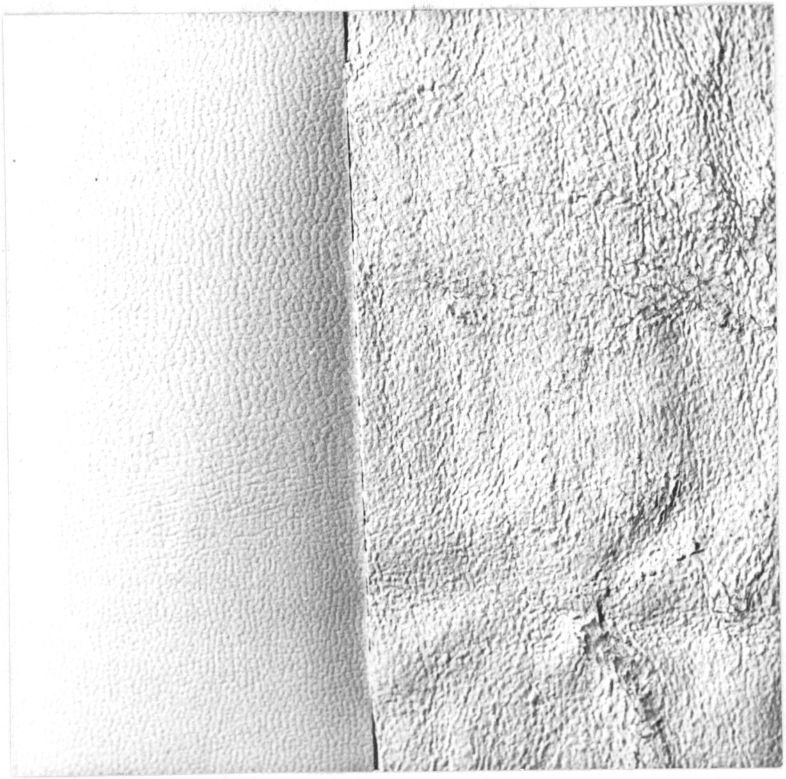


Figure 2. Control with sample treated with urea solution at 95°C for 6 hours.

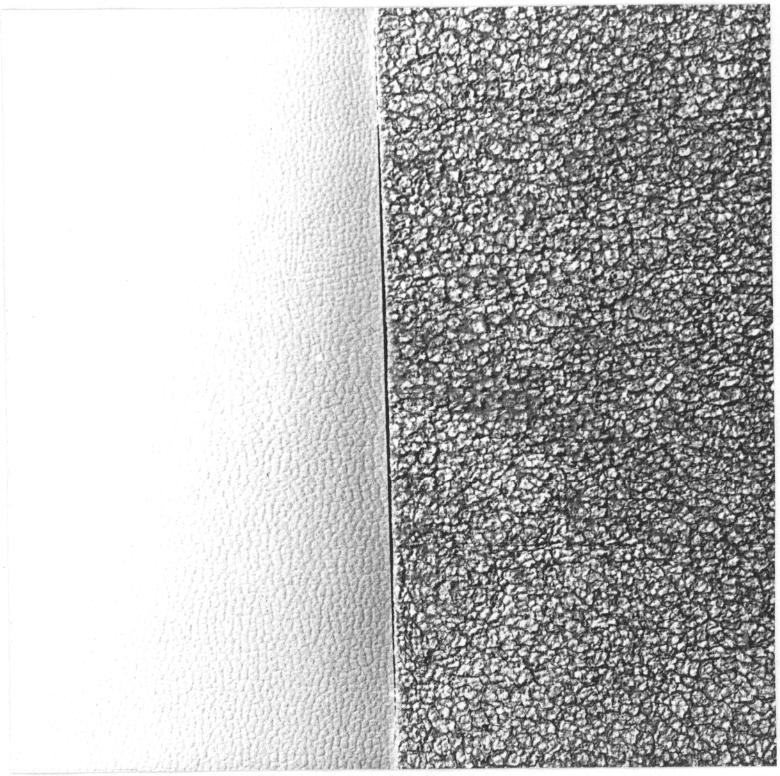


Figure 3. Control with sample treated with acid solution at 95°C for 6 hours.

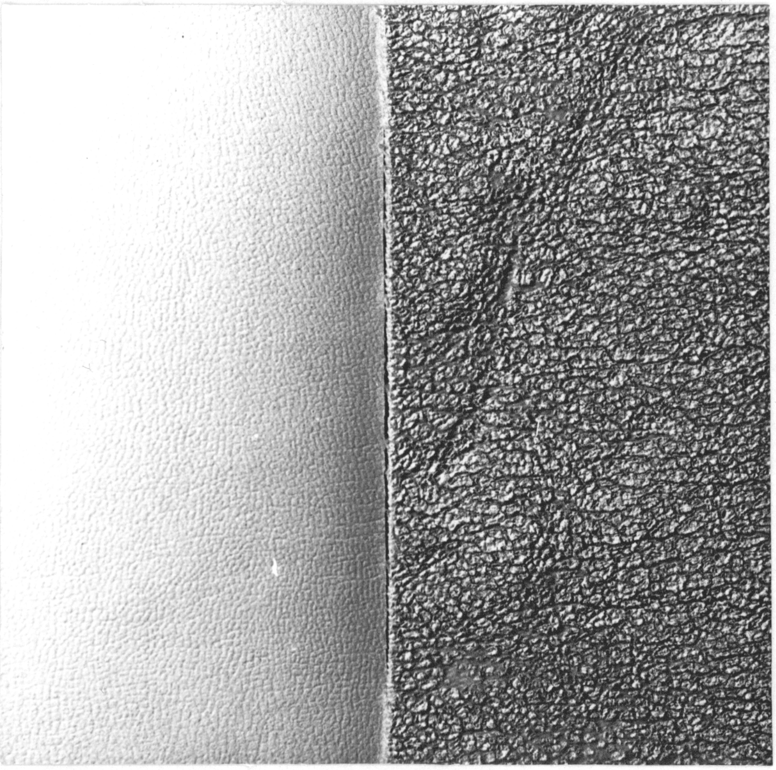


Figure 4. Control with sample treated with distilled water at 95°C for 6 hours.

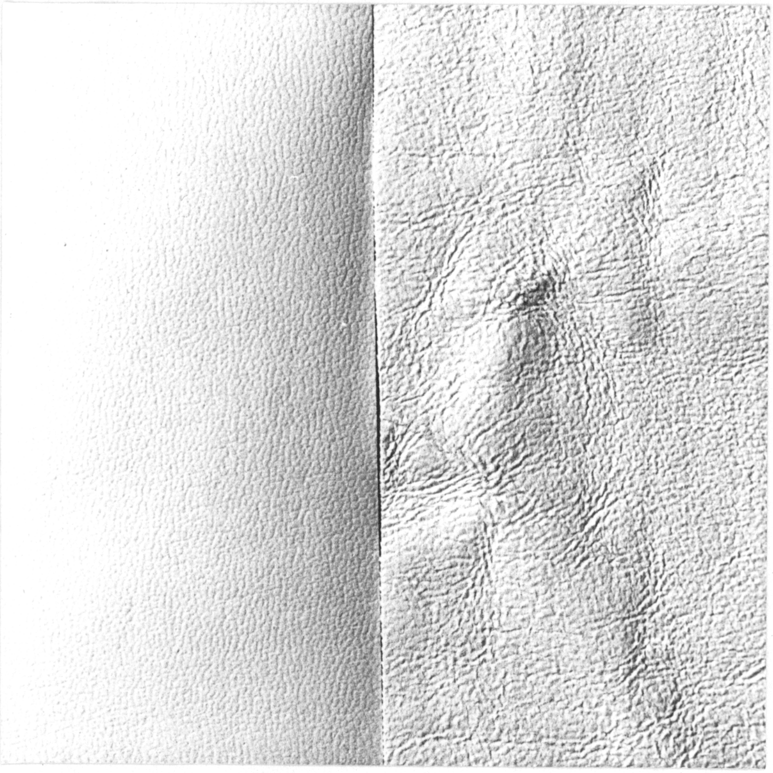


Figure 5. Control with sample treated with urea solution at 72^{o}C for 6 hours.

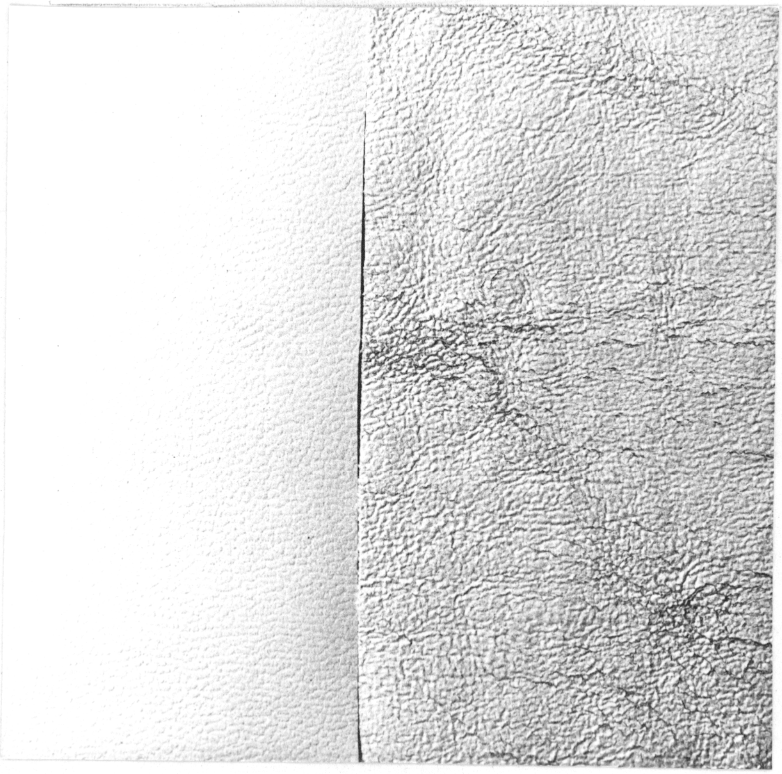


Figure 6. Control with sample treated with acid solution at 72°C for 6 hours.

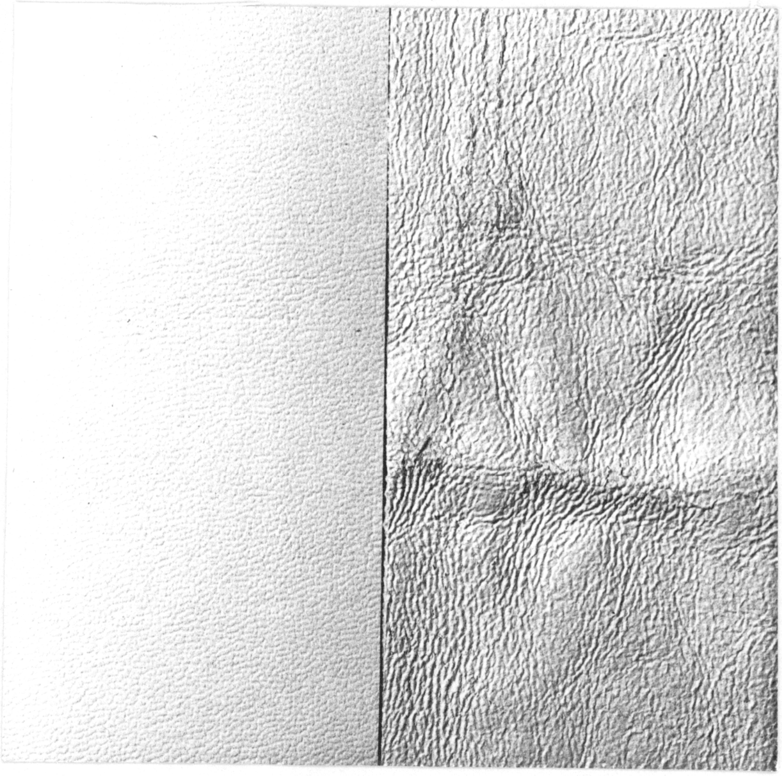


Figure 7. Control with sample treated with distilled water at $72^{o}C$ for 6 hours.

TABLE 8

ABRASION RESULTS WITH TEMPERATURE REPORTED IN CYCLES

Solution	Two Hour Test Time			
	Control	38°C	72°C	95°C
Urea		576[a]	306	
		623	221	Decomposed
Averages	583.3[b]	599.5	263.5	
Water		393	107	
		412	82	Decomposed
Averages	583.3	402.5	94.5	
Acid		212	72	
		235	61	Decomposed
Averages	583.3	223.5	66.5	

[a] Number of cycles until first film break.

[b] Average of untreated control.

Test Evaluation:

The problems encountered in rating samples on the Taber Abraser^R were similar to the problems noted under the Glass Plate Method. The effect of wrinkled areas and areas where slight abrasion had already occurred were discarded, which severely limited the areas for testing.

Data Interpretation:

Following the procedure outlined in Chapter III, the LaunderOmeter^R Method was repeated three times. Each run consisted of three samples treated for each test solution. The pH measurements were recorded before and after each treatment (Table 9) and the change in the abrasion resistance was demonstrated by the Taber Abraser^R results (Table 10).

Although the results were not significantly reproducible, definite trends emerged using the LaunderOmeter^R Method. It was evident that the samples treated with the urea solution had a higher abrasion resistance. It was not possible to determine whether more damage resulted from the water or acid solution. These results were also borne out by visual observations.

Further investigation might show a more pronounced correlation between the amount of change in pH and the amount of abrasion resistance gained or lost. It appeared, though, that the pH change must have affected the urethane sample differently depending on the solution. The pH of both the urea solution and distilled water increased during the treatment, but the urea solution appeared to protect the urethane film and keep it plastic, while the distilled water decomposed the

TABLE 9

MEASUREMENTS TAKEN OF pH BEFORE AND AFTER TREATMENTS

Solutions	72°C, Two Hour Test Time					
	Experiment 1		Experiment 2		Experiment 3	
	Before	After	Before	After	Before	After
Urea		7.02		7.40		7.21
		7.09		7.51		7.22
		7.03		7.50		7.22
Averages	5.70	7.05	5.68	7.47	5.85	7.22
Water		6.40		6.52		6.51
		6.51		6.71		6.70
		6.61		6.82		6.72
Averages	5.80	6.51	5.68	6.68	5.83	6.64
Acid		4.10		4.28		4.12
		4.12		4.30		4.13
		4.13		4.24		4.15
Averages	3.85	4.12	3.96	4.27	3.89	4.13

TABLE 10

ABRASION RESULTS REPORTED IN CYCLES AT 72°C FOR TWO HOUR TEST TIME

Solutions	Untreated Control	Experiment # 1	Experiment # 2	Experiment # 3
	Cycles	Cycles	Cycles	Cycles
Urea	564[a]	144	155	104
	624	126	103	150
	562	168	121	175
Averages	583.3	146.0	126.3	143.0
Water	564	82	99	97
	624	95	87	87
	562	70	80	58
Averages	583.3	82.3	88.7	80.7
Acid	564	87	79	89
	624	73	91	85
	562	111	67	73
Averages	583.3	90.3	79.0	82.3

[a] Number of cycles until first film break.

skin. The pH of the AATCC acid solution changed very little, but damage to the urethane skin was comparable to the damage caused by the distilled water.

The Effect of Urea

The urea solution was chosen for use in this research because SATRA has stated that it increased the rate of hydrolysis and simulated the action of perspiration on the polyurethane synthetic leathers (8). Distilled water was used as a control. Unexpectedly, the distilled water gave results comparable to the acid solution. The relatively good abrasion resistance obtained with the urea solution was even more unanticipated.

A sample of the polyurethane synthetic leather was treated in a solution made acidic (pH = 2.5) with phosphoric acid. Another was treated in a solution made alkaline (pH = 9) with sodium carbonate. On visual observation, the acid treated sample looked more yellow and more decomposed than the alkaline treated sample.

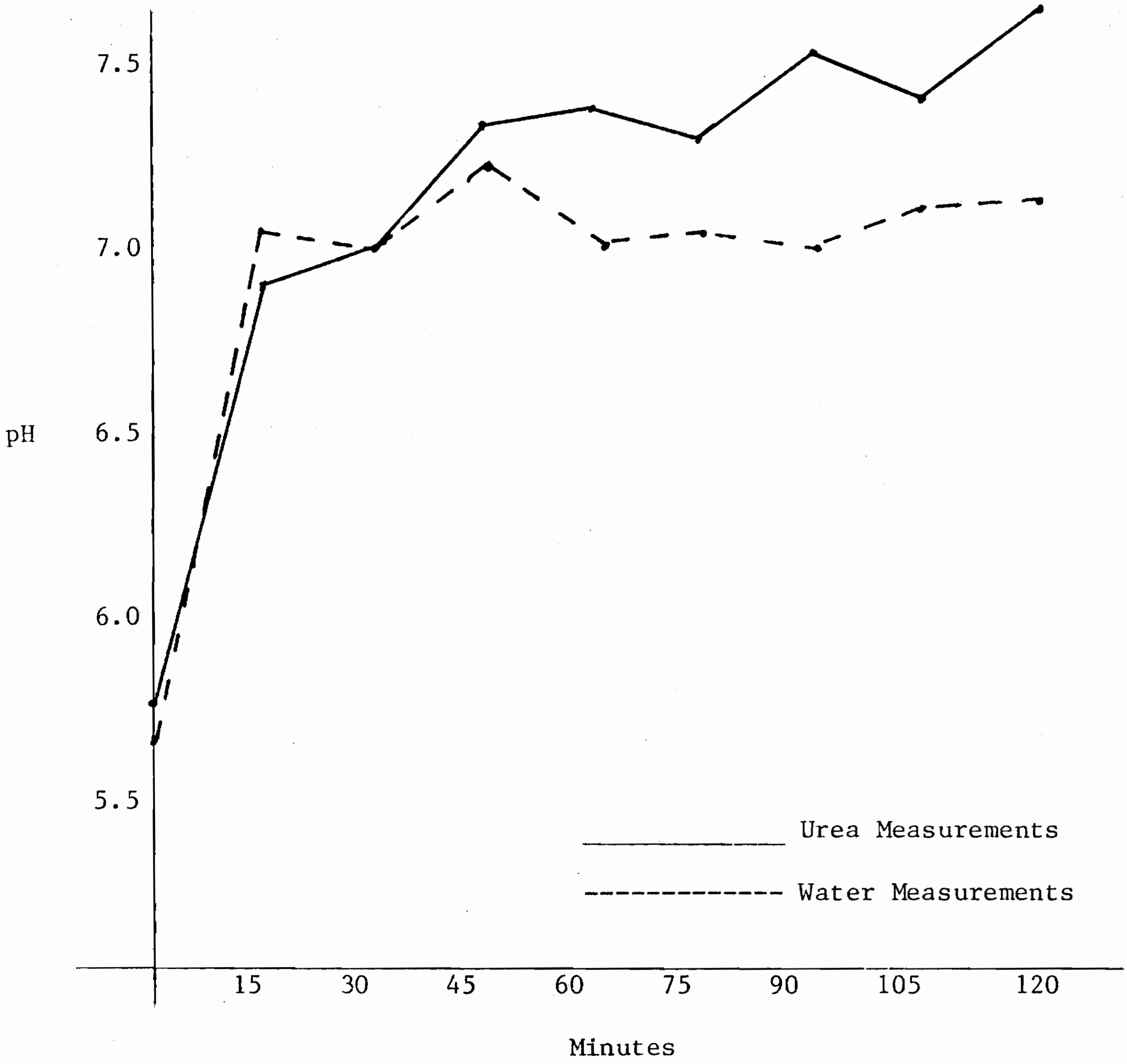
It was first thought that the apparent protection effect of the urea might be attributable to the large pH change for the urea solution from the acid to the alkaline side. Measurements were made at 15 minute intervals on the urea and water solutions at two temperatures. The acid solution was not measured as it had shown negligible change in earlier experimentation. The results (Table 11) showed that both solutions had sudden increases after which, they approached a more constant pH (Graphs 1 and 2). The distilled water leveled-off closer to the neutral pH of 7.0. It appeared that the urea pH might have

TABLE 11

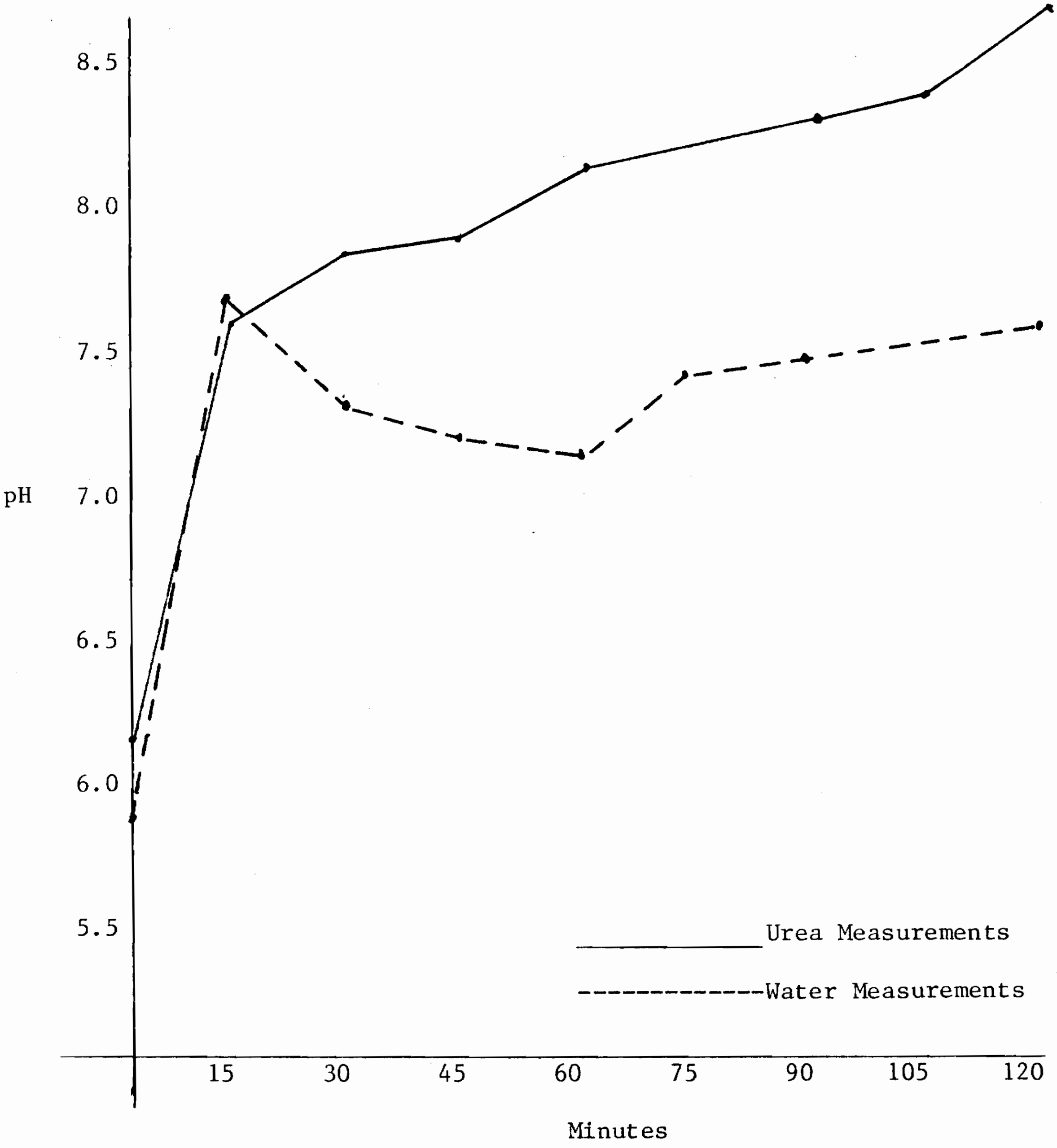
MEASUREMENTS OF pH AT 15 MINUTE INTERVALS TAKEN AT 72°C AND 95°C

72°C Solutions	Before	15	30	45	60	75	90	105	120
Urea	5.70	6.91	7.02	7.31	7.39	7.30	7.51	7.40	7.64
Water	5.68	7.02	7.00	7.21	7.02	7.05	7.01	7.11	7.12
95°C Solutions	Before	15	30	45	60	75	90	105	120
Urea	6.15	7.61	7.79	7.82	8.12	X[a]	8.29	8.34	8.59
Water	5.88	7.71	7.32	7.21	7.10	7.32	7.34	X	7.38

[a] Sample extract was destroyed in some manner.



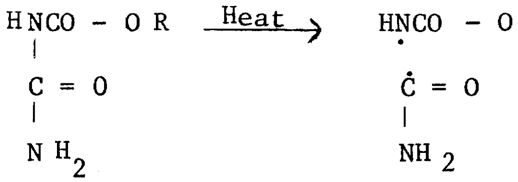
Graph 1. Measurement of pH with time at 72°C.



Graph 2. Measurement of pH with time at 95°C.

climbed slightly higher if more measurements had been taken. The neutral pH of the water can be explained since the water was acidic before treating the urethane coated fabric, probably with dissolved CO_2. The treatments were performed in a liquid tight, but not gas tight container. In the 72°C bath, the CO_2 escaped, leaving a neutral solution. The difference between the pH level of the distilled water and the urea solution did not seem great enough to warrant the dramatic differences in their effects on the urethane skin. The pH level of the acid solution was much lower, and gave effects very similar to the samples treated with the distilled water. Other factors involving the chemistry of the urea and the urethane polymer must be in effect.

From the previously stated chemical process for this particular polyurethane synthetic leather, it appears that allophanate linkages might be present in small amounts. These linkages are thermally weak.



$$\begin{array}{l} HNCO - 0\,R \\ | \\ C = 0 \\ | \\ NH_2 \end{array} \xrightarrow{Heat} \begin{array}{l} HNCO - 0 \\ \cdot \\ \dot{C} = 0 \\ | \\ NH_2 \end{array}$$

If the $-\underset{NH}{\underset{|}{C}} = 0$ group were cleaved from the structure, a site would be available for a reaction with urea. The reaction with the urea might make the polymer chain more stable to hydrolysis. However, the question of whether hydrolysis, or allophanate linkage cleavage would occur first should be investigated.

Strong forces exist between urea and urethane groups as discussed on page 10. It is possible that the urea from the solution is being bonded to this particular urethane and causing a crosslinking effect.

This would strengthen the polymeric chains, making them less subject to hydrolysis.

Although plasticizers are not used in polyurethane films, the urea solution seemed to be having a plasticizing effect in this case. Urea is slightly soluble in urethane and might be swelling the polymer. This would force the crosslinks further apart, making the urethane more flexible.

It has also been theorized that the urea might be acting as a mild acid scavenger. The hydrolytic process of urethanes is acid catalyzed (38). While urea will not react with acids, urea in solution will form some ammonia which might react with any acids in the solution and slow the rate of hydrolysis.

There also might be some question as to whether it was really hydrolysis that had taken place. Although the literature states that hydrolysis is the reaction that causes chain breakdown, very little research has been done on this aspect of the polyurethane synthetic leathers. Most sources label the information put forth on hydrolytic degradation of polyurethane synthetic leathers, as theories (9, 26).

CHAPTER V

SUMMARY AND RECOMMENDATIONS

This research has investigated the effects of a dilute urea solution, a simulated acid perspiration solution, and water on a polyurethane synthetic leather. A method of treatment was designed whereby the soaked samples were heated between glass plates. Treatment of samples was also attempted with the LaunderOmeter^{R}, where samples were treated in an enclosed system in a constant temperature bath.

In the Glass Plate Method, the degradative effects of the solutions used were measured by surface and flex abrasion. Surface abrasion was also used to measure the amount of degradation from the LaunderOmeter^{R} Method. pH before and after treatment in the LaunderOmeter^{R} was recorded.

Various time and temperature relationships were considered as they affected degradation and pH change of the samples and extracts from the LaunderOmeter^{R} Method. The effects of the solutions were also recorded visually by photographs.

This research has led into areas that apparently are not treated in the literature concerning polyurethane synthetic leathers. The inability to get reproducible degradation results, and the unexplained results obtained concerning the various solutions, suggest the following recommendations:

1. Due to technical and mechanical difficulties, the Glass Plate Method should not be used. It was shown that the weight of the glass plate coupled with high temperatures altered the surface of the polyurethane synthetic leather. This led to great variability in surface abrasion results. It is also felt that the change in abrasion resistance due to the smooth surface camouflaged the effects due to actual degradation.

2. Results obtained on the test fabric using the Taber Abraser^R had too much variability to analyze statistically. However, definite trends could be seen when the Taber Abraser^R was used with the LaunderOmeter^R Method. To be able to analyze the effect of the test solutions on abrasion resistance of the urethane skin statistically, another method should be designed. A more objective method should be chosen which would require less individual judgment on the part of the test operator. If the Taber Abraser^R is to be used, a rating panel might be employed to rate samples which have been abraded a specified number of times. Tests might also be run using the Accelerotor^R to show edge abrasion as a method of evaluating the surface degradation (37). These samples could be rated by a panel after being abraded at a specified revolutions per minute for a set time.

3. If the Taber Abraser^R Method for testing surface abrasion is to be used, a more stable sample surface should be maintained. Wrinkling, and abraded points should be eliminated, as these affect the surface abrasion results.

Accelerotor^R--Registered trademark of the Atlas Electric Devices Company.

4. Although the LaunderOmeter^{R} Method proved to be an acceptable method for showing the effect of the test solutions on the polyurethane synthetic leather, excessive wrinkling of the sample occurred because of the rotation action. This method should be adapted so that the samples could be treated in an unwrinkled condition. This might be accomplished by placing samples in the lower rack of the LaunderOmeter^{R} without rotation. A new treatment container might also be designed which would hold the samples in a completely flat condition.

5. Research concerning the feasibility of designing a chemical test to totally decompose the sample should be pursued. Degradation could be evaluated by rating the appearance of samples after a specified time has elapsed, or by measuring the time required to totally decompose the urethane top skin.

However, it must be remembered, that in accelerated testing, the time of testing and the temperature may actually change the state of the material. Separate states of the same material should not be compared, particularly if the state obtained in an accelerated test is not found in actual wear studies.

6. The results obtained in this research do not totally agree with results stated in the literature concerning urea and urethanes. This unexplained effect of urea on the polyurethane synthetic leather tested, illustrate the need for more research in this area. Both the chemical and physical mechanisms involved need to be explained. This may also lead to a better understanding of the complex chemistry of the polyurethane films.

7. In this research, large pH changes were observed when treating the polyurethane synthetic leather in the dilute urea solution. It should be determined whether this change occurred from the effect of urea on the polyurethane synthetic leather, or whether the change in pH caused the urea effect. The pH of the distilled water should also be investigated, as it changed a slightly lesser amount than the urea, but caused a much larger degradative effect. The acid solution barely changed pH, but caused degradation comparable to that observed with the distilled water.

8. The SATRA method of hydrolyzing polyurethane film with urea to simulate perspiration damage should be reconsidered. Although their test was not duplicated exactly in this research, the effect of urea on the polyurethane synthetic leather should have been similar. Results opposite to their findings were observed in this research, leading to the conclusion that their test method does not apply to all polyurethane synthetic leathers. They may be in error in some cases to state that the addition of urea increases the rate of hydrolysis of these urethane leathers.

However, if the urea is acting as an acid scavenger in the submerging treatments of this research, this effect might not be noticed in the high humidity treatments used by SATRA. The leaching effect of the solution should not occur very much in their treatments (38).

9. Results from this research show that the AATCC acid solution for simulated perspiration can be used to show degradation. Research should be carried out to determine if the degradative effects of this solution on polyurethane synthetic leather correlates with the

degradative effects of actual perspiration as measured by field studies. This researcher would recommend the substitution of .50g/l histidine monohydrochloride for the .25g/l as specified by AATCC.

CHAPTER VI

CONCLUSIONS

The major findings of this research were:

1. Treating for two hours, at 95°C, the test fabric was decomposed by both the acid and urea solutions, as well as the distilled water. However, the effect of the urea on the urethane film was much less damaging than were the other two solutions. Under some conditions the urea seemed to actually protect the urethane skin from decomposing.

2. The soaking technique used in the LaunderOmeter^R Method was more controllable than the treatment technique of the Glass Plate Method. However, the LaunderOmeter^R Method must be altered to eliminate wrinkling of the samples.

3. Results obtained for abrasion resistance using the Taber Abraser^R and Bally Flexometer^R were too erratic to statistically evaluate the effects of the test solutions on the durability of the polyurethane synthetic leathers.

4. The final pH of the urea solution was found to have increased to an alkaline pH after the polyurethane synthetic leather was treated and the urea appeared to degrade the urethane skin less than distilled water and an acid solution.

5. At present, there appears to be no suitable test method to show perspiration degradation of polyurethane synthetic leathers, since

through this research an exception has been shown to the only recognised test method available.

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Judith A. Peters

THE EFFECT OF A DILUTE UREA SOLUTION, AN ACID SIMULATED PERSPIRATION SOLUTION, AND DISTILLED WATER ON A POLYURETHANE COATED FABRIC

by

Judith Alleyne Peters

(ABSTRACT)

This research has investigated the effects of a dilute urea solution, an acid simulated perspiration solution and distilled water on a polyurethane coated fabric. Investigations were made into the feasibility of using the Glass Plate Method, where treated samples were heated between glass plates, and the LaunderOmeter^{R} Method where samples were treated with solutions in an enclosed system in a constant temperature bath. The degradative effects of the solutions when used with the Glass Plate Method were measured by flex and surface abrasion and the degradative effects of the solutions when used with the LaunderOmeter^{R} Method were measured by surface abrasion. The pH was observed before and after treatments in the LaunderOmeter^{R}.

It was found that the urethane film of the test fabric could be completely decomposed with all three solutions when treated at 95°C for six hours in the LaunderOmeter^{R}. However, those samples treated with urea had higher abrasion resistance and appeared less decomposed

visually. This was in conflict with reports that the addition of urea to distilled water would increase the rate of hydrolysis, and could be used to simulate perspiration. This is assuming that the effects of the solutions were indeed causing hydrolysis.

The LaunderOmeter^R Method was found to be more controllable than the Glass Plate Method. Replications of treatments at 72°C for two hours were carried out on the polyurethane synthetic leathers using the LaunderOmeter^R Method. Again, the urea treated samples demonstrated a higher abrasion resistance. Distilled water and the acid simulated perspiration solution gave comparable results.